

Synthesis and X-Ray Crystal Structure Determination of Thiotrithiazyl Iododichloride, $\text{S}_4\text{N}_3\text{ICl}_2$

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Thiotrithiazyl Iododichloride, Tetrasulfur Tetranitride, Rietveld Refinement

Thiotrithiazyl iododichloride, $\text{S}_4\text{N}_3\text{ICl}_2$, has been synthesized from molecular S_4N_4 and liquid ICl and structurally characterized by an X-ray Rietveld refinement. $\text{S}_4\text{N}_3\text{ICl}_2$ crystallizes in the monoclinic system ($P2_1/c$, $a = 611.548(7)$, $b = 877.336(8)$, $c = 1770.12(2)$ pm, $\beta = 92.3357(7)^\circ$, $Z = 4$), follows the crystal-chemical motif $(\text{S}_4\text{N}_3^+)(\text{Cl}\text{ICl}^-)$, and is thus isotypic with $(\text{S}_4\text{N}_3^+)(\text{Br}_3^-)$. The crystal structure contains a planar S_4N_3^+ ring and a linear ClICl^- unit.

1. Introduction

Polysulfurnitride, $(\text{SN})_x$, has been the first example of an artificial metal of polymeric nature composed purely of nonmetallic main group elements. It was first described almost a century ago [1] but the belated discovery of $(\text{SN})_x$'s superconductivity in the 1970s quickly boosted an interest in the chemistry of S/N-containing molecules such as tetrasulfur tetranitride, S_4N_4 , and its halogenated derivatives. While the chemistry and the physical properties of $(\text{SN})_x$ are extensively covered in the scientific literature [2, 3], our general knowledge concerning, for example, the structure of the brominated phase as well as other reaction products of various sulfur nitrides in combination with the halogens is far from being complete.

In 1977, Street *et al.* communicated [4] a reaction between S_4N_4 and bromine *vapor* that led to a metallically conducting solid which was similar in physical properties to the brominated derivatives of $(\text{SN})_x$. Shortly after, these reactions were extended by using related molecular educts, and they yielded similar conducting materials [5, 6]. It is worth mentioning that the corresponding reaction of S_4N_4 in *liquid* bromine, in contrast, gives access to a salt-like compound, namely $\text{S}_4\text{N}_3\text{Br}_3$ ($\equiv (\text{S}_4\text{N}_3^+)(\text{Br}_3^-)$), the crystal structure of which was first published [7] in 1979. In that particular paper, the authors mentioned the corresponding reaction between S_4N_4 and ICl but did not offer any struc-

tural details for the product. This was the starting point of our investigation.

In the course of our systematic studies on the temperature-dependent crystal structures [8] and chemical reactivity [9] of tetrasulfur tetranitride, we have reinvestigated the above mentioned reaction starting from S_4N_4 and liquid ICl. Here we report in detail about the synthesis and X-ray crystal structure analysis (Rietveld technique) of $\text{S}_4\text{N}_3\text{ICl}_2$.

2. Experimental Section

2.1. Synthesis

The title compound was made from crystalline S_4N_4 and ICl. ICl itself was prepared from the elements according to the procedure by Brauer [10]. In order to obtain a well-crystallized and pure single-phase product, all synthetic steps were carried out in an inert atmosphere of argon. At the beginning, 92 mg (0.5 mmol) of S_4N_4 was very carefully [11] powdered in an agate mortar. The powder was then mixed with an excess (≈ 5 ml) of freshly made ICl and sealed into a glass ampoule. The reaction mixture was heated to 80 °C for a period of 4 d. After that, excess ICl was distilled away in a vacuum, and the crude product of dark-red color was dried by evacuating the material a second time somewhat above room temperature. The final yield was 87 mg of a yellow material.

2.2. Structure determination

Since all selected crystals of $\text{S}_4\text{N}_3\text{ICl}_2$ turned out to be extremely soft and unsuitable (too strongly twinned or too small) for a single-crystal structure determination, a small

Table 1. Crystallographic Data of $\text{S}_4\text{N}_3\text{ICl}_2$.

Formula	$\text{S}_4\text{N}_3\text{ICl}_2$
Molecular weight	368.09 g/mol
Lattice parameters	$a = 611.548(7)$, $b = 877.336(8)$, $c = 1770.12(2)$ pm, $\beta = 92.3357(7)^\circ$
Space group	$P2_1/c$ (Nr. 14)
Formula units	4
X-ray density	2.576 g/cm ³
Absorption coefficient	39.45 mm ⁻¹
Sample dimension	flat sample
Instrument	Stoe STADI powder diffractometer, Cu-K α_1 rad., Ge monochromator, linear proportional counter
Scan type; range; step	2 θ ; $10.00^\circ \leq 2\theta \leq 89.99^\circ$; 0.01°
Scan speed	100 s/step
Temperature	293(1) K
Data points	8000
Bragg reflections	761
Background	manual & Fourier filtering
Structure refinement	Rietveld least-squares method
Profile function	pseudo-Voigt
η, X mixing params	0.41(2), -0.0042(5)
u, v, w halfwidth param.	0.044(3), -0.023(2), 0.0172(3)
Preferred orient. function	March-Dollase, $G = 0.869(1)$
Variables; constraints	45, 3
Zero point	-0.0109(3)
R_p ; R_{wp}	0.021; 0.028
$R_{\text{Bragg}}(I)$; GooF	0.057; 1.57
S_{corr}	3.86

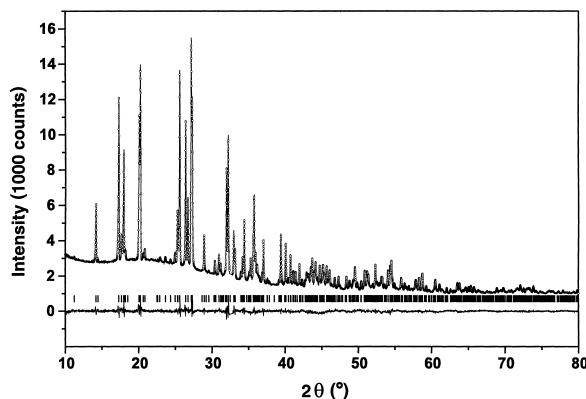


Fig. 1. Rietveld refinement of $\text{S}_4\text{N}_3\text{ICl}_2$; depicted are measured (circles) and calculated (line) diffraction patterns, the positions of the Bragg peaks, and the difference between observed and calculated intensities.

amount (about 10 mg) of the yellow substance was finely powdered, fixed between two rubberized Kapton foils (Dupont) and prepared as a flat sample for X-ray powder investigations. The diffraction pattern was recorded between 10.00 – 89.99° in 2θ using a Debye-Scherrer powder diffractometer (Stoe STADI), monochromatized

Table 2. Positional parameters (all atoms on Wyckoff position $4e$) and isotropic displacement parameters of $\text{S}_4\text{N}_3\text{ICl}_2$. Sulfur, nitrogen and halogen atoms were grouped using common displacement parameters during the refinement.

Atom	x	y	z	B_{iso} (\AA^2)
S(1)	0.4777(8)	0.8389(4)	0.1860(3)	3.20(6)
S(2)	0.2148(7)	0.7409(4)	0.2417(3)	"
S(3)	0.9968(8)	0.6060(5)	0.1040(3)	"
S(4)	0.3671(8)	0.7464(4)	0.0290(3)	"
N(1)	0.461(2)	0.825(1)	0.0945(7)	2.0(2)
N(2)	0.052(2)	0.645(1)	0.1847(8)	"
N(3)	0.135(2)	0.639(1)	0.0445(7)	"
I	0.2215(2)	0.2101(1)	0.12489(9)	4.07(3)
Cl(1)	0.5123(8)	0.4329(4)	0.1444(2)	"
Cl(2)	0.9468(7)	0.0004(3)	0.1068(3)	"

Cu-K α_1 radiation (focusing germanium monochromator), and a linear proportional counter.

Twenty sharp reflections with high intensities were selected from the data set to determine the lattice parameters of $\text{S}_4\text{N}_3\text{ICl}_2$. Unfortunately, all available indexing algorithms failed such that no reasonable lattice could be obtained. Hence we continued the structure calculations using the previously published [7] lattice parameters of $\text{S}_4\text{N}_3\text{Br}_3$ ($a = 610.5$, $b = 879.2$, $c = 1806$ pm, $\beta = 91.58^\circ$) because Street *et al.* [5] predicted $\text{S}_4\text{N}_3\text{ICl}_2$ to be isotypic with $\text{S}_4\text{N}_3\text{Br}_3$. These four lattice parameters were then varied in a stepwise manner using the POWDERCELL program [12] to fit the measured reflections of $\text{S}_4\text{N}_3\text{ICl}_2$ as closely as possible. The result of this procedure ($a = 608$, $b = 872$, $c = 1761$ pm, $\beta = 92.3^\circ$) was subsequently used as an input for the Rietveld profile refinement of the whole pattern using the FULLPROF package [13].

The background of the data set was first manually subtracted by linear interpolation and afterwards smoothed by linear, nonrecursive filtering in the last refinement cycle (1% filter width of all data points). The data were refined in the monoclinic space group $P2_1/c$, and the atomic positions were taken from the crystal structure of $\text{S}_4\text{N}_3\text{Br}_3$ [7]. An overview of the refinement is given in Fig. 1 while all important numerical details may be found in Table 1. Positional as well as isotropic displacement factors are listed in Table 2. All standard deviations need to be multiplied with the parameter S_{corr} for possible comparison with single crystal results [14]*.

* A list of the observed and calculated X-ray intensities can be obtained from either Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the registry number CSD-412 782, or directly from R. D.

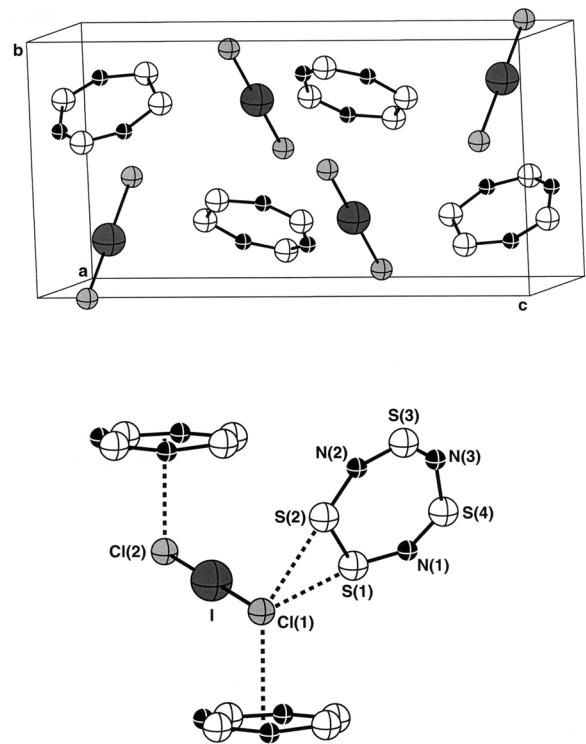


Fig. 2. Top: Packing of cations and anions in the crystal structure of $\text{S}_4\text{N}_3\text{ICl}_2$. S, N, I, and Cl atoms are given as open, black, dark- and light-grey balls. Bottom: Coordination motifs in $\text{S}_4\text{N}_3\text{ICl}_2$.

3. Results and Discussion

Fig. 2 offers a view of the crystal structure and the coordinations of $\text{S}_4\text{N}_3\text{ICl}_2$ while all important bond lengths and angles are given in Table 3.

There are four formula units per unit cell, and the structural motif is made up from planar S_4N_3^+ rings together with ClICl^- units. The alternating stacks of cations and anions are packed along the b axis. Within the S_4N_3^+ ring, the intramolecular S–N distances scatter around an average (and quite typical [15]) value of *ca.* 156 pm. The larger spectrum for the bond lengths involving the lightest atom (N) simply reflects the limited resolution of the powder refinement and should not be overinterpreted. On the other side, the average S–N bond length of 156 pm is roughly 6 pm shorter than within molecular S_4N_4 and 18 pm shorter than the sum of the covalent radii of S and N [16]. The one S–S bond

Table 3. Important bond lengths (pm) and angles ($^\circ$) of $\text{S}_4\text{N}_3\text{ICl}_2$.

$\text{S}(1)-\text{N}(1)$	162(1)	$\text{S}(1)-\text{S}(2)-\text{N}(2)$	112.4(6)
$\text{S}(1)-\text{S}(2)$	210.4(7)	$\text{S}(2)-\text{N}(2)-\text{S}(3)$	145.3(9)
$\text{S}(2)-\text{N}(2)$	162(1)	$\text{N}(2)-\text{S}(3)-\text{N}(3)$	123.3(7)
$\text{S}(3)-\text{N}(2)$	149(2)	$\text{S}(3)-\text{N}(3)-\text{S}(4)$	138.6(8)
$\text{S}(3)-\text{N}(3)$	141(1)	$\text{N}(3)-\text{S}(4)-\text{N}(1)$	115.6(7)
$\text{S}(4)-\text{N}(1)$	145(1)	$\text{S}(4)-\text{N}(1)-\text{S}(1)$	147.3(8)
$\text{S}(4)-\text{N}(3)$	174(1)	$\text{N}(1)-\text{S}(1)-\text{S}(2)$	114.8(5)
$\text{S}(1)-\text{Cl}(1)$	311.2(6)	$\text{I}-\text{Cl}(1)-\text{S}(1)$	85.2(1)
$\text{S}(2)-\text{Cl}(1)$	306.8(6)	$\text{I}-\text{Cl}(1)-\text{S}(2)$	91.4(1)
$\text{I}-\text{Cl}(1)$	265.6(4)	$\text{Cl}(1)-\text{I}-\text{Cl}(2)$	179.8(5)
$\text{I}-\text{Cl}(2)$	250.3(4)		

is 210 pm, *i.e.*, a regular single bond taking into account the covalent radius of S (104 pm) [16].

The anionic unit ClICl^- is linear within instrumental resolution. The two I–Cl bonds are indeed different (250 and 266 pm), a result which certainly goes back to their differing coordinations. While the Cl(1) atom exhibits two contacts (307 and 311 pm) to the S(2) and S(1) atoms (that is, more than 50 pm shorter than the sum of the van-der-Waals radii [16]), the distances between Cl(2) and the atoms of the cationic ring (more than 346 pm) are probably nonbonding. Mayerle and coworkers already exemplified [7] that within the asymmetric trihalides the terminal halogen atom involved in the longest bond – Cl(1) inside $(\text{S}_4\text{N}_3^+)(\text{ClICl}^-)$ – is most closely surrounded by neighboring atoms. The orientation of cations and anions is not fully parallel; the ClICl^- unit is slightly canted (13°) with respect to the S_4N_3^+ rings between which it is sandwiched.

It is interesting to note that the lattice parameters of $\text{S}_4\text{N}_3\text{ICl}_2$ compare astonishingly well with those of $\text{S}_4\text{N}_3\text{Br}_3$; in fact, only the c axis is significantly (2%) shorter for the title compound. The decrease in molecular volumes when going from $\text{S}_4\text{N}_3\text{Br}_3$ to $\text{S}_4\text{N}_3\text{ICl}_2$, however, is also a bit larger ($3 \text{ cm}^3/\text{mol}$) than what would be expected based on tabulated [17] volume increments ($1 \text{ cm}^3/\text{mol}$).

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