

In addition to the engagement in the hydrogen-bond system each water molecule is coordinated to two $\text{Na}^+(3)$ ions with different distances $\text{O}(W)\cdots\text{Na}(3)$ of 2.338 (7) and 2.854 (7) Å respectively (Fig. 5) and angle $\text{Na}(3)\cdots\text{O}(W)\cdots\text{Na}(3) = 104.46(8)^\circ$; hence it may be assigned to class 2A in the classification given by Ferraris & Franchini-Angela (1972).

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The Structure of 1,5-Dichlorocyclotetra(azathiene)

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Abstract

The structure of monoclinic $\text{S}_4\text{N}_4\text{Cl}_2$ [space group $P2_1/c$, $a = 9.077(4)$, $b = 6.580(2)$, $c = 13.311(6)$ Å, $\beta = 108.46(4)^\circ$, $U = 754.1$ Å³, $Z = 4$, $M_r = 255.19$, $D_m = 2.25$, $D_x = 2.25$ Mg m⁻³] was refined to $R = 0.094$ for 1235 densitometer intensities. The structure consists of $\text{S}_4\text{N}_4\text{Cl}_2$ molecules with covalent S–Cl bonds. The average bond lengths are S–N 1.59 and S–Cl 2.18 Å; the angles are S–N–S 119, N–S–N 109 and N–S–Cl 104°.

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Introduction

According to Meuwesen (1931) the chlorination of S_4N_4 yields 1,3,5-trichlorocyclotri(azathiene), $\text{S}_3\text{N}_3\text{Cl}_3$. However, the kinetics of the reaction in CS_2 (Nelson & Heal, 1970) suggests that the process proceeds *via* some intermediate, which decomposes to $\text{S}_3\text{N}_3\text{Cl}_3$ and SNCl . Its composition has been proposed, by analogy with $\text{S}_4\text{N}_4\text{F}_4$ and from the stoichiometry of the chlorination, as $\text{S}_4\text{N}_4\text{Cl}_4$. Zbořilová & Gebauer (1979a,b) have isolated the intermediate and identified

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it as 1,5-dichlorocyclotetra(azathiene), $S_4N_4Cl_2$. Because of interest in its ring configuration we have undertaken an X-ray structure analysis.

Experimental

Single crystals of $S_4N_4Cl_2$ were prepared by the reaction of Cl_2 with S_4N_4 in CS_2 solution (Zbořilová & Gebauer, 1979a) and sealed in thin-walled quartz capillaries in an atmosphere of dry N_2 .

The crystal data on $S_4N_4Cl_2$ have already been published (Gebauer, Žák & Zbořilová, 1979) and are summarized in the *Abstract*. Although the compound is fairly stable at room temperature, it decomposes slowly in X-rays even at low temperature and several crystals had to be used for the data collection. The crystals were mounted with c parallel to the rotation axis of a Nonius Weissenberg goniometer. The reciprocal levels $hk0-h, k, 10$ were recorded by an integrating equi-inclination method with Ni-filtered Cu $K\alpha$ radiation. The intensities were measured photometrically on a Zeiss-Jena densitometer; weak diffractions were estimated visually. The data were reduced to 1235 symmetry-independent diffractions including 199 unobserveds, which were substituted by statistical values (Hamilton, 1955). The independent data were converted to structure amplitudes by applying Lorentz and polarization corrections and an absorption correction assuming cylindrical crystals ($\mu = 17.00 \text{ mm}^{-1}$) (Weber, 1967). Scattering factors for S^0 , N^0 , and Cl^0 were taken from Cromer & Mann (1968).

Structure determination and refinement

The structure was solved by direct methods. The phases of 159 E 's ≥ 1.3 from 160 input were determined by *TANFOR* (Drew & Larson, 1968). On the basis of these 159 phases, an additional 114 phases with $E \geq 1.0$ were determined by *TANEXT*. An E map based on 273 known phases revealed the positions of all atoms. The isotropic full-matrix least-squares refinement was ended at $R = 0.18$. Anisotropic temperature factors were introduced, which decreased R to 0.114. After rescaling the observed structure factors on $\sum |F_o| / \sum |F_c|$ for every recorded level, additional refinement gave a final R of 0.094; $R_w = 0.136$ $\{R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}\}$. * The weighting scheme was derived by plotting $|\Delta F|$ (mean) versus $|F_o|$ (mean) for groups of 50–60 diffractions of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35621 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* ($\times 10^4$) and *isotropic thermal parameters*, with *e.s.d.'s* in parentheses

$$\langle U^2 \rangle = \frac{1}{3}(8\pi^2)^{-1} \text{trace } B.$$

Individual B 's are related to refined β 's by $B_{ij} = 4\beta_{ij}/(a_i^* \cdot a_j^*)$ where a_i^* , a_j^* represent reciprocal-lattice translations.

	x	y	z	$\langle U^2 \rangle (\text{\AA}^2)$
S(1)	3549 (2)	2595 (3)	7771 (2)	0.04
S(2)	452 (2)	3667 (3)	7101 (2)	0.04
S(3)	2683 (2)	5467 (3)	6510 (2)	0.04
S(4)	3296 (2)	1898 (3)	5651 (2)	0.04
N(1)	2001 (8)	2543 (10)	7964 (7)	0.05
N(2)	1065 (8)	5604 (10)	6637 (7)	0.05
N(3)	2540 (8)	4077 (10)	5469 (7)	0.05
N(4)	3465 (9)	1053 (10)	6804 (7)	0.05
Cl(1)	5743 (2)	2510 (4)	5877 (2)	0.06
Cl(2)	477 (2)	6584 (3)	9222 (2)	0.05

similar magnitudes. The weight was taken as proportional to $1/|\overline{\Delta F}|^2$ (Stout & Jensen, 1968). R and R_w for observed data only were 0.086 and 0.123 respectively. No extinction correction was made and all independent diffractions, except unobserveds, were included in the refinement. The maximum shift in positional parameters during the last cycle was 0.2σ , the average 0.05σ . The programs used in the refinement were *TLS* and *TLIS* (Novák, 1973), based on *ORFLS* (Busing, Martin & Levy, 1962). Those employed during the solution of the structure are part of our *UNIBOX* system for the Tesla 200 computer (Žák, 1977). The final atomic parameters are given in Table 1.

Description and discussion of the structure

The structure of $S_4N_4Cl_2$ is composed of discrete molecules (Fig. 1) with approximate C_s symmetry through Cl(1), S(4), S(2), and Cl'(2') [symmetry code: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$] (Table 2). The average S–N distance, 1.59 Å, is comparable with those found in other azathiene compounds (1.57–1.62 Å) (Banister, 1975) and the S–Cl length, 2.18 Å, is similar to that in $S_3N_2Cl^+$ (2.17 Å) (Zalkin, Hopkins & Templeton, 1966). Table 3 lists the bond lengths and angles.

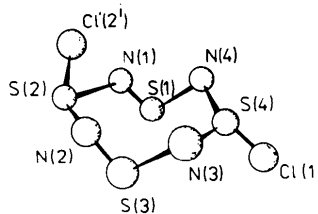


Fig. 1. A perspective view of a molecule of $S_4N_4Cl_2$.

Table 2. *Best planes through the S₄N₄Cl₂ molecule referred to orthogonal axes with distances (Å) of relevant atoms from the planes*

The errors (in parentheses) are taken as equal to the absolute isotropic errors in atomic positions.

Plane A: Cl(1), S(4), S(2), Cl'(2')

$$-0.0701x + 0.7800y - 0.0622z = -3.51$$

Cl(1) -0.008 (2); S(4) 0.012 (2); S(2) 0.002 (2);
Cl'(2') -0.006 (2); N(1) -1.328 (8); N(2) 1.287 (8);
S(1) -1.249 (2); S(3) 1.231 (2); N(3) 1.316 (8); N(4) -1.315 (8)

Plane B: S(1), N(1), S(2), N(2), S(3)

$$0.0250x - 0.6371y - 0.7704z = -8.70$$

S(1) 0.048 (2); N(1) -0.142 (8); S(2) 0.190 (2); N(2) -0.163 (8);
S(3) 0.067 (2)

Plane C: S(1), N(4), S(4), N(3), S(3)

$$-0.9530x - 0.2594y - 0.1563z = -1.89$$

S(1) -0.039 (2); N(4) 0.105 (8); S(4) -0.136 (2); N(3) 0.107 (8);
S(3) -0.038 (2)

Angles between planes (°)

A/B 91.1 (8) A/C 92.2 (8) B/C 105.2 (9)

Table 3. *Interatomic distances (Å) and angles (°)*

The interatomic distances and angles were computed with *ORFFE* (Busing, Martin & Levy, 1964). They include the cell-parameter errors but averaging over the thermal motion of the atoms was not considered to be appropriate. The atom marked by a prime is from a neighbouring unit cell.

S(1)—N(1)	1.5071 (6)	S(1)—S(2)	2.758 (2)
S(1)—N(4)	1.6217 (5)	S(1)—S(3)	2.484 (1)
S(2)—N(1)	1.679 (1)	S(1)—S(4)	2.796 (1)
S(2)—N(2)	1.5903 (4)	S(2)—S(3)	2.670 (1)
S(3)—N(3)	1.6310 (5)	S(2)—S(4)	3.859 (2)
S(3)—N(2)	1.5336 (6)	S(3)—S(4)	2.7448 (7)
S(4)—N(3)	1.5753 (5)	Cl(1)—Cl'(2')	7.985 (2)
S(4)—N(4)	1.5931 (7)	Cl(2)—Cl'(2')	3.244 (1)
S(2)—Cl'(2')	2.179 (1)		
S(4)—Cl(1)	2.183 (1)		
S(1)—N(1)—S(2)	119.80 (3)	N(1)—S(2)—N(2)	107.37 (3)
S(2)—N(2)—S(3)	117.41 (2)	N(2)—S(3)—N(3)	107.80 (4)
S(3)—N(3)—S(4)	117.75 (3)	N(3)—S(4)—N(4)	111.75 (2)
S(4)—N(4)—S(1)	120.81 (3)	N(4)—S(1)—N(1)	108.00 (4)
N(3)—S(4)—Cl(1)	103.19 (2)	N(1)—S(2)—Cl'(2')	107.56 (4)
N(4)—S(4)—Cl(1)	98.55 (6)	N(2)—S(2)—Cl'(2')	106.51 (3)

Table 4. *Comparison of average bond lengths (Å) and angles (°) in S₄N₄, S₄N₄(Ph₃PN)₂, S₄N₄Cl₂, and S₄N₄²⁺*

	S—N	S—S	N—S—N	S—N—S
S ₄ N ₄	1.62	2.58	104.5	112.8
S ₄ N ₄ (Ph ₃ PN) ₂	1.62	2.45 3.73	111	120
S ₄ N ₄ Cl ₂	1.59	2.48 3.86	109	119
S ₄ N ₄ ²⁺	1.54 1.57	—	119.5 127	150.5 143

The shape of the S₄N₄ group was discussed by Gleiter (1970). S₄N₄, an eight-centre system with 12 electrons, can possess only a three-dimensional cage structure (Sharma & Donohue, 1963; DeLucia & Coppens, 1979), while the dication S₄N₄²⁺, a 10π-electron system, must be planar with *D*_{4h} symmetry. Ionization of S₄N₄ to S₄N₄²⁺ can be achieved by the action of the strong Lewis acids SbCl₅ and SbF₅ and the actual structure of S₄N₄²⁺ is a flat or almost flat ring (Gillespie, Slim & Tyrer, 1977). By the same reasoning, the structure of S₄N₄Cl₂ must possess a partially opened S₄N₄ cage since the action of Cl₂ on S₄N₄ cannot cause its full ionization but only breaks a S—S bond and new, more or less covalent, bonds between these S and Cl atoms are formed. The same is valid for (Ph₃PN)₂S₄N₄ (Bojes, Chivers, MacLean, Oakley & Cordes, 1979), whose structure is very close to that of S₄N₄Cl₂. Table 4 summarizes average bond lengths and angles in S₄N₄, S₄N₄Cl₂, (Ph₃PN)₂S₄N₄, and S₄N₄²⁺. Although no general conclusion about the bond order of the S—N bond in azathiene compounds can be drawn from the S—N lengths (Gleiter, 1970), in this closely related group the change in the S—N length reflects the change in its double-bond character.

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Compounds with Perovskite-Type Slabs.

IV. Ferroelectric Phase Transitions in $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ ($x \simeq 0.12$) and $\text{Sr}_2\text{Ta}_2\text{O}_7$

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Abstract

Ferroelectric phase transitions in $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ ($x \simeq 0.12$) and $\text{Sr}_2\text{Ta}_2\text{O}_7$ were investigated by the single-crystal X-ray diffraction technique. The structures of $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ ($x \simeq 0.12$) at 300, 573, 773 and 1073 K and $\text{Sr}_2\text{Ta}_2\text{O}_7$ at 123 K have been determined from three-dimensional X-ray diffraction data and refined to final R values of 0.047, 0.070, 0.087, 0.097 and 0.033 for 907, 748, 663, 598 and 520 observed reflexions, respectively. The structures above the Curie points, approximately 675 K for $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ ($x \simeq 0.12$) and 166 K for $\text{Sr}_2\text{Ta}_2\text{O}_7$, have the symmetries of the space group $Cmcm$. All atoms are on the mirror planes at $z = 0.25$ and 0.75 . Below the Curie points, the structures lose the mirror planes at $z = 0.25$ and 0.75 and the metal atoms move along the c axis on the mirror planes at $x = 0$ and 0.5 . The space group becomes $Cmc2_1$. A slight deformation of the O atom framework in a perovskite-type slab can be regarded as a small rotation of $(\text{Ta}, \text{Nb})\text{O}_6$ octahedra around axes parallel to the a axis. A distinct difference in the temperature dependence of the thermal parameters of the metal atoms in $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ ($x \simeq 0.12$) was found below and above the Curie point.

Introduction

Several ferroelectric $A_2B_2O_7$ compounds have been revealed to form a structural family related to the

perovskite structure. The members include $\text{Sr}_2\text{Ta}_2\text{O}_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1976), $\text{Sr}_2\text{Nb}_2\text{O}_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975; Scheunemann & Müller-Buschbaum, 1975a), $\text{La}_2\text{Ti}_2\text{O}_7$ (Scheunemann & Müller-Buschbaum, 1975b; Gasperin, 1975), $\text{Ca}_2\text{Nb}_2\text{O}_7$ (Scheunemann & Müller-Buschbaum, 1974; Ishizawa, Marumo, Iwai, Kimura & Kawamura, 1980) and $\text{Nd}_2\text{Ti}_2\text{O}_7$ (Scheunemann & Müller-Buschbaum, 1975c). The structures are composed of perovskite-type slabs stacked along the b axis. The slabs contain corner-shared BO_6 octahedra and A cations in twelve-coordination, and are linked by A cations lying at the boundaries of the slabs. These compounds have various polymorphs which are assumed to originate from a prototype structure whose space group is $Cmcm$ (Ishizawa *et al.*, 1980). The Curie temperatures (T_c) of these compounds are higher than 1500 K except for $\text{Sr}_2\text{Ta}_2\text{O}_7$ ($T_c = 166$ K) (Nanamatsu, Kimura & Kawamura, 1975). $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ forms a complete solid-solution system and T_c varies continuously from 166 K ($x = 0$; $\text{Sr}_2\text{Ta}_2\text{O}_7$) to 1615 K ($x = 1.0$; $\text{Sr}_2\text{Nb}_2\text{O}_7$) (Nanamatsu *et al.*, 1975). The space groups $Cmcm$ and $Cmc2_1$ were reported for the respective end members of the system at room temperature (Ishizawa *et al.*, 1975, 1976). Thus, the ferroelectric phase transition in $\text{Sr}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_7$ was expected to accompany a structural change from $Cmcm$ to $Cmc2_1$ (Ishizawa *et al.*, 1976). Recently, new phases were found for $\text{Sr}_2\text{Nb}_2\text{O}_7$ below 493 K and for $\text{Sr}_2\text{Ta}_2\text{O}_7$ below 443 K (Yamamoto, Yagi, Honjo, Kimura & Kawamura, 1980). Studies related to the phase transition in $\text{Sr}_2\text{Nb}_2\text{O}_7$ were also carried out by Ohi, Kimura, Ishida & Kakinuma (1979) and Kojima,

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