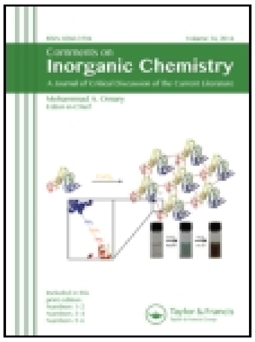


Taylor & Francis
Taylor & Francis Group

Comments on Inorganic Chemistry

ISSN: 0260-3594 (Print) 1548-9574 (Online) Journal homepage: http://www.tandfonline.com/loi/gcic20

Small Reactive Sulfur-Nitrogen Compounds and Their Transition Metal Complexes

Max Herberhold

To cite this article: Max Herberhold (1988) Small Reactive Sulfur-Nitrogen Compounds and Their Transition Metal Complexes, Comments on Inorganic Chemistry, 7:2, 53-72, DOI: 10.1080/02603598808072300

To link to this article: http://dx.doi.org/10.1080/02603598808072300

Small Reactive Sulfur-Nitrogen Compounds and Their Transition Metal Complexes

MAX HERBERHOLD
Laboratorium für Anorganische Chemie
der Universtität Bayreuth,
D-8580 Bayreuth,
Federal Republic of Germany

Salts containing thiazyl (SN^+), dithionitronium (S_2N^+) and sulfur diimide (SN_2^{2-}) ions can be used as sources for these small sulfur-nitrogen units in synthetic studies. The highly reactive molecules sulfur nitride (SN) and dinitrogen sulfide (N═N═S) are known as transients in the gas phase, and the existence of anionic species such as the radical $SN_2^{\overline{\cdot}}$ or dithionitrite (S_2N^-) has been deduced from electrochemical studies. The thionitroysl group (NS) is a versatile three-electron acceptor system in transition metal complexes; it is generally coordinated as a linear terminal ligand.

Key Words: *sulfur-nitrogen compounds, thiazyl salts, sulfur diimides, sulfur nitrides, thionitrosyl complexes*

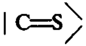
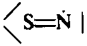
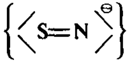
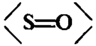
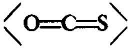
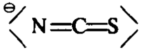
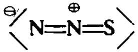
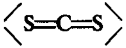
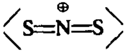
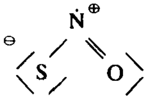
INTRODUCTION

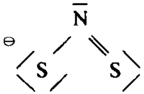
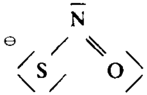
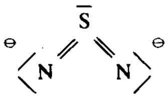
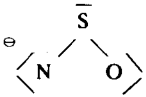
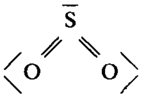
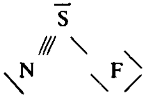
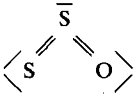
The generation and characterization of highly reactive molecules and ions is a challenge to both synthetic and structural chemistry. The following account deals with some small inorganic species containing sulfur-nitrogen multiple bonds. Table I contains a compilation of di- and triatomic species which are formally obtained

Comments Inorg. Chem.
1988, Vol. 7, No. 2, pp. 53–72
Reprints available directly from the publisher
Photocopying permitted by license only

TABLE I

Di- and triatomic species containing CS, SN and SO multiple bonds[a]

Number of Valence Electrons	CS	SN	SO
10			
11			
12			
16	 		
16			
16			
17			

18			
18			
18			

---

*Only one of the possible valence bond formulations is given in each case.

by combining the element sulfur with the representative nonmetal elements carbon, nitrogen, oxygen and fluorine.

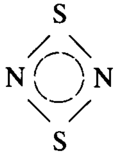
Following the pioneering work of M. Goehring and co-workers,[1] the chemistry of the sulfur-nitrogen compounds has undergone an astonishingly rapid development during the last two decades. In particular, the electron-rich sulfur-nitrogen rings and cages have attracted much interest.[2–5] Among the acyclic sulfur-nitrogen compounds, the conducting polymer polythiazyl, $(SN)_x$,[6] and the transition metal complexes of simple inorganic sulfur-nitrogen ligands[7,8] have been extensively studied.

In connection with these developments, the questions about existence, structure, stability and reactivity of the simple sulfur-nitrogen species presented in Table I have become of general interest. The following preparative approaches have been used:

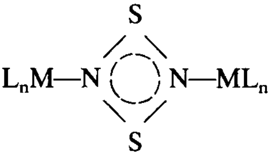
1. Synthetic procedures under rigorous exclusion of air and moisture and the use of suitable solvents have allowed the isolation of stable salts such as $SN^+AsF_6^-$, $SN_2^+SbF_6^-$ and K_2SN_2.
2. The (thermal or photochemical) generation of highly reactive molecules from suitable precursors has allowed the spectroscopic characterization of transients such as SN and SN_2, either in the gas phase at low pressures or in a low-temperature matrix.
3. The electrochemical reduction of stable sulfur-nitrogen species has allowed the identification of anions such as SN_2^- and S_2N^-.
4. The synthesis of transition metal complexes containing reactive molecules as ligands has allowed us to study species such as SN and HNS in coordination compounds. The reactive ligands can be generated or constructed in the protecting coordination sphere of the metal.

PREPARATION AND STRUCTURAL CHARACTERIZATION OF THE SULFUR-NITROGEN COMPOUNDS

Sulfur-nitrogen rings consisting of only three atoms are unknown (cf. Ref. 9). The smallest homoleptic ring known to exist is the strained disulfur dinitride, S_2N_2, which is the most important precursor for polythiazyl, $(NS)_x$.[6] A series of complexes containing S_2N_2 ligands has been described since 1980 (cf. Refs. 7 and 8); in most cases, the square-planar molecule is coordinated through both nitrogen atoms,[8] forming bridging ligands in which the SNS angle is found to be close to 95°.



∢SNS ca. 90°

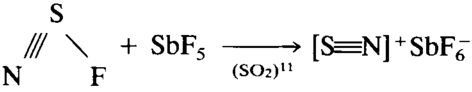


∢SNS ca. 95°

Although simple homoleptic compounds such as SN, SN_2 and S_2N are not available under normal conditions, stable salts of the cations SN^+ and S_2N^+ and of the anion SN_2^{2-} are known.

1. SALTS OF THE THIAZYL (SN^+) AND DITHIONITRONIUM (S_2N^+) CATIONS

The small sulfur-nitrogen cations are very sensitive towards nucleophiles and are therefore best prepared in liquid sulfur dioxide. Thiazyl salts were first obtained by Glemser and Koch[10] in 1971 and later investigated in more detail by Mews.[11–14] They are formed upon fluoride abstraction from thiazyl fluoride by Lewis acids, e.g.,[10,11]



The usual salts of the NS^+ cation contain anions such as AsF_6^- and SbF_6^-,[10,11] FSO_3^- and $CF_3SO_3^-$.[11] A more convenient starting material than NSF is the trimeric thiazyl chloride: Reaction of $N_3S_3Cl_3$ with $AgPF_6$ (1:3) in nitromethane gives solutions containing $SN^+PF_6^-$ which can be used *in situ*.[16] The analogous reaction of $N_3S_3Cl_3$ with excess $AgAsF_6$ in liquid sulfur dioxide leads to the pure salt $SN^+AsF_6^-$ in ca. 75% yield.[17]

$$N_3S_3Cl_3 + 3\ AgAsF_6 \xrightarrow[(SO_2)]{} 3\ AgCl + 3\ SN^+AsF_6^-$$

The SN bond in the SN^+ cation is stronger than in NSF, as may be deduced from the stretching frequencies (ν(SN) = 1437 cm^{-1} (R) in $SN^+AsF_6^-$ and 1361 cm^{-1} in NSF gas).[18] The internuclear distance in the NS^+ cation is now generally assumed to be 1.44 Å[19]; this calculated bond length agrees well with the experimental values from photoelectron spectroscopy (1.44 Å)[20] and from an X-ray structure determination of $NS^+Sb_2F_{11}^-$ at −151°C (1.42 Å).[15]

Short sulfur-nitrogen bonds are also observed for the linear dithionitronium cation, $[S{=}N{=}S]^+$, first described in 1978.[21] Thus, in the salt $S_2N^+SbCl_6^-$ the SN distance of 1.463(4) Å[21] has been taken to indicate some triple bond character. Similar short distances (1.464(5) and 1.472(5) Å) were reported for $S_2N^+AlCl_4^-$.[22] The corresponding bond length in the isoelectronic molecule carbon disulfide, $S{=}C{=}S$, is 1.55 Å.[23]

A practicable synthesis of the salt $S_2N^+AsF_6^-$ starting from tetrasulfur tetranitride has been developed,[24] giving reasonable yields (77%) in the presence of traces of bromine:

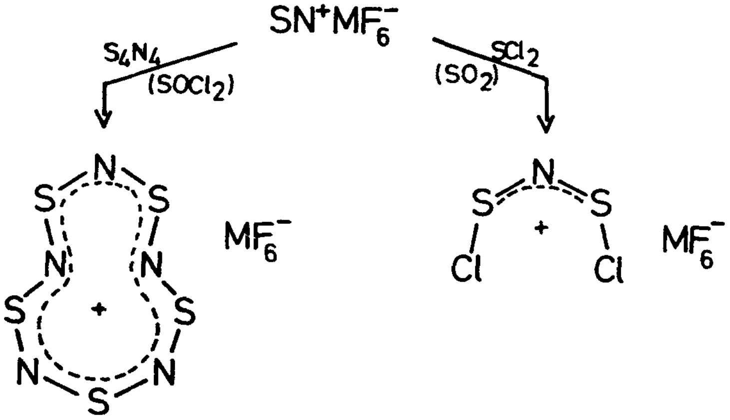
$$S_8 + 2\ S_4N_4 + 12\ AsF_5 \xrightarrow[(SO_2)]{(Br_2)} 8\ S_2N^+AsF_6^- + 4\ AsF_3$$

A particularly convenient preparation of the salt $S_2N^+SbCl_6^-$ is based on the reaction[25]

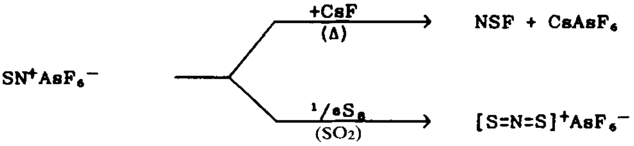
$$N_3S_3Cl_3 + 3\ SbCl_5 + \frac{3}{8}S_8 \xrightarrow[(SO_2)]{} 3\ S_2N^+SbCl_6^-$$

The yield (ca. 35%) is low, but pure samples are obtained since the side-products ($S_3N_2Cl^+SbF_6^-$ and $N(SCl)_2^+SbF_6^-$) can be extracted by liquid sulfur dioxide.[25]

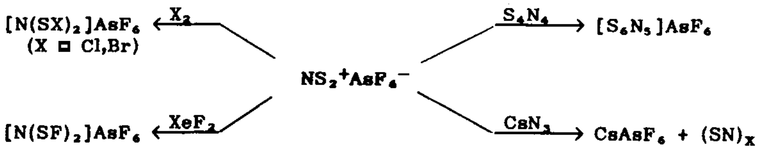
The cations SN^+ and S_2N^+ can be used to prepare other sulfur-nitrogen cations. Thus, the salts $SN^+MF_6^-$ (M = As, Sb) react[11] with S_4N_4 and SCl_2 under formal addition (cf. Ref. 18):



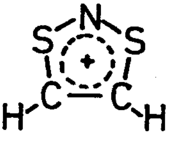
The insertion of SN^+ into the polar S–Cl bond of sulfenyl chlorides, RS–Cl (R = CF_3, $(CF_3)_2C{=}N$, Cl), appears to be a general reaction.[11,18] Treatment of $SN^+AsF_6^-$ with CsF and with elemental sulfur leads to the expected products[17]:

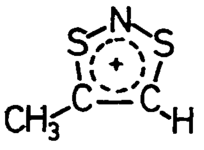


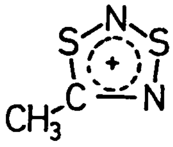
A series of reactions is similarly known to convert $[S{=}N{=}N]^+AsF_6^-$ into various sulfur-nitrogen derivatives[26]:



The preparation of heterocyclic cations by cycloaddition of the S_2N^+ cation (from $S_2N^+AsF_6^-$) to acetylene, propyne and acetonitrile is an essentially quantitative reaction[26]:







The hexafluoroarsenate salts of the small sulfur-nitrogen cations (SN^+, S_2N^+, $N(SCl)_2^+$) are efficient initiators for the polymerization of tetrahydrofuran.[27]

The thiazyl salts $SN^+MF_6^-$ (M = As,[13] Sb[12]) and solutions containing $SN^+PF_6^-$[16] have also been used to prepare cationic thionitrosyl complexes such as $[Re(CO)_5NS]^{2+}$,[12,13] $[CpMn(CO)_2NS]^+$,[13] $[CpFe(CO)_2NS]^{2+}$ [13] and $[Cr(CN^tBu)_5NS]^{n+}$ (n = 1, 2).[16] Insertion of thiazyl cations into metal halide bonds appears to open a new route to thiazyl halide complexes[28]:

$$Re(CO)_5X + SN^+AsF_6^- \longrightarrow [Re(CO)_5(NSX)]AsF_6$$

$$[X = Cl, Br)$$

2. SULFUR NITRIDE (SN) AND TRANSITION METAL THIONITROSYL COMPLEXES

In contrast to nitric oxide, NO, the monomeric radical sulfur nitride, SN, is only known as a short-lived transient in the gas phase. It is nevertheless a well-known molecule (cf. Refs. 29 and 30) as it is readily formed in electric discharges passing through sulfur vapor and dinitrogen, as well as by the interaction of "active nitrogen" or nitrogen atoms with a variety of sulfur compounds, e.g., S_8, S_2, H_2S, SCl_2 and S_2Cl_2. It has also been observed in methane flames doped with NH_3 and H_2S.[31] The optical spectra of SN both from the ground state and several electronically excited states have repeatedly been investigated (cf. Refs. 29 and 30) as have the vibrational and rotational states of the molecule and the EPR spectrum.

In Table II some characteristic parameters of the molecule SN and the cation SN^+ are compared with those of the related diatomic molecules N_2, CS, SO and S_2. Both NO and SN possess an unpaired electron in an antibonding molecular orbital, and a bond order in the range between 2 and 3 can be assigned to both molecules.

The formation of sulfur nitride, SN, in the controlled pyrolysis of S_4N_4 at 10^{-4} mbar has been studied by photoelectron spectroscopy.[32] Thermolysis over silver wool leads primarily to the cyclic dimer S_2N_2, which decomposes preferentially to SN at lower

TABLE II

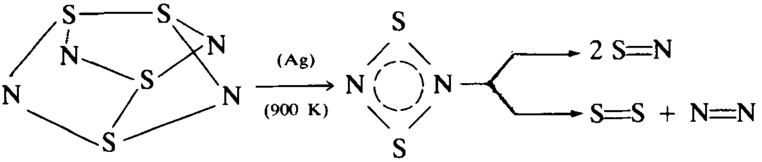
Characteristic data for SN and SN^+, and related diatomic molecules

	NN	CS	SN^+	SN	SO	SS
Number of valence electrons	10	10	10	11	12	12
Nuclear Distance [Å]	1.098	1.535	1.44	1.495	1.481	1.887
Stretching Frequency [cm^{-1}]	2330	1274	1437	1205	1136.7	719
Force Constant [$N\cdot cm^{-1}$][(a)]	22.39	8.35	11.86	8.34	8.12	4.88
Bond Enthalpy [$kJ\cdot mol^{-1}$][(b)]	945.33 ±0.59	698.7 ±8.4		464 ±21	521.70 ±0.13	425.28
Dipole Moment [D]	0	1.958 ±0.005	(3.89)	1.83 ±0.03	1.55 ±0.02	0

(a) Calculated from the stretching frequencies.

(b) D°_{298}, from J. A. Kerr, "*Strengths of Chemical Bonds*," in *Handbook of Chemistry and Physics*, 67th Edition (CRC Press, 1986-87), F-167.

temperatures (ca. 900 K) while S_2 and N_2 are obtained as main products at higher temperatures (ca. 1100 K):



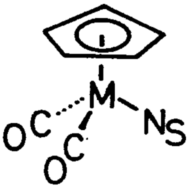
Mass spectral studies[33] on the pyrolytic decomposition of S_4N_4 also indicate that the (red) radical SN is generated via the (colorless) heterocycle S_2N_2 and slowly polymerizes to the (lustrous golden) chain-polymer polythiazyl, $(SN)_X$, which consists of alternating sulfur and nitrogen atoms.

Although free sulfur nitride SN is a highly reactive radical, it can also play the role of a stable three-electron acceptor ligand in transition metal compounds. Nearly 100 thionitrosyl–metal complexes have been characterized since 1974, and several reviews are available.[7,8,30,34] The preparative development of the field was certainly hampered by the fact that the free ligand is not available under normal conditions, and indirect methods are required to build the thionitrosyl ligand within the coordination sphere, e.g., by sulfurization of nitrido-metal complexes or by halide abstraction from either thiazyl fluoride or thiazyl chloride complexes. In most cases $N_3S_3Cl_3$, and occasionally S_4N_4, have been used as sources for the thionitrosyl ligand. The direct introduction of the SN group via thiazyl compounds $NS^+MF_6^-$ (M = P,[16] As,[13] Sb[12]) is possible but limited to the synthesis of cationic thionitrosyl complexes.

Transition metal complexes containing more than one thionitrosyl ligand (e.g., *cis*-$MCl_4(NS)_2$, M = Ru,[35] Os[36]) are still rare.

Thionitrosyl ligands are generally coordinated as terminal, linear units. In all structural studies reported so far (cf. Refs. 8 and 35), the metal-N-S angles are always found between 169° and 180°. In contrast to the transition metal nitrosyl complexes where both bent and bridging NO ligands are well known, no authentic cases of either bent or bridging thionitrosyl complexes are available so far.

Like the nitrosyl ligand, the thionitrosyl ligand is able to vary its donor–acceptor properties considerably, and NS stretching absorptions can be found in the wide range between 1050 and 1400 cm^{-1} (cf. free SN 1205 cm^{-1}, FSN 1361 cm^{-1}, SN^+ 1437 cm^{-1}).[18] The N–S bond distances vary between 1.45 and 1.59 Å (cf. Refs. 8 and 35). It is not helpful, however, to make a formal distinction between NS^+, NS and NS^- ligand systems. The charge of the complex has a decisive influence upon the extent of the metal-to-NS back donation, as may be seen from the ν(NS) frequencies of the isoelectronic half-sandwich complexes[13] of the type $[CpM(CO)_2NS]^{n+}$:



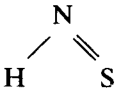
	ν(NS)[cm^{-1}]
$CpCr(CO)_2NS$	1154
$[CpMn(CO)_2NS]AsF_6$	1284
$[CpFe(CO)_2NS](AsF_6)_2$	1388

A comparison of analogous nitrosyl and thionitrosyl complexes[13,16,37] is particularly suited to demonstrate the electronic versatility of the thionitrosyl group.

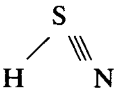
3. SULFIMIDE (HNS) AND THIAZYL HYDRIDE (NSH)

It is assumed that the radical nitrogen sulfide, SN, is able to take up one electron to give the anion $[SN]^-$. The large reduction of the (calculated) dipole moment from Sn (1.73 D) to $[SN]^-$ (0.09 D) is consistent with the expectation that the electron should be primarily attached to the sulfur end of the molecule.[38]

Salts containing the anion $[SN]^-$ are unknown, and protonated derivatives, i.e., the three-atomic molecules HNS or NSH, are not known in the free state either. According to *ab initio* MO calculations,[39] the sulfur imide isomer (a) is more stable than the thiazyl hydride form (b).

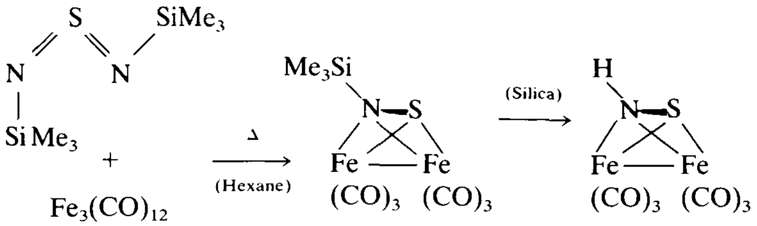


(a)



(b)

A coordination compound of sulfimide (a) has been obtained[40] by stepwise degradation of bis(trimethylsilyl) sulfurdiimide in the presence of carbonyliron complexes:



The trimethylsilyl derivative $Fe_2(CO)_6(Me_3SiNS)$ formed initially is converted to the sulfimide complex $Fe_2(CO)_6(HNS)$ by chromatography on silica. The HNS unit behaves as a six-electron ligand, it undergoes H/D exchange in D_2O to give $Fe_2(CO)_6(DNS)$ and is methylated by diazomethane to give $Fe_2(CO)_6(MeNS)$. Similar tetrahedrane complexes of the type $Fe_2(CO)_6(RNS)$, (R = ^{t}Bu,[41,42] p-tolyl,[42] phenyl[41]) have been described earlier. The tert-butyl complex $Ru_2(CO)_6(^tBuNS)$ has been structurally characterized[43]; the N–S bond (1.716 Å) is essentially a single bond and is arranged perpendicular to the Ru–Ru axis.

Sulfimide, HNS (a), is the parent compound of the organic thionitroso compounds which are, in general, unstable. However, N-thionitrosamines (= sulfinylamines) such as $Me_2N{-}NS$ have been synthesized,[44] and several complexes are known in which the ligand N-thionitroso-dimethylamine, $Me_2N{-}NS$, is always end-on coordinated through the sulfur atom.[45–47] The structures of $Cr(CO)_5(SN{-}NMe_2)$,[45] *cis*-$[PdCl_2(PPh_3)(SN{-}NMe_2)]$[46b] and $OsCl(tolyl)(CO){-}(PPh_3)_2(SN{-}NMe_2)$[47b] have been determined by X-ray structure analyses.

The isomeric ligand thiazyl-dimethylamine, $Me_2N{-}SN$, which is formally a derivative of thiazyl hydride, HSN (b), can be generated in transition metal complexes. Thus, the thiazyl fluoride complex $[Re(CO)_5(NSF)]AsF_6$[12] reacts under substitution of fluoride to a thiazyl amide compound in which the ligand $Me_2N{-}SN$ is end-on coordinated through the nitrogen atom[48]:

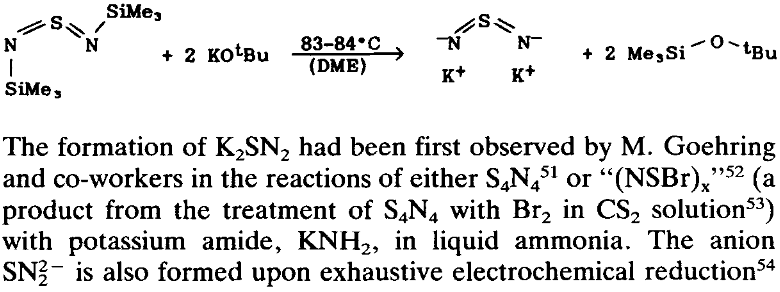
$$[\mathrm{Re(CO)_5(NSF)}]\mathrm{AsF_6} + \mathrm{Me_3Si{-}NMe_2} \xrightarrow[(\mathrm{SO_2})]{-30^\circ\mathrm{C}} [\mathrm{Re(CO)_5(NS{-}NMe_2)}]\mathrm{AsF_6} + \mathrm{Me_3SiF}$$

The analogous fluoride substitution using $(Me_3Si)_2NMe$ leads to a binuclear complex $[(CO)_5Re(NS{-}N(Me){-}SN)Re(CO)_5](AsF_6)_2$ which contains a bis(thiazyl)amine bridge.[48]

A number of coordination compounds containing thiazyl fluoride are known (cf. Refs. 7, 8 and 18), and many complexes containing thiazyl chloride (in the form of the "chlorothionitrene" ligand) have been synthesized by Dehnicke and co-workers since 1982 (cf. Refs. 7, 8 and 49). The pentacarbonylrhenium salts $[Re(CO)_5(NSX)]AsF_6$, $(X = F, Cl, Br)$[28] are particularly good model compounds.

4. THE SULFURDIIMIDE ($SN_2{}^{2-}$) ANION AND ITS DERIVATIVES

Pure samples of the light-yellow salt K_2SN_2 are prepared starting from bis(trimethylsilyl) sulfurdiimide in boiling dimethoxyethane (DME) solution in ca. 85% yield.[50]

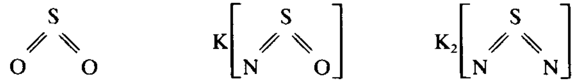


The formation of K_2SN_2 had been first observed by M. Goehring and co-workers in the reactions of either S_4N_4[51] or "$(NSBr)_x$"[52] (a product from the treatment of S_4N_4 with Br_2 in CS_2 solution[53]) with potassium amide, KNH_2, in liquid ammonia. The anion SN_2^{2-} is also formed upon exhaustive electrochemical reduction[54] of the cage compound S_4N_4:

$$S_4N_4 + 8\,e^- \xrightarrow[(CH_3CN)]{} 2\,SN_2^{2-} + 2\,S^{2-}$$

It is characterized by a strong ultraviolet absorption at $\lambda_{max} = 254$ nm ($\epsilon \approx 4 \times 10^4$ L/mol·cm).

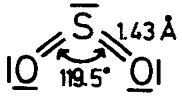
The sulfurdiimide dianion, SN_2^{2-}, is isoelectronic with the thionylimide anion, NSO^-, and with sulfur dioxide, SO_2. The frequencies of the three fundamental vibrations are comparable[50]:

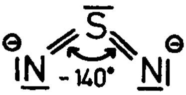


	(a)	(b)	(c)
$\nu_{as}[cm^{-1}]$	1360vs	1270vs	1198vs
$\nu_s[cm^{-1}]$	1151m	990vs	1001m
$\delta[cm^{-1}]$	518m	515vs	528m

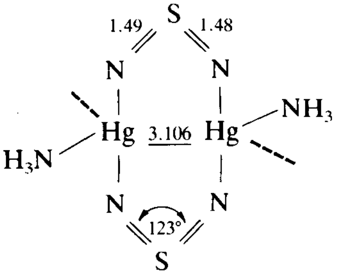
(a) Gas phase. (b) Ref. 55. (c) Nujol/Kel-F-3.

The valence force constant of the S=N bonds in K_2SN_2 (f = 6.5 N/cm) is considerably smaller than that of the S=O bond in SO_2 (f = 10.02 N/cm). The angle at the central sulfur(IV) in the SN_2^{2-} dianion may be estimated from the IR intensities of the ν_{as} and ν_s absorptions to be around 142°; calculations by Hartree–Fock–Slater methods indicate a flat energy minimum around 135°.[56] The corresponding angle in SO_2 is 119°. Both the reduced force constant and the large angle at sulfur indicate that the negative charge in the anion SN_2^{2-} is essentially localized at the terminal nitrogen atoms.



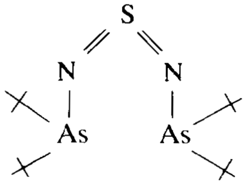


Aside from K_2SN_2 no other salts containing the sulfur diimide dianion are known (cf. Refs. 7, 8, 57 and 58). The mercury(II) derivatives $HgSN_2 \cdot NH_3$[59] and $HgSN_2$[52,60] contain Hg–N bonds. The yellow 1:1 adduct with ammonia consists of dimeric molecules $Hg_2(SN_2)_2(NH_3)_2$ which are connected to give a two-dimensional network.[58]

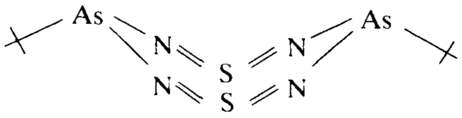


The salt K_2SN_2 can be used to prepare new sulfur diimide derivatives. Thus, the reactions with bulky organoarsines such as

^{t}Bu$_2$AsCl and ^{t}BuAsCl$_2$ lead to the pseudo-cyclic derivative ^{t}Bu$_2$As(NSN)As^{t}Bu$_2$[61] and to the eight-membered heterocycle ^{t}BuAs(NSN)$_2$As^{t}Bu,[62] respectively.

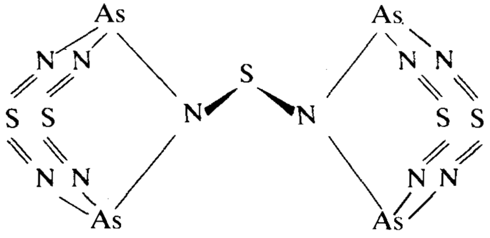


^{t}Bu$_2$As(NSN)As^{t}Bu$_2$[61]

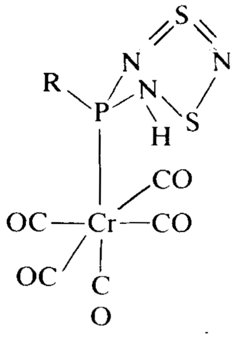


^{t}BuAs(NSN)$_2$As^{t}Bu[62]

A more complicated cage system, $As_4S_5N_{10}$, is obtained from the reaction (3:2) of K_2SN_2 with arsenic trihalides, AsX_3 (X = Cl, Br).[63] Cyclothiazene derivatives of phosphorus(III) are accessible from the reaction of the phosphorus halide complexes $Cr(CO)_5$ P^{t}BuCl$_2$ and $Cr(CO)_5PCl_3$ with excess K_2SN_2[64]:



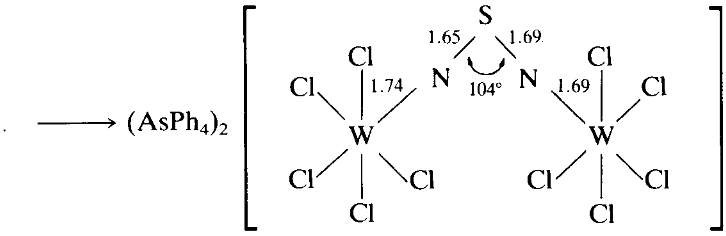
As_4 S_5N_{10}[63]



$Cr(CO)_5[P(R)S_2N_3H]$[64]
(R = ^{t}Bu, NH_2)

Attempts to incorporate the intact sulfurdiimide dianion, SN_2^{2-}, into coordination compounds have not been successful so far. However, a binuclear tungsten complex, $(AsPh_4)_2[Cl_5W(NSN)WCl_5]$ has been prepared by Dehnicke and co-workers[65] starting from chlorothionitrene compounds:

$$[WCl_4(NSCl)_2]_2 + 2\ AsPh_4Cl \xrightarrow[(CH_2Cl_2)]{} 2\ AsPh_4[WCl_5(NSCl)]$$

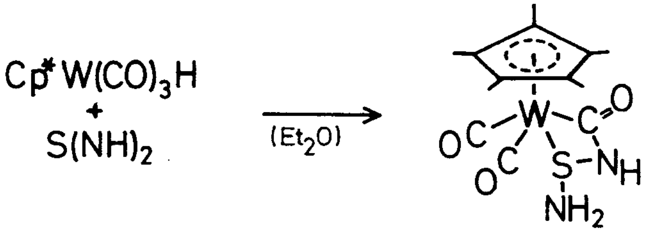


According to the X-ray structure analysis, the binuclear anion should not be considered as an adduct of the SN_2^{2-} anion with two WCl_5 units; the short W–N and long S–N distances as well as the small N–S–N angle are more compatible with a sulfur(II) bridging two nitridotungsten moieties,[65] e.g., $[Cl_5W{\equiv}N{-}S{-}N{\equiv}WCl_5]^{2-}$.

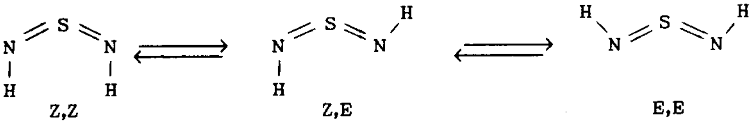
Protonation of the anion SN_2^{2-} by stoichiometric amounts of acetic acid in diethyl ether or THF gives yellow solutions containing $S(NH)_2$, the unstable parent compound of the sulfur diimides[66]:

$$K_2SN + 2\ CH_3COOH \xrightarrow[\text{(Ether)}]{} S(NH)_2 + 2\ CH_3COOK$$

Although $S(NH)_2$ cannot be isolated free from solvent, its structure may be deduced from that of the stable orange 1:1 adduct with the half-sandwich complex η^5-pentamethylcyclopentadienyl hydrido tricarbonyltungsten, $Cp^*W(CO)_3H$[67]:



Like all sulfur diimides bearing identical substituents, the parent compound $S(NH)_2$ can be present in three isomeric forms:

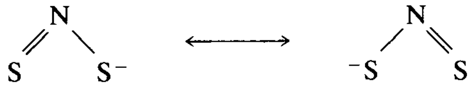


According to *ab initio* MO calculations[68] the configuration Z,Z is somewhat more stable than Z,E, while E,E is expected to possess considerably higher energy. Solutions of $S(NH)_2$ (in [D_8]-toluene) show temperature-dependent ^1H NMR spectra which have been interpreted to indicate mixtures of the Z,Z and Z,E isomers with the Z,Z form predominating.[66]

The formation of a radical anion $SN_2^{\overline{\cdot}}$ has been postulated both in chemical reactions[69,70] and in the electrochemical reduction of the $S_4N_5^-$ anion.[71] EPR studies show a five-line spectrum with a large coupling constant a_N in the range of 0.506 to 0.53 mT (cf. Ref. 71). The EPR spectra are consistent with delocalization of an electron over two equivalent nitrogen centers in a bent structure of C_{2v} symmetry.

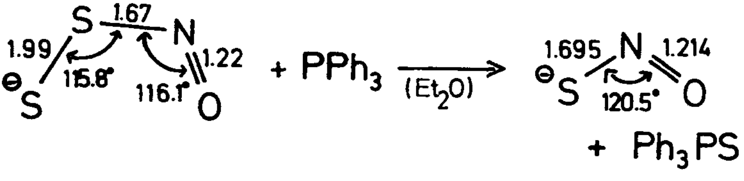
5. THE DITHIONITRITE (S_2N^-) ANION AND RELATED SPECIES

Electrochemical studies by Chivers and Hojo[72] have indicated that an anionic species S_2N^- is formed upon reduction of S_7NH and 1,4-$S_6(NH)_2$ at a platinum electrode, in addition to the anions S_4N^- and S_3N^- which can also be used as precursors. The S_2N^- anion is characterized by a strong UV absorption at λ_{max} 375 nm. According to HFS calculations[73] the ground state of this anion is expected to possess C_{2v} symmetry (with SN distances of ca. 1.57 Å and an NSN angle around 110°):



Addition of S_8 to an acetonitrile solution of the S_2N^- anion (375 nm) generates the S_4N^- anion (580 nm) immediately.[72]

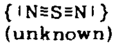
A bis(triphenylphosphane)iminium salt of the related monothionitrite anion, $PNP^+[SNO]^-$, has been structurally characterized.[74] The monothionitrite (= nitroso-sulfide) anion is obtained upon desulfurization of the perthionitrite (= nitroso-disulfide) ion[74,75]:

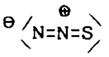


Salts of the nitroso-disulfide ion such as $PNP^+[S_2NO]^-$ are formed by nitrosation of polysulfide anions,[74,75] e.g., by the reaction of $(PNP)_2S_{12}$ with either NO or $PNP^+[NO_2]^-$.

6. DINITROGEN SULFIDE (N=N=S)

All attempts have been unsuccessful to oxidize the 18-electron sulfur diimide dianion, SN_2^{2-}, to the unknown 16-electron molecule sulfur dinitride, N≡S≡N. The formation of sulfur and dinitrogen in these experiments (e.g., with iodine, Ag^+ or NO^+ salts) is not unexpected, since *ab initio* MO calculations indicate that both linear and bent symmetrical NSN species are unstable.[39,76] The lowest-energy arrangement for the composition SN_2 is a linear NNS molecule of symmetry $C_{\infty v}$.





Dinitrogen sulfide, N=N=S, has been identified as the carrier of a CS_2/N_2 laser.[77] It is also assumed to be formed in the ion molecule reaction between azide and carbon disulfide in a flowing afterglow apparatus[78]:

$$[N{=}N{=}N]^- + S{=}C{=}S \longrightarrow [N{=}C{=}S]^- + N{=}N{=}S$$

In addition, convincing arguments for the generation of N=N=S can be deduced from the flash vacuum pyrolysis of 5-phenyl-1,2,3,4-thiatriazole and the corresponding photolysis (at 254 nm).[79] Both mass spectroscopy (m/e 60) and matrix-IR spectroscopy ($\nu = 2030$ cm^{-1}) support the formation of the reactive molecule N=N=S:

Although the species N=N=S is stable at 77 K, it decomposes upon slow warming to 160 K. A bimolecular decomposition process

$$2\,N{=}N{=}S \longrightarrow 2\,N_2 + S_2$$

appears to be plausible.[79]

CONCLUDING REMARKS

A large amount of information on small reactive molecules and ions of the sulfur-nitrogen family has been collected during the last few years. In further studies, electrochemical generation of paramagnetic species and matrix isolation techniques may become increasingly important. X-ray crystallographic studies of transition metal complexes may help to characterize ligands in the free state. It must be kept in mind, however, that "stabilization" of an unstable species in the coordination sphere of a metal may considerably alter its structure and electronic nature. Thus, a thionitrosyl ligand is quite different from the free radical sulfur nitride, and the bridging six-electron ligand HNS in the binuclear carbonyliron complex $Fe_2(CO)_6(HNS)$ may not really be comparable with the (elusive) free sulfimide molecule. It cannot be expected that "liberation" of unusual ligands from a transition metal complex will become a suitable method to generate reactive species.

References

1. M. Goehring, *Ergebnisse und Probleme der Chemie der Schwefel-Stickstoff-Verbindungen, Scientia Chimica*, Vol. 9 (Akademie-Verlag, Berlin, 1957).
2. H. G. Heal, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus* (Academic Press, London, 1980).
3. H. W. Roesky, Adv. Inorg. Chem. Radiochem. **22**, 239 (1979); Angew. Chem. **91**, 112 (1979); Angew. Chem. Int. Ed. Engl. **18**, 91 (1979).
4. R. Gleiter, Angew. Chem. **93**, 442 (1981); Angew. Chem. Int. Ed. Engl. **20**, 444 (1981).
5. T. Chivers, Acc. Chem. Res. **17**, 166 (1984); Chem. Rev. **85**, 341 (1985).
6. M. M. Labes, P. Love and L. F. Nichols, Chem. Rev. **79**, 1 (1979).
7. P. F. Kelly and J. D. Woollins, Polyhedron **5**, 607 (1986).
8. T. Chivers and F. Edelmann, Polyhedron **5**, 1661 (1986).
9. 1,2-Bis(fluoroalkyl)cyclo-1,2-diaza-3-sulfanes, $R_F\overline{NSN}R_F$ ($R_F = C_2F_5, CF_2Cl$) are assumed to exist in the form of a three-membered heterocycle: R. C. Kumar and J. M. Shreeve, J. Chem. Soc. Chem. Commun. 658 (1983); Inorg. Chem. **23**, 238 (1984).
10. O. Glemser and W. Koch, Angew. Chem. **83**, 145 (1971); Angew. Chem. Int. Ed. Engl. **10**, 127 (1971); An. Asoc. Quim. Argent. **59**, 143 (1971).
11. R. Mews, Angew. Chem. **88**, 757 (1976); Angew. Chem. Int. Ed. Engl. **15**, 691 (1976).
12. R. Mews and C. S. Liu, Angew. Chem. **95**, 156 (1983); Angew. Chem. Int. Ed. Engl. **22**, 158 (1983).
13. G. Hartmann and R. Mews, Angew. Chem. **97**, 218 (1985); Angew. Chem. Int. Ed. Engl. **24**, 202 (1985).

14. R. Hoppenheit and R. Mews, Chem. Ber. **118**, 4276 (1985).
15. W. Clegg, O. Glemser, K. Harms, G. Hartmann, R. Mews, M. Noltemeyer and G. M. Sheldrick, Acta Crystallogr., Sect. B **37**, 548 (1981).
16. M. Herberhold and L. Haumaier, Z. Naturforsch. **35b**, 1277 (1980).
17. A. Apblett, A. J. Banister, D. Biron, A. G. Kendrick, J. Passmore, M. Schriver and M. Stojanac, Inorg. Chem. **25**, 4451 (1986).
18. O. Glemser and R. Mews, Angew. Chem. **92**, 904 (1980); Angew. Chem. Int. Ed. Engl. **19**, 883 (1980).
19. C. Zirz and R. Ahlrichs, Inorg. Chem. **23**, 26 (1984).
20. J. M. Dyke, A. Morris and I. R. Trickle, J. Chem. Soc. Faraday Trans. II **73**, 147 (1977).
21. R. Faggiani, R. J. Gillespie, C. J. L. Lock and J. D. Tyrer, Inorg. Chem. **17**, 2975 (1978).
22. U. Thewalt, K. Berhalter and P. Müller, Acta Crystallogr., Sect. B **38**, 1280 (1982).
23. A. H. Guenther, T. A. Wiggins and D. H. Rank, J. Chem. Phys. **28**, 682 (1958).
24. A. J. Banister, R. G. Hey, G. K. MacLean and J. Passmore, Inorg. Chem. **21**, 1679 (1982).
25. A. J. Banister and A. G. Kendrick, J. Chem. Soc. Dalton Trans. 1565 (1987).
26. G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington and L. H. Sutcliffe, J. Chem. Soc. Dalton Trans. 1405 (1985).
27. S. A. Fairhurst, A. Hulme-Lowe, K. M. Johnson, L. H. Sutcliffe, J. Passmore and M. J. Schriver, Magn. Res. Chem. **23**, 828 (1985).
28. G. Hartmann and R. Mews, Z. Naturforsch, **40b**, 343 (1985).
29. H. G. Heal, Adv. Inorg. Chem. Radiochem. **15**, 375 (1972).
30. H. W. Roesky and K. K. Pandey, Adv. Inorg. Chem. Radiochem. **26**, 337 (1983).
31. J. B. Jeffries and D. R. Crosley, Combust. Flame **64**, 55 (1986); Chem. Abstr. **104**, 151 883g (1986).
32. H. Bock, B. Solouki and H. W. Roesky, Inorg. Chem. **24**, 4425 (1985).
33. E. Besenyei, G. K. Eigendorf and D. C. Frost, Inorg. Chem. **25**, 4404 (1986).
34. M. Herberhold, Nachr. Chem. Tech. Lab. **29**, 365 (1981).
35. U. Demant, W. Willing, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem. **532**, 175 (1986).
36. R. Weber, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem. **504**, 13 (1983).
37. M. Minelli, J. L. Hubbard, D. L. Lichtenberger and J. H. Enemark, Inorg. Chem. **23**, 2721 (1984).
38. P. A. G. O'Hare, J. Chem. Phys. **54**, 4124 (1971).
39. M. P. S. Collins and B. J. Duke, J. Chem. Soc. Dalton Trans. 277 (1978).
40. M. Herberhold and W. Bühlmeyer, Angew. Chem. **96**, 64 (1984); Angew. Chem. Int. Ed. Engl. **23**, 80 (1984).
41. S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem. **7**, 1833 (1968).
42. R. Meij, D. J. Stufkens, K. Vrieze, A. M. F. Brouwers, J. D. Schagen, J. J. Zwinselman, A. R. Overbeek and C. H. Stam, J. Organomet. Chem. **170**, 337 (1979).
43. M. Herberhold, W. Bühlmeyer, A. Gieren, T. Hübner and J. Wu, Z. Naturforsch. **42b**, 65 (1987).
44. W. J. Middleton, J. Am. Chem. Soc. **88**, 3842 (1966).
45. (a) H. W. Roesky, R. Emmert, W. Clegg, W. Isenberg and G. M. Sheldrick, Angew. Chem. **93**, 623 (1981); Angew. Chem. Int. Ed. Engl. **20**, 591 (1981).

(b) H. W. Roesky, R. Emmert, W. Isenberg, M. Schmidt and G. M. Sheldrick, J. Chem. Soc. Dalton Trans. 183 (1983).
46. (a) G. Tresoldi, G. Bruno, F. Crucitti and P. Piraino, J. Organomet. Chem. **252**, 381 (1983). (b) G. Tresoldi, G. Bruno, P. Piraino, G. Faraone and G. Bombieri, J. Organomet. Chem. **265**, 311 (1984).
47. (a) M. Herberhold and A. F. Hill, J. Organomet. Chem. **315**, 105 (1986). (b) A. Gieren, C. Ruiz-Perez, T. Hübner, M. Herberhold and A. F. Hill, J. Chem. Soc. Dalton Trans. (1988), in press.
48. G. Hartmann, R. Mews and G. M. Sheldrick, Angew. Chem. **95**, 753 (1983); Angew. Chem. Int. Ed. Engl. **22**, 723 (1983); Angew. Chem. Suppl. 945 (1983).
49. K. Dehnicke and U. Müller, Comments Inorg. Chem. **4**, 213 (1985).
50. M. Herberhold and W. Ehrenreich, Angew. Chem. **94**, 637 (1982); Angew. Chem. Int. Ed. Engl. **21**, 633 (1982); Angew. Chem. Suppl. 1346 (1982).
51. W. Berg and M. Goehring, Z. Anorg. Allg. Chem. **275**, 273 (1954).
52. W. Berg, M. Goehring and H. Malz, Z. Anorg. Allg. Chem. **283**, 13 (1956).
53. H. Vincent, Y. Monteil and M. P. Berthet, Synth. React. Inorg. Met.-Org. Chem. **10**, 99 (1980).
54. T. Chivers and M. Hojo, Inorg. Chem. **23**, 1526 (1984).
55. D. A. Armitage and J. C. Brand, J. Chem. Soc. Chem. Commun. 1078 (1979).
56. M. Conti, M. Trsic and W. G. Laidlaw, Inorg. Chem. **25**, 254 (1986).
57. J. Weiss, Fortschr. Chem. Forsch. **5**, 635 (1966).
58. H. Martan and J. Weiss, Z. Anorg. Allg. Chem. **515**, 225 (1984).
59. O. Ruff and E. Geisel, Ber. Dt. Chem. Ges. **37**, 1573 (1904).
60. D. Hänssgen and B. Ross, Z. Anorg. Allg. Chem. **473**, 80 (1981).
61. M. Herberhold, W. Ehrenreich and K. Guldner, Chem. Ber. **117**, 1999 (1984).
62. A. Gieren, H. Betz, T. Hübner, V. Lamm, M. Herberhold and K. Guldner, Z. Anorg. Allg. Chem. **513**, 160 (1984).
63. M. Herberhold, K. Guldner, A. Gieren, C. Ruiz-Perez and T. Hübner, Angew. Chem. **99**, 81 (1987); Angew. Chem. Int. Ed. Engl. **26**, 82 (1987).
64. B. Wrackmeyer, K. Schamel, K. Guldner and M. Herberhold, Z. Naturforsch. **42b**, 703 (1987).
65. U. Kynast, W. Willing, U. Müller and K. Dehnicke, Z. Anorg. Allg. Chem. **529**, 129 (1985).
66. M. Herberhold, W. Jellen, W. Bühlmeyer, W. Ehrenreich and J. Reiner, Z. Naturforsch. **40b**, 1229 (1985).
67. M. Herberhold, W. Jellen, W. Bühlmeyer and W. Ehrenreich, Z. Naturforsch. **40b**, 1233 (1985).
68. K. Raghavachari and R. C. Haddon, J. Phys. Chem. **87**, 1308 (1983).
69. D. Chapman and A. G. Massey, Trans. Faraday Soc. **58**, 1291 (1962).
70. R. Appel, I. Ruppert, R. Milker and V. Bastian, Chem. Ber. **107**, 380 (1974).
71. H. P. Fritz and R. Bruchhaus, Electrochim. Acta **29**, 947 (1984).
72. T. Chivers and M. Hojo, Inorg. Chem. **23**, 2738 (1984).
73. M. Trsic and W. G. Laidlaw, Theochem. **24**, 259 (1985); Chem. Abstr. **103**, 166 349r (1985 II).
74. F. Seel, R. Kuhn, G. Simon, M. Wagner, B. Krebs and M. Dartmann, Z. Naturforsch. **40b**, 1607 (1985).
75. F. Seel and M. Wagner, Z. Naturforsch. **40b**, 762 (1985).
76. W. G. Laidlaw and M. Trsic, Inorg. Chem. **20**, 1792 (1981).
77. F. X. Powell, Chem. Phys. Letters **33**, 393 (1975).
78. S. R. Kass and C. H. DePuy, J. Org. Chem. **50**, 2874 (1985).
79. C. Wentrup, S. Fischer, A. Maquestiau and R. Flammang, J. Org. Chem. **51**, 1908 (1986).