tions, 783 parameters, $wR2(F^2) = 0.081$, $R1$ (7545 data with $I > 2\sigma(I)$) = 0.039. All non-hydrogen atoms were refined anisotropically, the B-bonded hydrogen atoms isotropically. All other H atoms were considered with the riding model.

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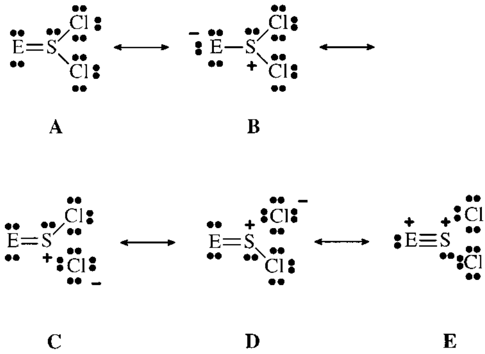
$NSCl_2^-$: Thiazyl Dichloride—An Aza Analogue of Thionyl Dichloride[**]

Elmar Keßenich, Felix Kopp, Peter Mayer, and Axel Schulz[*]

Formally, the $NSCl_2^-$ ion can be regarded as the isoelectronic aza analogue of thionyl dichloride ($OSCl_2$) with sulfur in the oxidation state +IV. $OSCl_2$ represents a highly polarized electron-rich species with a strong S–O bond and two labile S–Cl bonds (Scheme 1). Exchanging the oxygen atom for an N^- ion should result in S–Cl bonds which are further destabilized, and a strong N–S bond with a large amount of π character (bond order between 2 and 3).



Scheme 1. VB representation of $OSCl_2$ and $NSCl_2^-$ ($E = O, N^-$).

The $NSCl_2^-$ ion belongs to a new class of very labile ternary anions NSX_2^- (X = halogen) of which, to the best of our knowledge, no representative containing the "naked" anion has been structurally characterized[1] or synthesized in high yield. Most compounds containing the NSX_2 unit are stabilized by covalent interaction of the N atom with either a metal center, for example, $[Hg(NSF_2)_2]$[2–4] or organic groups as in $RNSCl_2$ ($R = R'C, R''SO_2, C_6F_5$, etc.).[5]

First we undertook a theoretical study of the acceptor properties of the Cl^- ion and the thermodynamics of NSCl. Ab initio (CCSD(T)) and density functional (B3LYP) calculations indicate a barrier-free attack of the Cl^- ion at the NSCl molecule resulting in the formation of the highly polarized $NSCl_2^-$ ion. This reaction represents an exothermic Lewis acid Lewis base reaction with an estimated molar enthalpy ΔH_{298} of $-124.6\ kJ\,mol^{-1}$ and a charge transfer Q_{CT} of 0.385 e

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[+] X-ray investigation

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

(B3LYP/6-311+G(3df)).[6] Therefore, it was our idea to start the synthesis of $NSCl_2^-$ from NSCl and Cl^- donors with bulky cations in polar solvents.

An easily accessible source for generating NSCl is the trimer $(NSCl)_3$. The chemistry of $(NSCl)_3$ shows a great diversity and has been investigated intensively. It has been known for a long time that the $(NSCl)_3$/NSCl equilibrium [Eq. (1)] strongly determines the chemistry of $(NSCl)_3$ and

$$(NSCl)_3 \rightleftarrows 3\,NSCl \qquad (1)$$

NSCl in solution.[7] On the basis of ^{14}N NMR spectroscopy studies Passmore et al. estimated the thermodynamic quantities of the $(NSCl)_3$/NSCl equilibrium (1) in solution to be $\Delta H^o = 65 \pm 13\ kJ\,mol^{-1}$ and $\Delta S^o = 206 \pm 20\ J\,mol^{-1}\,K^{-1}$.[8] Moreover, they concluded that both the forward and reverse reactions are kinetically very hindered. Impurities were assumed to "facilitate" the monomerization of the trimer. The influence of Cl^-, NH_4^+, and Cl_2 on the equilibrium has been investigated and, as a result, these compounds were ruled out as "facilitating agents" for the monomerization. The conclusion concerning the influence of the Cl^- ion is in contrast to our computational results, and indeed, upon adding a solution of $(NSCl)_3$/NSCl in CH_2Cl_2 to a solution of Ph_4PCl in CH_2Cl_2 an immediate reaction occurs as demonstrated by ^{14}N NMR spectroscopic studies [Eq. (2), Table 1].

$$NSCl + Cl^- \xrightarrow[RT,\ 24\,h]{CH_2Cl_2} NSCl_2^- \qquad (2)$$

Table 1. ^{14}N NMR chemical shifts (δ) and line widths ($\Delta\nu^{1/2}$).[a]

Species		δ	$\Delta\nu^{1/2}$ [Hz]
$[Ph_4P]^+[NSCl_2]^-$	^{14}N	+153	140
$[Ph_4P]^+[NSCl_2]^-$	^{15}N	+148	–
$[Ph_4P]^+[NSCl_2]^-$	^{15}N MAS[d]	+147	–
$[Ph_3BzP]^+[NSCl_2]^-$[b]	^{14}N	+153	140
$[(Ph_3PN)_2SCl]^+[NSCl_2]^-$	^{14}N	+153	140
$(NSCl)_3$[c]	^{14}N	−263	260
NSCl[c]	^{14}N	+329	80

[a] Chemical shift values are reported relative to neat nitromethane, solvent: CH_2Cl_2. [b] Bz = benzyl. [c] See Passmore et al.:[8]: δ (in CCl_4) = −264 ($(NSCl)_3$), +352 (NSCl); δ (in SO_2) = −259 ($(NSCl)_3$), +19 ($ClSNSCl^+$), +196 (NSF), +202(NS^+), +323 (NSCl).[d] MAS = magic angle spining.

Within seconds of adding the Ph_4PCl solution the dark green $(NSCl)_3$/NSCl solution turned bright yellow. After 24 h only one ^{14}N resonance signal was detected ($\delta = +153$) which can be assigned to the $NSCl_2^-$ ion. This resonance lies between those of NSCl $\delta = +329$ and $(NSCl)_3$ $\delta = -263$. The solution Raman spectrum showed a new very strong band at 1343 cm^{-1} assigned to the stretching mode of the S–N moiety. After removing the solvent a pale yellow solid was isolated, the Raman spectrum of which was consistent with pure $[Ph_4P]^+[NSCl_2]^-$. By comparison to the theoretically obtained data five new normal modes could be assigned to the C_s symmetric $NSCl_2^-$ ion (Table 2).[9] Compared to monomeric NSCl ($\nu_1 = 1323\ cm^{-1}$) the wave number of the S–N stretching mode ($\nu_1 = 1339\ cm^{-1}$) is increased indicating a shorter S–N bond. The normal modes ν_3 and ν_6 represent the symmetric and antisymmetric deformation vibrations of the entire $NSCl_2^-$ ion. The ν_2 and ν_5 motions can be described as the symmetric and antisymmetric stretch of the SCl_2 units, and ν_4 represents a deformation of the SCl_2 moiety. It is interesting to compare the IR/Raman data of the isoelectronic pair NSF_2^- and OSF_2 as well as $OSCl_2$ and $NSCl_2^-$.[1, 9, 10] Both NSX_2^- ions show a higher wave number for ν_1 than the OS analogue whereas the S–X (X = Cl, F) stretching modes appear at lower wave numbers.

Using $[Me_4N]Cl$, which is only very sparingly soluble in CH_2Cl_2, instead of $[Ph_4P]Cl$ results in a slow conversion of the white $[Me_4N]Cl$ suspension into a pale yellow precipitate. This pale yellow precipitate was found to be pure $[Me_4N][NSCl_2]$, regardless of the reaction stoichiometry ($[Me_4N]Cl$:NSCl = 1:1, 1:2, and 1:3). This result was confirmed by C,H,N analysis, Raman spectroscopy, and X-ray powder diffraction experiments.[11] When an excess of NSCl was used, unreacted NSCl/$(NSCl)_3$ remained in solution in accord with the stoichiometry. The $NSCl_2^-$ ion with $[(Ph_3PN)_2SCl]^+$[12] was also found as a side product (yield 10 %) in the reaction of $Ph_3PNSiMe_3$ with NSCl in a 1:3 ratio. The reaction of $(NSCl)_3$ with $Ph_3PNSiMe_3$ is very complex and depending on the reaction conditions different products are formed.[13]

To date, no structural data for a compound containing a "naked" NSX_2^- ion (X = halogen) have been published. In $[Hg(NSF_2)_2]$, the NSF_2 group is covalently attached to the Hg atom (d(N–S) = 1.439 Å).[4b] The single-crystal X-ray study of $[(Ph_3PN)_2SCl]^+[NSCl_2]^-$ revealed a slightly distorted C_s

Table 2. Experimental and calculated Raman and IR data.

Compound[a]					$\tilde{\nu}_{exp}$ [cm^{-1}][b]		
Assignment			$\tilde{\nu}_{calcd}$ [cm^{-1}]				
NSF_2^-	OSF_2	$OSCl_2$	$NSCl_2^-$		for C_s $NSCl_2^-$		B3LYP/6-311+G(3df)[c,d]
IR	IR	IR	IR	Raman			
1368	1333	1251	1338 (s)	1339 [10][e]	$\nu_1(A')$	$\nu(SN)$	1405 (96) [116][f]
500 (br)	808	492	302 (m)	308 [2]	$\nu_2(A')$	$\nu_s(SCl)$	304 (48) [9]
500 (br)	748	455	293 (m)	293 [2]	$\nu_5(A'')$	$\nu_{as}(SCl)$	300 (155) [1]
325 (br)	530	344	220 (m)	222 [4]	$\nu_3(A')$	$\delta_s(NSCl_2)$	210 (16) [15]
325 (br)	390	284	–	160 [3]	$\nu_6(A'')$	$\delta_{as}(NSCl_2)$	164 (84) [11]
–	410	194	–	–	$\nu_4(A')$	$\delta(ClSCl)$	69 (0.2) [11]

[a] Taken from refs. [1] and [9]; with $[(Me_2N)_3S]^+$ as counter ion of NSF_2^-. [b] cf. $(NSCl)_3$ (IR: $\tilde{\nu}$ = 1017(vs), 698(ms), 621(w), 514(m), 493(m), 385(m), 320(m) cm^{-1}).[31] [c] Unscaled frequencies; IR intensities [$km\,mol^{-1}$] in round brackets, Raman activities [$Å^4\,amu^{-1}$] in square brackets. [d] CCSD(T)/6-311+(2d): $\tilde{\nu}$ = 1310, 295, 311, 211, 169, 64 cm^{-1}. [e] cf. SN^+: $\nu_1(\Sigma_g) = 1434\ cm^{-1}$.[9] [f] Besides ν_1 there is a good agreement between experiment and theory. A similar large difference was found for the ν(S–N) in NSCl: B3LYP/6-311+G(3df): ν_1(S-N) = 1386(51) [41], ν_2(SCl) 406(128) [10], ν_3(N-S-Cl, bending) 268(14) [15]; exp.: NSCl (IR): $\tilde{\nu}$ = 1324(s), 415(m), 272(m) cm^{-1}).[32]

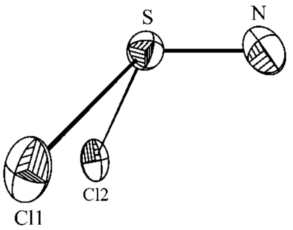

Figure 1. ORTEP drawing of the NSCl$_2^-$ ion in the [(Ph$_3$PN)$_2$SCl]$^+$ salt. Thermal ellipsoids set at the 25% probability level at 200 K.

symmetric anion (Figure 1) with a very short S–N bond (d(S–N) = 1.436 Å, cf. 1.416 in NSF$_3$(g),[14] 1.444 in OSCl$_2$(g),[15] 1.446 in NSF(g),[16] 1.450 in NSCl(g),[17] 1.42 in SN$^+$(s)[18]) and two loosely bound chlorine atoms d(S–Cl) = 2.423 Å, cf. 2.014 in SCl$_2$(g),[19] 2.076 in OSCl$_2$(g),[15] 2.161 in NSCl(g);[17] Table 3). NSCl$_2^-$ shows a relatively small Cl-S-Cl angle (93.3°) and a large N-S-Cl angle (112.8°) which is a consequence of the repulsive interaction between the S–N π bonds and the S–Cl σ bonds.

Table 3. Experimentally and theoretically obtained structural data of NSCl$_2^-$.

	[(Ph$_3$PN)$_2$SCl][NSCl$_2$]	B3LYP 6-311+G(3df)[a]	CCSD(T) 6-311+G(3df)[a]
S–N [Å]	1.436(6)	1.445	1.456
S–Cl [Å]	2.423(2), 2.427(2)	2.487	2.453
∢N-S-Cl [°]	112.76(19), 113.8(3)	114.4	113.9
∢Cl-S-Cl [°]	93.26(8)	102.4	99.9

[a] It should be emphasized that the computation was carried out for a single, isolated (gas-phase) anion in C_s symmetry. There may well be significant differences between gas-phase and solid-state data because of lattice effects. See also ref. [33].

The intriguing structural features of NSCl$_2^-$ can be rationalized by a qualitative valence bond (VB) consideration (Scheme 1). Canonical Lewis structures of types **A**–**E** are easily anticipated. In the structure **A**, the sulfur atom has expanded its valence shell to use d atomic orbitals (d-AO) to form an electron-pair π bond to either the oxygen or nitrogen atom. However, because natural atomic populations of the d$_{xy}$-, d$_{xz}$-, and d$_{yz}$-AOs are so small,[20] Lewis structures with an expanded valence-shell (such as **A**) would be expected to make very minor contributions to the ground-state resonance scheme.[21, 22] The calculated natural atomic population (NAO) net charges are $Q_S = +1.01$ e on sulfur, $Q_N = -0.79$ e on nitrogen, and $Q_{Cl} = -0.61$ e on both the chlorine atoms. These partial charges and the calculated bond orders (BO(NS) = 2.21, BO(SCl) = 0.23; cf. BO(SN, SN$^+$) = 2.76, BO(SN,NSCl) = 2.16, BO(SCl, NSCl) = 0.45, BO(SCl, OSCl$_2$) = 0.74, BO(SO, OSCl$_2$) = 0.98)[23] support the conclusion that resonance structures **C**–**E** are the primary structures for NSCl$_2^-$.[24] This is in accord with the short S–N bond and the long S–Cl bonds. For OSCl$_2$ a larger SCl bond order is estimated indicating that structure **E** is less important. Moreover, formal charge consideration for OSCl$_2$ indicate that the resonance structures **B**–**D** are the primary canonical Lewis structures.[25] Hence, the difference between the primary resonance scheme of OSCl$_2$ and NSCl$_2^-$ is the weight of structure **B** in the resonance scheme for OSCl$_2$ and the weight of structure **E** in the resonance scheme of NSCl$_2^-$. The NBO analysis of NSCl$_2^-$ corresponds to structure **E**. As indicated by an investigation of the noncovalent effects,[26] there is a significant interaction of the lone pairs (p-LP, localized in p-AOs) on both chlorine atoms with the two unoccupied, antibonding π* orbitals of the S–N triple bond. This intramolecular p-LP(Cl) → π*(N–S) donor–acceptor interaction (hyperconjugation) describes the rather long S–Cl bond[27] and corresponds to resonance between structures **C** ↔ **D** ↔ **E**. According to the NBO analysis, each of these interactions will involve a concerted delocalization of the two chlorine electrons. As indicated by Harcourt the concerted two-electron delocalization could have a higher energy than has a concerted one-electron delocalization. If this is the case, then increased-valence structures will provide a better primary VB representation of the electronic structure.[28]

Investigation of the molecular orbitals (MO) of C_s symmetric NSCl$_2^-$ ion revealed two MOs with N–S π-bonding character, one MO for the π_x electrons and one for the π_y electrons which, however, are further delocalized over the SCl$_2$ moiety stabilizing the weak S–Cl σ bonds, (Figure 2).[29] This can best be understood as the interaction of the π system of the SN$^+$ unit (S–N triple bond) with one lone pair of each Cl$^-$ ion. For the system: NS$^+$ + Cl1$^-$ + Cl2$^-$, the doubly occupied 3p$_x$(Cl1)-AO overlaps in a σ manner with the singly occupied 3p$_x$(S)-AO, and the doubly occupied 3p$_y$(Cl2)-AO also overlaps in a σ manner with the singly occupied 3p$_y$(S)-AO. The 3p$_x$(S)- and 3p$_y$(S)-AOs also overlap in a π_x and a π_y manner with the singly occupied 2p$_x$(N)- and 2p$_y$(N)-AOs, respectively. Therefore two 4-electron 3-center bonding units arise, with fractional S–Cl1 and S–Cl2 σ bonding, and fractional S–N π_x and π_y bonding.[28, 30] It is interesting to note that the resulting bonding MOs are composed of mostly p-AOs (on N, S and Cl; *no* d orbitals) whereas the nonbonding MOs are stabilized by a small amount of d-AOs localized on the S atom.

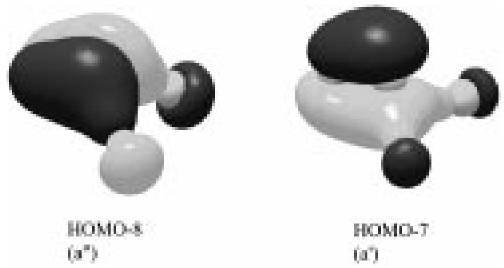

Figure 2. Delocalized bonding molecular orbitals of NSCl$_2^-$ describing the S–N π and the weak S–Cl σ bonds.

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[24] See also the discussion of on hypervalent sulfur compounds of the type NSX_mY_n (X, Y = O, Cl, F; $m = 1$; $n = 0$, 1, 2) in C. Ehrhardt, R. Ahlrichs, *Chem. Phys.* **1986**, *108*, 429 – 439.

[25] Because the oxygen possesses a positive formal charge structure **E** is counter intuitive and should have a very low weight.

[26] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO, Version 3.1, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI; b) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211 – 7218; c) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066 – 4073; d) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735 – 746; e) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926; f) A. E. Reed, P. von R. Schleyer, *J. Am. Chem. Soc.* **1987**, *109*, 7362 – 7373; g) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum, New York, **1988**, p. 227.

[27] NBO analysis: The second-order perturbation energy was computed according to Equation (3) (h^F = Fock operator). $2 \times \text{p-LP(Cl)} \rightarrow \pi_x^*(NS)$: $E^{(2)} = 30.0$ kcal mol^{-1} and $2 \times \text{p-LP(Cl)} \rightarrow \pi_y^*(NS)$: $E^{(2)} = 19.5$ kcal mol^{-1}.

$$\Delta_{\varphi\varphi^*}E^{(2)} = -2\frac{(\langle\varphi|h^F\varphi*\rangle)^2}{\varepsilon_{\varphi*} - \varepsilon_{Gf}} \qquad (3)$$

[28] a) R. D. Harcourt, *Eur. J. Inorg. Chem.* **2000**, 1901 – 1916; b) R. D. Harcourt in *Valence Bond Theory and Chemical Structure* (Eds.: D. J. Klein, N. Trinajstic), Elsevier, New York, **1990**; c) R. D. Harcourt, *Qualitative Valence Bond Descriptions of Electron-Rich Molecules*, Springer, Berlin, **1982**, p. 30.

[29] The N and S atoms are assumed to lie on the *z*-axis.

[30] This description is the simplest one, idealized for 90° bond angles. One elaboration would involve replacing $3p_x(Cl1)$ and $3p_y(Cl2)$ with the hybrid AOs ($3p_x + k3s$) on Cl1 and ($3p_y + k3s$) on Cl2 (k = mixing coefficient).

[31] G. G. Alange, A. J. Banister, B. Bell, *J. Chem. Soc. Dalton Trans.* **1972**, *22*, 2399 – 2400.

[32] A. Müller, N. Mohan, S. J. Cyvin, N. Weinstock, O. Glemser, *J. Mol. Spectrosc.* **1976**, *59*, 161 – 170.

[33] B3LYP/aug-cc-pvTZ: S−N = 1.453, S−Cl = 2.503 Å; ∢(N-S-Cl) = 114.0, ∢(Cl-S-Cl) = 104.0°; B3LYP/aug-cc-pv5Z: S−N = 1.443, S−Cl = 2.485 Å; ∢(N-S-Cl) = 114.3, ∢(Cl-S-Cl) = 102.9°.

A Homoleptic Carbene–Lithium Complex[**]

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The coordination chemistry of N-heterocyclic carbenes was given great impetus by the isolation of stable, free species by Arduengo.[1] Since then carbene complexes of nearly all the metals of the periodic table have been synthesized and studied in detail.[2, 3] As strongly nucleophilic two-electron donors the N,N-carbenes even form stable complexes with metals that normally show no tendency for π back-donation. Thus, a few years ago, Arduengo et al. were able to prepare a series of carbene complexes from the elements of Group 2.[4] However, to date there are very few examples of carbene complexes with Group 1 metals;[5–8] this is surprising as for the formation of "free" carbenes from the corresponding formamidinium and imidazolinium salts, even by the ammonia method of Herrmann et al.,[9] alkali metal containing bases such as KO*t*Bu, NaH, or lithiumdiisopropylamide are used in stoichiometric amounts as deprotonating agents. Thus, knowledge of the interactions between carbenes and alkali metals is essential for the understanding of the reactivity and properties of these complexes in solution.

In 1995 we were able to synthesize, for the first time, an Fe^{III} complex of the monoanionic, tridentate hydrotris(3-methyl-

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[+] X-ray analysis

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