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

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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[1] and crystallizes as an unstable orange material containing puckered S_8 rings with exocyclic oxygen atoms in axial positions.[2] 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 *Pcmn*, $a = 1052(5)$, $b = 880(3)$, $c = 1621(6)$ pm, $Z = 4$, $D_c = 2{\cdot}53$ g cm^{-3} (-100 °C), $M = 571{\cdot}5$ (Mo-K_α, $\lambda = 71{\cdot}069$ pm, $\mu = 37{\cdot}7$ cm^{-1}). Data were collected at -100 °C using a Syntex $P2_1$ diffractometer. The intensities of 1621 reflections were measured ($2\theta < 50°$), 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 $R = 0{\cdot}083$ using anisotropic thermal parameters but without absorption correction.†

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut fur Anorganische Chemie, Universitat, 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).

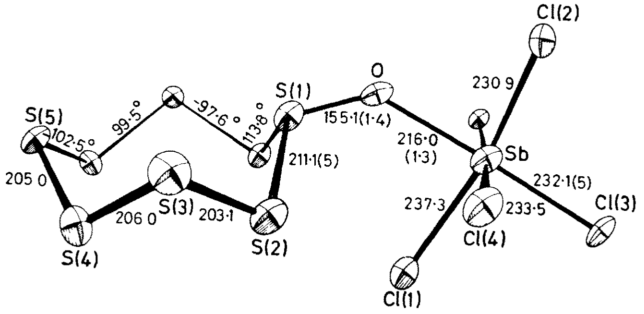

FIGURE 1 Molecular structure, bond lengths (pm) and torsional angles of $S_8O{\cdot}SbCl_5$.

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).

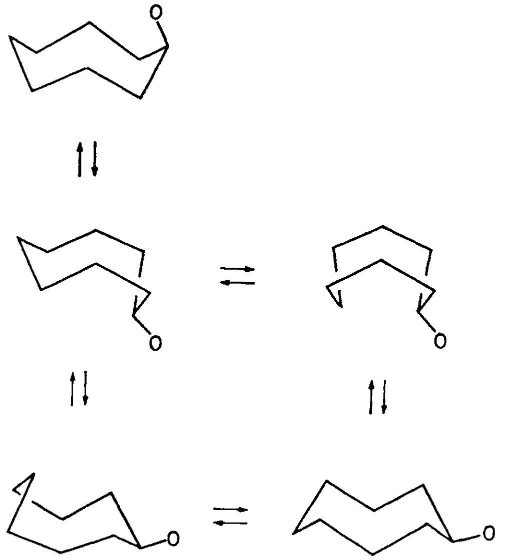

FIGURE 2. Possible pathway for the exchange of the oxygen atom between axial and equatorial positions by S_8 ring inversion.

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