$S_2N_3^+$: An Aromatic SN Cation with an N_3 Unit**

Sebastian Herler, Peter Mayer, Heinrich Nöth,
Axel Schulz,* Max Suter, and Martin Vogt

During a study of the known[1] thiazyl dichloride ion, $[NSCl_2]^-$, we investigated the Cl^- ion donor–acceptor properties of thiazyl chloride (NSCl). Since the NSX_2 group (X = F, Cl) can also act as a ligand and is stabilized by a covalent interaction of the N atom with metals (e.g. $Hg(NSF_2)_2$),[2] it was of interest to study the reaction of $NSCl/(NSCl)_3$ with $HgCl_2$ in CH_2Cl_2 as a potential route to $Hg(NSCl_2)_2$. By ^{14}N NMR spectroscopy small amounts of the NS^+ ion ($\delta = +201$), as well as the starting material ($NSCl/(NSCl)_3$), were detected, which indicates that in this reaction NSCl can function as a Cl^- ion donor. Surprisingly, crystals were obtained from the yellow CH_2Cl_2 solution. Raman, infrared (IR), and single-crystal X-ray studies of these crystals revealed a ring-shaped planar $S_2N_3^+$ ion (Figure 1) and an $Hg_2Cl_6^{2-}$ ion.[3]

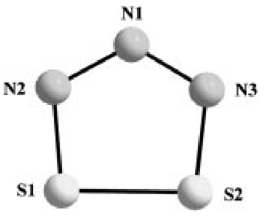

Figure 1. Molecular structure of the $S_2N_3^+$ ion.

The $S_2N_3^+$ ion represents the first binary SN ring with an N_3 unit. The other ring isomer of the $S_2N_3^+$ ion with one N atom between the two S atoms is not known. Although, the isovalence-electronic $S_3N_2^{2+}$ ion has been observed in the solid state by vibrational spectroscopy, this ring readily dissociates in liquid SO_2 into SN^+ and SNS^+ ions.[4] In contrast, the $\{[S_2N_3]^+\}_2[Hg_2Cl_6]^{2-}$ salt is stable at room temperature, is neither heat nor shock sensitive, and decomposes only above 80 °C. The formation of the $S_2N_3^+$ ion in the reaction of $NSCl/(NSCl)_3$ with $HgCl_2$ indicates a complex reaction. The $S_2N_3^+$ ion might be regarded as the product of a [3+2] cycloaddition of N_3^- and S_2^{2+} ions but this is rather unlikely in view of the starting materials. No evidence was found for the intermediate formation of N_3^- and S_2^{2+} ions. We assume that in the first step a Cl^- ion is abstracted from NSCl by dissolved $HgCl_2$ resulting in the formation of NS^+ and $HgCl_4^{2-}$ ions [Eq. (1)]. In the second step the NS^+ ion could formally react with two NSCl molecules yielding $S_2N_3^+$ and SCl_2 [Eq. (2)]. The formation of the anion [Eq. (3)] gives the overall reaction in Equation (4).

$$2\,NSCl + HgCl_2 \longrightarrow 2\,NS^+ + HgCl_4^{2-} \qquad (1)$$

$$2\,NS^+ + 4\,NSCl \longrightarrow 2\,S_2N_3^+ + 2\,SCl_2 \qquad (2)$$

$$HgCl_4^{2-} + HgCl_2 \longrightarrow Hg_2Cl_6^{2-} \qquad (3)$$

$$6\,NSCl + 2\,HgCl_2 \longrightarrow 2\,S_2N_3^+ + Hg_2Cl_6^{2-} + 2\,SCl_2 \qquad (4)$$

Interestingly, upon layering the CH_2Cl_2 solution with hexane, the $S_2N_3^+$ ion crystallizes with the previously unknown $Hg_3Cl_{10}^{4-}$ counterion (Figure 2). Because of the low solubility of $HgCl_2$ in CH_2Cl_2, the yield strongly depends on the reaction time and only small yields of the $S_2N_3^+$ salts were obtained (5–12 %). In addition, the formation of $S_4N_3^+$ salts was observed. However, the formation of both salts, $\{[S_2N_3]^+\}_4[Hg_3Cl_{10}]^{4-}$ and $\{[S_2N_3]^+\}_2[Hg_2Cl_6]^{2-}$, can be reproduced.

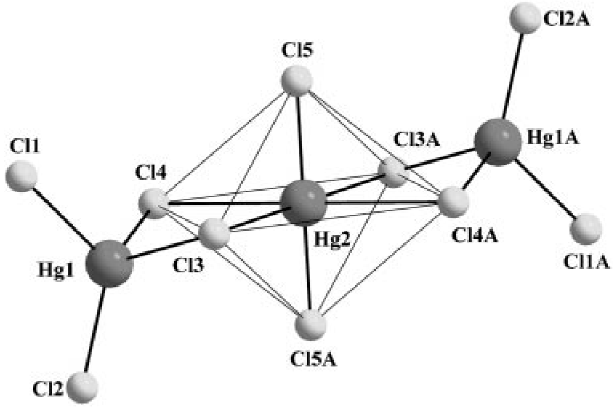

Figure 2. Molecular structure of the $Hg_3Cl_{10}^{4-}$ ion.

Ab initio (CCSD(T)) and density functional theory (DFT) calculations (B3LYP) indicate that the isolated $S_2N_3^+$ ion in the gas phase possesses a planar C_{2v} structure (Table 1). This prediction turns out to be correct for the salts as well: $\{[S_2N_3]^+\}_2[Hg_2Cl_6]^{2-}$ crystallizes in the triclinic space group $P\bar{1}$ with one independent $S_2N_3^+$ ion; $\{[S_2N_3]^+\}_4[Hg_3Cl_{10}]^{4-}$ crystallizes in the monoclinic space group $P2_1/n$ with two symmetry independent $S_2N_3^+$ ions. The C_{2v} structure of the $S_2N_3^+$ ion in $\{[S_2N_3]^+\}_2[Hg_2Cl_6]^{2-}$ is slightly distorted; the same holds for one $S_2N_3^+$ ion in $\{[S_2N_3]^+\}_4[Hg_3Cl_{10}]^{4-}$, whereas the second has almost exact C_{2v} symmetry (Table 1). The N–N bond lengths of 1.329–1.363 Å are substantially shorter than the sum of the covalent radii ($d_{cov}(N{-}N) = 1.4$ Å, $d_{cov}(N{=}N) = 1.2$ Å;[5] cf. 1.318–1.364 Å in tetrazoles),[6] which indicates partial double bond character for the N_3 unit. A similar situation is found for the N–S bonds (1.574–1.596 Å) which also lie in the range between a single and a double bond ($d_{cov}(S{-}N) = 1.74$, $d_{cov}(S{=}N) = 1.54$ Å;[6] cf. 1.572–1.593 Å in $S_4N_4Cl^+$, 1.58 Å in $S_3N_2^{2+}$, and 1.55 Å in $S_4N_3^+$).[4c, 7] The S–S bond length of 2.016–2.031 Å corresponds to a single bond ($d_{cov}(S{-}S) = 2.08$, $d_{cov}(S{=}S) = 1.88$ Å).[5] The N-N-N angle (ca. 120°) is rather

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[*] Dr. A. Schulz, S. Herler, Dr. P. Mayer,[+] Prof. Dr. H. Nöth,[+]
M. Suter,[+] M. Vogt[+]
Department Chemie
Ludwig-Maximilians-Universität München
Butenandtstrasse 5–13 (Haus D), 81377 München (Germany)
Fax: (+ 49) 89-21807492
E-mail: Axel.Schulz@cup.uni-muenchen.de

[+] X-ray investigation

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Table 1. Experimental and theoretical structural data for the $S_2N_3^+$ ion.

	$[S_2N_3]^+_2[Hg_2Cl_6]^{2-}$	$[S_2N_3]^+_4[Hg_3Cl_{10}]^{4-}$		B3LYP[a]	
		cation 1	cation 2	6-311+G(3df)	6-31G(d)
d(N1-N2) [Å]	1.329(9)	1.329(8)	1.336(8)	1.297	1.299
d(N1-N3) [Å]	1.348(10)	1.363(8)	1.337(9)	1.297	1.299
d(N2-S1) [Å]	1.574(6)	1.583(5)	1.582(5)	1.622	1.633
d(N3-S2) [Å]	1.583(5)	1.576(5)	1.596(6)	1.622	1.633
d(S1-S2) [Å]	2.016(2)	2.031(2)	2.023(3)	2.026	2.050
$\sphericalangle$(N2-N1-N3) [°]	119.9(6)	119.6(5)	120.3(6)	118.3	118.7
$\sphericalangle$(N1-N2-S1) [°]	114.9(5)	115.4(4)	114.6(4)	117.3	117.3
$\sphericalangle$(N1-N3-S2) [°]	114.3(5)	114.3(4)	114.5(5)	117.3	117.3
$\sphericalangle$(N2-S1-S2) [°]	95.7(2)	95.0(2)	95.6(2)	93.6	93.3
$\sphericalangle$(N3-S2-S1) [°]	95.3(2)	95.7(2)	95.0(2)	93.6	93.3

[a] CCSD(T)/6-31G(d): d(N1-N2) = 1.318, d(N1-S1) = 1.652, d(S1-S2) = 2.038 Å; $\sphericalangle$(N2-N1-N3) = 118.3, $\sphericalangle$(N1-N2-S1) = 117.0, $\sphericalangle$(N2-S1-S2) = 93.9°.

large compared to the N-N-S (114–115°) and N-S-S angles (95–96°; cf. N-N-N angles in tetrazoles ca. 113°).[6]

Over the past 30 years a large number of planar, binary molecules and ions containing only the elements sulfur and nitrogen have been isolated and characterized.[8, 9] This class of planar ring systems (e.g. $S_2N_2(6\pi)$, $S_3N_2^+(7\pi)$, $S_3N_3^-(10\pi)$, $S_4N_3^+(10\pi)$, $S_4N_4^{2+}(10\pi)$, $S_5N_5^+(14\pi)$), to which the novel $S_2N_3^+$ ion (6π) belongs, has electronic structures that are related to those of aromatic hydrocarbons.[10] With the exception of the radical cation $S_3N_2^+$, which is stabilized by a $\pi^*-\pi^*$ interaction upon dimerization,[4, 9, 11] these planar SN rings have $(4n+2)$ π electrons and therefore formally obey the Hückel rule for aromatic hydrocarbons.[12]

The π molecular orbitals (MOs) of the $S_2N_3^+$ ion are related to those of $C_5H_5^-$ and P_5^-. Both sulfur and nitrogen are more electronegative than carbon and phosphorous and therefore the π MOs of the $S_2N_3^+$ ion are of lower energy than those of the $C_5H_5^-$ and P_5^- ions.[4b] The degeneracy of the e_1'' and e_2'' π MOs is removed because of the lower symmetry of the C_{2v} $S_2N_3^+$ ion (Figure 3). Inspection of the occupied π MOs and the calculated electron-density distribution indicate that the π-electron density is mainly localized between the N–N and N–S centers. The calculated sulfur and nitrogen atoms-in-molecules (AIM) net charges are $Q_{S1/S2} = +0.89\,e$, $Q_{N1} = +0.12\,e$, and $Q_{N2/N3} = -0.45\,e$, respectively. These partial charges and the calculated bond orders (BO(N–S) = 1.72, BO(N–N) = 1.60, and BO(S–S) = 1.23) are in agreement with the experimentally observed short S–N and N–N bonds and the S–S single bond. The rather large positive partial charges (resulting in a large nuclear–nuclear repulsion) on both S atoms also contribute to the longer S–S bond, whereas, because of the small amount of S–S π overlap a shorter S–S bond would be expected.

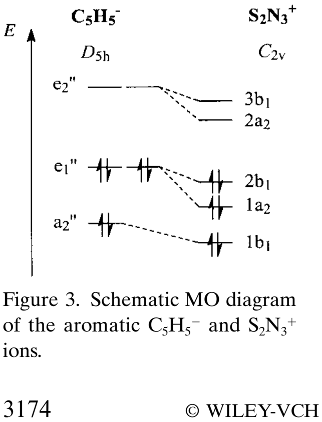

Figure 3. Schematic MO diagram of the aromatic $C_5H_5^-$ and $S_2N_3^+$ ions.

Structural variety within the chloro-mercurate(II) anions is surprisingly large.[13, 14] The formal stoichiometry rarely reflects the nature of the chloro-mercurate(II) anions in the crystal lattice. This diversity stems from the ability of mercury to form $Hg_xCl_y^{n-}$ ions with coordination numbers from three to six with chloro-mercury fragments connected through chloro bridges. Hence, mono- ($HgCl_4^{2-}$), di- ($Hg_2Cl_6^{2-}$, $Hg_2Cl_7^{3-}$), tri- ($Hg_3Cl_9^{3-}$, $Hg_3Cl_{12}^{6-}$), tetra- ($Hg_4Cl_{14}^{6-}$) oligo-, or polynuclear chloro-mercurate(II) anions have been observed. To our best knowledge, the $Hg_3Cl_{10}^{4-}$ ion is a new species. It can be assumed that in the reaction mixture of $NSCl/HgCl_2$ different chloro-mercurate(II) anions coexist in equilibrium.[13a]

The salts of the known $Hg_2Cl_6^{2-}$ ion (edge-sharing tetrahedra) crystallize from the polar solvent CH_2Cl_2 and have been identified in many compounds.[13, 14] Upon layering the CH_2Cl_2 solution with hexane the novel $Hg_3Cl_{10}^{4-}$ ion crystallizes (Figure 2). The decrease of the solvent polarity causes the insertion of a neutral $HgCl_2$ molecule between two $HgCl_4^{2-}$ ions. The interaction between these three fragments can be considered as a closed-shell interaction.[15, 16] Selected structural data of the $Hg_2Cl_6^{2-}$ and $Hg_3Cl_{10}^{4-}$ ions are summarized in Tables 2 and 3. The $Hg_3Cl_{10}^{4-}$ ion consists of two strongly distorted tetrahedral $HgCl_4^{2-}$ units each sharing one edge unsymmetrically (d(Cl3–Hg2) = 2.958 Å and d(Cl4–Hg2) = 3.079 Å; Table 3) with the $HgCl_2$ unit resulting in a formal highly distorted octahedral environment for the central mercury atom (Hg2). The $Hg_3Cl_{10}^{4-}$ ion has inversion symmetry and shows a great variety of different Hg–Cl bond lengths (2.335–3.079 Å; cf. 2.25–2.34 Å in $HgCl_{2(gas)}$, 2.25 Å

Table 2. Experimental structural data for the $Hg_2Cl_6^{2-}$ ion.

Bond lengths [Å]		Angles [°]	
Hg1-Hg1A	3.948(2)	Hg1-Cl3-Hg1A	92.11(4)
Hg1-Cl1	2.3662(13)	Cl1-Hg1-Cl2	144.40(7)
Hg1-Cl2	2.369(2)	Cl3-Hg1-Cl3A	87.89(4)
Hg1-Cl3	2.629(2)	Cl1-Hg1-Cl3	111.51(5)
Hg1-Cl3A	2.851(1)	Cl1-Hg1-Cl3A	97.77(5)

Table 3. Experimental structural data for the $Hg_3Cl_{10}^{4-}$ ion.

Bond lengths [Å]		Angles [°]	
Hg1-Hg2	3.865(0)	Cl1-Hg1-Cl2	113.86(5)
Hg1-Cl1	2.578(1)	Cl1-Hg1-Cl3	93.28(5)
Hg1-Cl2	2.406(1)	Cl1-Hg1-Cl4	106.71(5)
Hg1-Cl3	2.635(1)	Cl2-Hg1-Cl3	105.06(4)
Hg1-Cl4	2.433(2)	Cl2-Hg1-Cl4	130.43(5)
Hg2-Cl3	2.958(1)	Cl3-Hg1-Cl4	99.67(5)
Hg2-Cl4	3.079(1)	Cl3-Hg2-Cl4	79.84(4)
Hg2-Cl5	2.335(1)	Cl3-Hg2-Cl4A	100.16(4)

in $HgCl_{2(solid)}$)[17] and Cl-Hg-Cl bond angles ($\sphericalangle$Cl-Hg-Cl ca. 80–180°). Both bridging Hg1–Cl bonds (2.635 and 2.433 Å) and the terminal Hg1–Cl bonds (2.578 und 2.406 Å) are considerably longer than the axial Hg2–Cl5 bond (2.335 Å).

Experimental Section

General remarks: all experiments and manipulations were carried out under argon (Schlenk techniques). Prior to use all solvents were freshly distilled, dried, and stored under nitrogen. The starting material $(NSCl)_3$ was prepared according to the literature method.[18] $HgCl_2$ was purchased from Merck and dried under vacuum before use. NMR: Jeol Eclipse 400 (^{14}N NMR chemical shifts refer to $\delta(CH_3NO_2) = 0.00$); IR: Nicolet 520 FT-IR; Raman: Perkin Elmer Spectrum 2000R NIR FT.

$\{[S_2N_3]^+\}_4[Hg_3Cl_{10}]^{4-}$ (**1**): A solution of $(NSCl)_3$ (0.25 g, 1.02 mmol) in CH_2Cl_2 (10 mL) was added to $HgCl_2$ (0.42 g, 1.55 mmol). The light yellow mixture was stirred at ambient temperature for 16 h. The color changed to bright orange. The mixture was filtered through a glass sinter (G4). The clear yellow filtrate was allowed to stand for crystallization after layering with hexane (5 mL). (Besides the $[S_2N_3]^+$ salt we were able to isolate the $[S_4N_3]^+$ salt which was identified by its Raman spectrum.) Yield: 0.04 g (0.03 mmol, 11 %, based on $(NSCl)_3$); Raman (400 mW, RT): $\tilde{\nu} = 1180\,cm^{-1}$ (0.1, ν_a (NNN)), 859 (9, $\delta_{in\text{-}plane}$ (NNN)), 815/812 (2, ν_s (SN)), 516 (10, $\delta_{in\text{-}plane}$ ($S_2N_3^+$)), 443 (1, ν (SS)); $Hg_3Cl_{10}^{4-}$: 387 (3, br), 287(1), 157(2), 132(2), 130(2) cm^{-1}; IR (KBr): $\tilde{\nu} = 1238$ (s, br, ν_s (NNN)), 846 (s, $\delta_{in\text{-}plane}$ (NNN)), 812 (s, br, ν_s (SN)), 801 (vs, br, ν_a (SN)), 570 cm^{-1} (m, br, $\delta_{in\text{-}plane}$ ($S_2N_3^+$)).

Crystal structure analysis of **1**: $Hg_3Cl_{10}N_{12}S_8$, $M = 1380.91$, crystal size: $0.46 \times 0.05 \times 0.04$ mm, yellow rod, monoclinic, space group $P2_1/n$, $a = 8.8890(1)$, $b = 9.5688(1)$, $c = 17.1702(2)$ Å, $\beta = 95.3469(4)°$, $V = 1454.09(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.15397(7)\,Mg\,m^{-3}$, $\lambda = 0.448\,mm^{-1}$, $F(000) = 1244$. Nonius Kappa CCD, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 200(3)$ K, θ range $= 2.38$ to $27.49°$ in $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-22 \leq l \leq 22$, reflections collected: 29665, independent reflections: 3337 ($R_{int} = 0.0575$), observed reflections: 3014 ($F > 4\sigma(F)$). Structure solution program: SIR97,[19] direct methods, final R indices ($F > 4\sigma(F)$): $R1 = 0.0298$, $wR2 = 0.0937$ (all data), GOF on $F^2 = 1.269$, largest difference peak/hole: 3.583, -1.508 e Å^{-3}, program used: SHELXL-97.[20, 21]

$\{[S_2N_3]^+\}_2[Hg_2Cl_6]^{2-}$ (**2**): A solution of $(NSCl)_3$ (0.25 g, 1.02 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a suspension of $HgCl_2$ (0.42 g, 1.55 mmol). The light yellow mixture was stirred at ambient temperature for 16 h. The color changed via light green to orange. The mixture was filtered through a glass sinter (G4). The clear yellow CH_2Cl_2 phase was allowed to stand for crystallization. (Besides the $[S_2N_3]^+$ salt we were able to isolate the $[S_4N_3]^+$ salt which was identified by its Raman spectrum.) Yield: 0.05 g (0.06 mmol, 12 %, based on $(NSCl)_3$); Raman (400 mW, RT): $\tilde{\nu} = 1180\,cm^{-1}$ (0.1, ν_a (NNN)), 859 (9, $\delta_{in\text{-}plane}$ (NNN)), 812 (2, ν_s (SN)), 514 (10, $\delta_{in\text{-}plane}$ ($S_2N_3^+$)), 448 (1, ν (SS)); $Hg_2Cl_6^{2-}$: 381 (0.5, br); 286 (2, br), 142 (3, br), 120 (2) cm^{-1}; IR (KBr): $\tilde{\nu} = 1238$ (s, br, ν_s (NNN)), 846 (s, $\delta_{in\text{-}plane}$ (NNN)), 812 (s, br, ν_s (SN)), 801 (vs, br, ν_a (SN)), 570 cm^{-1} (m, br, $\delta_{in\text{-}plane}$ ($S_2N_3^+$)).

Crystal structure analysis of **2**: $Hg_2Cl_6N_6S_4$, $M = 826.2$, crystal size: $0.20 \times 0.04 \times 0.04$ mm, yellow rod, triclinic, space group $P\bar{1}$, $a = 6.0086(1)$, $b = 8.2445(2)$, $c = 9.2830(2)$ Å, $\alpha = 105.0320(11)$, $\beta = 99.2003(11)$, $\chi = 106.4211(14)°$, $V = 412.289(15)$ Å^3, $Z = 1$, $\rho_{calcd} = 3.32766(12)\,Mg\,m^{-3}$, $\mu = 20.062\,mm^{-1}$, $F(000) = 368$. Nonius Kappa CCD, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $T = 200(3)$ K, θ range $= 2.72$ to $27.48°$ in $-7 \leq h \leq 7$, $-10 \leq k \leq 10$, $-12 \leq l \leq 12$, reflections collected: 7569, independent reflections: 1881 ($R_{int} = 0.0581$), observed reflections: 1722 ($F > 4\sigma(F)$). Structure solution program: SIR97,[19] direct methods, final R indices ($F > 4\sigma(F)$): $R1 = 0.0330$, $wR2 = 0.0836$ (all data), GOF on $F^2 = 1.073$, largest difference peak/hole: 1.957, -1.979 e Å^{-3}, program used: SHELXL-97.[20, 21]

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