Fundamental chemistry of binary S,N and ternary S,N,O Anions: analogues of sulfur oxides and nitrogen oxido-anions

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Binary S,N anions, e.g., NSN− and SSNSS−, and related ternary S,N,O anions such as the structural isomers NSO/SNO− and SSNO are rarely mentioned in inorganic chemistry textbooks, despite the fact that their salts were synthesised and structurally characterised more than 30 years ago. These fundamentally important species and their conjugate acids, e.g. HNSO and HSNO, have been the focus of numerous investigations in recent years in view of their significance in disciplines as diverse as atmospheric chemistry and cell biology. This tutorial review provides a consolidated account of the fundamental chemistry including synthesis, spectroscopic characterisation, molecular and electronic structures, and properties of these intriguing species, and compares these aspects of their behaviour with those of isoelectronic sulfur oxides and nitrogen oxo-anions. A final section draws attention to the significance and applications of these simple S-N species in a broader context.

Key learning points
- Synthetic approaches for isolation and characterisation of thermally labile molecules
- Isoelectronic relationships between binary S,N anions, ternary S,N,O species and sulfur oxides or nitrogen oxo-anions
- Applications of 15N labelling for interpretation of vibrational and NMR spectra
- Relative stabilities of structural isomers of S,N,O molecules
- Significance of simple sulfur-nitrogen species in the gunpowder reaction, metal complexes, qualitative and quantitative analysis, atmospheric chemistry and cell biology

1 Introduction: historical background

Binary sulfur oxides, e.g. SO2 and SO3, and oxo-anions of nitrogen such as nitrite (NO−2), nitrate (NO−3) and peroxynitrite (OONO−) are simple, fundamentally important species of sulfur and nitrogen, respectively, that are discussed thoroughly in inorganic chemistry textbooks. The conjuction of sulfur and nitrogen chemistry generates a number of anionic species with sulfur–nitrogen bonds that are either isoelectronic (or isovalent) with these sulfur oxides or nitrogen oxo-anions, e.g. the structural isomers NSO/SNO−, the diion NSN−2, and the monoanions NSO2− and SSNO−. These anions receive scant attention in textbooks despite the fact that most of them have been known for more than thirty years (Chart 1).

The protonated molecules H(N=S)=NH, HNSO, HSNO and HNSO2 depicted in Chart 2 are the conjugate acids of the corresponding anions. Although HNSNH was identified spectroscopically in 1985, the experimentally difficult synthesis and characterisation of the three neutral S,N,O species have only been achieved in the last few years (see Section 2.2 for details).

Only one resonance form has been depicted for each species shown in Charts 1 and 2. The bonding in the molecules is generally more complicated and has been demonstrated by the bond parameters in different crystal structure determinations (Section 4) and by a number of molecular orbital calculations (Section 5). The bonding description is exemplified for HNSO in Scheme 1.

The impetus for the renewed interest in S,N and ternary S,N,O anions and their conjugate acids comes, in part, from biological communities, including biochemists. Indeed, the evidence for the involvement of the anions SNO− and SSNO− in the biological

![Chart 1 Binary S,N and ternary S,N,O anions. Only one resonance form has been depicted in each case.](image-url)
role of nitric oxide as a signaling molecule has been covered comprehensively in a recent Perspective by Feilisch et al. An up-to-date seminal contribution to this area of investigation is the identification of the neutral molecule HSNO as a “crucial intermediate linking H2S and nitroso chemistries” (Section 2.2). The coordination chemistry of ternary S,N,O anions is also of current interest. For example, it has been shown that transition-metal complexes of these anions are involved in the Gmelin test for the analysis of sodium nitroprusside Na3[Fe(CN)6NO] solutions (Section 6.2.2) and (b) the reaction of a terminal nickel(II) sulfide complex and nitric oxide (Section 6.2.3). In the context of atmospheric chemistry, binary S,N anions have been invoked as chromophores responsible for Jupiter’s Great Red spot.

The conjugate acids of S,N,O anions have also been the subject of contemporary experimental and computational investigations. Coordination to a main group element centre played a key role in the solid-state structural characterisation of the labile HNSO molecule (Section 2.2). The combination of flash vacuum photolysis coupled with matrix isolation IR spectroscopy has enabled the identification of monomeric HNSO, as well as the NSO and NO radicals (Section 2.2). As a complement to the experimental studies, the factors determining the relative stabilities of ternary S,N,O anions and their conjugate acids have been elucidated through quantum chemical computational investigations (Section 5).

In this Tutorial Review our objective is to discuss the fundamental chemistry of the S,N and S,N,O anions and their conjugate acids illustrated in Charts 1 and 2, respectively, in the context of isoelectronic (or isovalent) sulfur oxides or oxo-anions of nitrogen. The account will begin with a discussion of synthetic approaches to these species, which will be followed by sections describing their spectroscopic characterisation (including NMR, vibrational and electronic spectra) and molecular structure determinations by X-ray crystallography or microwave spectroscopy (for gaseous species). The contributions of computational studies to the elucidation of electronic structures and the relative stabilities of structural isomers are considered next. A final instalment will draw attention to the significance of these species in a variety of settings, including the gunpowder reaction, the formation of metal complexes, Lassaigne’s test and the Gmelin reaction, atmospheric chemistry and cell biology. For a general introduction to the area of sulfur-nitrogen chemistry the reader is referred to a recent book.

2 Synthesis

2.1 Binary S,N and ternary S,N,O anions

A versatile approach to the preparation of salts of binary S,N and ternary S,N,O anions in high yields entails the reactions of silylated derivatives with potassium tert-butoxide in ether solvents such as tetrahydrofuran (THF) or boiling dimethylether (DME), as exemplified by the high-yield syntheses of K[NSO] and K2[NSN] reported by Armitage and Herberhold, respectively: this process is favoured by the formation of the strong Si–O bond in the Me3SiO’Bu by-product [eqn (1) and (2)]. Other alkali-metal salts M[NSO] (M = Na, Rb, Cs) have also been prepared by the method shown in eqn (1), while Mews accomplished the synthesis of the soluble tris(dimethylamino)sulfonium (TAS) salt in liquid SO2; the latter transformation is driven by the elimination of volatile trimethylsilyl fluoride [eqn (3)].

\[
KO’Bu + Me3SiNSO → K[NSO] + Me3SiO’Bu \tag{1}
\]

\[
2KO’Bu + Me3SiNSNNSiMe3 → K2[NSN] + 2Me3SiO’Bu \tag{2}
\]

\[
[[Me2N]3S][Me2SiF2] + Me3SiNSO → [[Me2N]3S][NSO] + 2Me3SiF \tag{3}
\]

Although the sulfur-centred anions, NSO- and NSN2-, can be isolated as alkali-metal salts (vide supra), the nitrogen-centered SNO- and the catenated SSNE- (E = O, S) anions are much more labile and the use of a very large organic cation, e.g. bis(triphenylphosphino)iminium (PPN+), Ph4As+ or R3N+, is necessary for their successful manipulation in the solid state. For example, Seel demonstrated that the red anion SSNO- anion is produced by the reaction of an ionic nitride such as KNO2 with elemental sulfur or a polysulfide in acetone, dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) and can be isolated as the PPN+ salt (Section 4). Thirty years later Filipovic et al. re-investigated this synthesis using K3NO2, which allows monitoring the progress of the reaction by 31N NMR spectroscopy (Section 3.1). A resonance at -67 ppm (cf. 348 ppm for SSNO-), which is associated with a visible absorption band at 428 nm (cf. 448 nm for SSNO-), was assigned to the mononitrate ion SNO2- formed in the first step of the reaction [eqn. (4)]. Stable salts of SNO2- have not yet been isolated.

\[
1/8S8 + NO2^- → SNO2^- \tag{4}
\]
The propensity of Ph₃P for cleavage of S–S bonds with the formation of Ph₃P⁺S⁻ can be used to generate a new anion from a sulfur-rich precursor. Thus, Chivers et al., showed that the rapid reaction of Ph₃P with blue solutions of [PPN][SSNS] or [Ph₃As][SSNS]\(^{21}\) in acetonitrile produces the corresponding salts of the SSNS⁻ anion, which form orange solutions [eqn (5)].\(^{22}\) Similarly, Seele prepared the monothionitrite ion SNO⁻ by treatment of SSNO with one equivalent of Ph₃P in acetonitrile and isolated it as a PPN⁺ salt [eqn (6)].\(^{3}\) However, this simple procedure cannot be used to generate the dithionitrite ion S₂N⁻ from SSNS⁻ and the isolation of this important member of the family of binary S–N anions remains elusive (Section 3.3).\(^{23}\)

\[\text{SSNS}^- + \text{PPh}_3 \rightarrow \text{SSNS}^+ + \text{SPPH}_3 \quad (5)\]

\[\text{SSNO} + \text{PPh}_3 \rightarrow \text{SNO}^- + \text{SPPH}_3 \quad (6)\]

Although the NSO₂⁻ ion, isoelectronic with SO₃⁻, has been generated by the gas-phase reaction of the NH₂⁻ anion with SO₂F₂ [eqn (7)] and identified by a combination of experimental and theoretical methods,\(^4\) this fundamentally important species has escaped characterisation in the solid state (Section 3.2). The azidosulfurane anion SO₂N₃⁻, which has been isolated by Christe and co-workers as thermally unstable cesium and tetramethylammonium salts [eqn (8)],\(^{23}\) is a potential precursor for NSO₂⁻ via loss of N₂. However, mild heating of Cs[SO₂N₃] leads directly to the evolution of SO₂ and formation of cesium azide.\(^{23}\) This transformation is attributed to the remarkably long S–N bond in M[SO₂N₃] salts (M = Cs, 1.981(12) Å;\(^{23}\) M = Me₄N, 2.005(2) Å).\(^{24}\) Typical S–N bond lengths are given in Table 2. For comparison, the S–N bond in Cs[SO₂N₃] is substantially shorter (by 0.23 Å) as a result of the stronger Lewis acidity of SO₃ than that of SO₂.\(^{23}\)

\[\text{NH}_2^- + \text{SO}_2\text{F}_2 \rightarrow \text{NSO}_2^- \rightarrow \text{2HF} \quad (7)\]

\[\text{[Me}_4\text{N}]^+\text{N}_3^- + \text{SO}_2 \rightarrow \text{[Me}_4\text{N}]\text{SO}_2\text{N}_3^- \quad (8)\]

### 2.2 The conjugate acids HNSO, HNSNH, HSNO and HNSO₂

The neutral molecules HNSO, HNSNH, HNSNH and HNSO₂ are conjugate acids of the anions discussed in the previous section. In the absence of a stabilising cation, however, the chemical and isotopic isolation of these labile molecules is a challenging undertaking. Nevertheless, these targets have been accomplished in the last few years for the three S,N,O species by a combination of creative synthetic methodology and sophisticated characterisation methods.

The obvious route of direct protonation of the corresponding anion was employed by Herberhold to generate sulfur diimide HNSNH by treatment of K₁[NSN] with stoichiometric amounts of acetic acid [eqn (9)]; however, characterisation of this thermally labile molecule was limited to variable temperature \(^1\)H NMR spectra, which indicated the presence of two isomers in solution.\(^5\)

\[\text{K}_1[\text{NSN}] + 2\text{CH}_3\text{COOH} \rightarrow \text{HNSNH} + 2\text{CH}_3\text{COOK} \quad (9)\]

Monomeric thionylimide HNSO is a gas which, at low temperatures, forms a colourless liquid that quickly polymerises to a brown solid, polythionilimide ([HNSO]₄), at ambient temperature.\(^{25}\) In 2015 Schulz and co-workers invoked adduct formation with B(C₆F₅)₃ to stabilise HNSO, which was formed \textit{in situ} by protonation of K[NSO] with stearic acid (Scheme 2).\(^6\) Transition-metal complexes of the HNSO ligand, characterised only by IR and NMR spectra, were reported earlier by Mews et al.\(^26\)

In a biological environment S-nitrosothiols RSNO are important species for the storage and transport of nitric oxide with potential applications in the treatment of blood circulation problems (for a comprehensive discussion of the chemistry of RSNOs and HNSO, see ref. 9). In this context the simplest derivative thionitrous acid HSN₂O, a structural isomer of HNSO (Section 5.2), has been suggested to result from the reaction of H₂S with protein S-nitrosothiols. In 2012 Filipovic et al. confirmed the existence of HSN₂O under physiologically relevant conditions by a combination of spectroscopic techniques.\(^7\) Four years later McCarthy et al. showed that HSN₂O is formed in high concentration when NO and H₂S are mixed at room temperature on metallic surfaces.\(^10\)

Similar to the observations for HNSO, the parent N-sulfonylamine HNSO₂ has a tendency to associate in the condensed state and the cyclic trimer (HNSO₂)₃ has been isolated in early work.\(^{27}\) This behaviour mirrors the well-established trimerisation of the isoelectronic molecule sulfur trioxide SO₃ in the solid state. Monomeric HNSO₂ remained elusive until 2016 when Zeng et al. used flash vacuum photolysis of methoxysulfonyl azide CH₃OS(O)N₃ at ca. 1000 K to generate this simple N-sulfonylamide in the gas phase; the monomer was characterised by matrix isolation IR spectroscopy.\(^8\) This stepwise transformation occurs via a nitrene intermediate (Scheme 3). Upon 193 nm laser irradiation, HNSO₂ isomerises into the structural isomer N-hydroxysulfonilamine HONSNO (Section 5.2).

### 3. Spectroscopic characterisation

#### 3.1 NMR spectra

Nitrogen has two NMR-active isotopes ([¹⁴N], I = 1, 99.6%; [¹⁵N], I = ½, 0.4 %). Although the quadrupolar [¹⁴N] nucleus gives rise to broad lines, the [¹⁴N] chemical shift of the simple S,N and S,N,O species described in the previous sections is informative in view of the small N–S bond length which results in a reduced shielding. The weak nitrogen–sulfur bond in the dithionitrite ion S₂N⁻ stabilises the N backbonding in HNSO which explains the upfield shift of the [¹⁵N] resonance in the solid state compared to that of SO₂ (by 0.23 Å) as a result of the stronger Lewis acidity of SO₂.\(^{23}\)
of the broad range of values for this parameter.\textsuperscript{28} For example, the \textsuperscript{14}N NMR spectrum of a liquid ammonia solution of cyclo-S\textsubscript{3}N\textsubscript{2}H\textsubscript{3} containing KNH\textsubscript{3} shows well-separated signals for the acyclic SNSS and SSNSS anions as well as a singlet for the cyclic anion S\textsubscript{3}N\textsubscript{2}J.\textsuperscript{29}

The expense involved in the synthesis of \textsuperscript{15}N-enriched sulfur-nitrogen compounds, is justified by the advantage offered by \textsuperscript{15}N-labelled precursors for the characterisation of species with more than one nitrogen environment.\textsuperscript{28a} This benefit is nicely demonstrated by the identification of the acyclic SNSNH\textsuperscript{−} anion in the \textsuperscript{15}N NMR spectrum of a liquid ammonia solution of S\textsubscript{3}N\textsubscript{2}H\textsubscript{3} treated with two equiv. of KNH\textsubscript{3}. This spectrum is comprised of two mutually coupled resonances \(\textsuperscript{15}J(\textsuperscript{15}N, \textsuperscript{14}N) = 2\) Hz one of which exhibits a \(\textsuperscript{15}J(\textsuperscript{15}N, \textsuperscript{14}H)\) coupling of 55 Hz (Fig. 1).\textsuperscript{29}

The SNSS\textsuperscript{−} anion has not been characterized in the solid state. However, treatment of the cyclic tetraamide S\textsubscript{4}N\textsubscript{2}H\textsubscript{4} with two equivalents of the Wittig reagent Ph\textsubscript{3}P=CH\textsubscript{2} in THF produces a yellow solid, presumably \([\text{Ph}_3\text{P}]\text{S}[\text{S}\textsubscript{4}N\textsubscript{2}H\textsubscript{4}]\), which serves as an \textit{in situ} reagent for the preparation of the homoleptic nickel(II) complex Ni(S\textsubscript{4}N\textsubscript{2}H\textsubscript{4})\textsubscript{2} (Scheme 4).\textsuperscript{30}

In the absence of \textsuperscript{15}N-labelling, polarisation transfer techniques can be used to enhance the sensitivity of \textsuperscript{15}N NMR experiments. For example, the \textsuperscript{1}H-\textsuperscript{15}N HMQC (heteronuclear multiple quantum coherence) spectrum of a mixture of the cyclic diimide isomers 1,3-, 1,4-, and 1,5-S\textsubscript{3}N\textsubscript{2}(NH\textsubscript{2}), together with the trimides 1,3,5- and 1,3,6-S\textsubscript{3}N\textsubscript{2}(NH\textsubscript{2}), provides well-resolved \textsuperscript{1}H and \textsuperscript{15}N chemical shifts for each component; the \(\textsuperscript{15}J(\textsuperscript{15}N, \textsuperscript{1}H)\) values are in the range 91-94 Hz.\textsuperscript{32} This technique is also informative in discerning the presence of cis and trans isomers in a D\textsubscript{2}-toluene solution of the adduct HNSO-\textsubscript{2}B(\textsubscript{6}C\textsubscript{5}F\textsubscript{5})\textsubscript{2} (Scheme 3); the distinctive NMR parameters for the two isomers are \(\delta(\textsuperscript{1}H) = 10.4 \) and 10.6 ppm, \(\delta(\textsuperscript{15}N) = -95 \) and -106 ppm, and \(\textsuperscript{15}J(\textsuperscript{15}N, \textsuperscript{1}H) = 65 \) and 70 Hz.\textsuperscript{6}

The quadrupolar \(^{17}O\) nucleus (\(I = 5/2\)) has a very low natural abundance (0.04\%). In a singular example of the application of \(^{17}O\) NMR spectroscopy to the chemistry of S,N,O anions, Wu and co-workers have utilised the \(^{17}O\)-enriched complex to monitor the progress of the well-known Gmelin reaction between nitroprusside \([\text{Fe(CN)}\textsubscript{5}\text{NO}]\) and an aqueous solution of sodium sulfide [Section 6.2.2, eqn (10)].\textsuperscript{11} Significantly, time-dependent \(^{17}O\) NMR spectra led to the identification of the transient red-violet and blue intermediates that are formed in this reaction, \([\text{Fe(CN)}\textsubscript{5}\text{N}(\text{O})]\)\textsuperscript{4} and \([\text{Fe(CN)}\textsubscript{5}\text{N}(\text{O})\text{SS}]\)\textsuperscript{4}, respectively.

### 3.2 Vibrational (IR and Raman) spectra

Vibrational (IR and Raman) spectroscopy is a powerful characterisation method for S,N and N,S,O anions, e.g. for distinguishing structural isomers, since the polar S–N, S–O and N–O bonds are all IR-active. Raman spectroscopy is particularly useful for those containing S–S linkages because of the high polarisability of those bonds. Investigations of \(^{15}N\)-enriched samples is especially instructive, since vibrations involving the nitrogen atom can be unambiguously identified by the presence of satellite bands. Some examples of the application of these techniques are given below.

The bent (\(C_2\)) NO\textsuperscript{−} and NSO\textsuperscript{2−} anions give rise to simple IR spectra comprised of asymmetric and symmetric stretching modes (\(\nu_{as}\) and \(\nu_{s}\)) and a bending mode (\(\delta\)). The experimental values are compared with those of the isoelectronic SO\textsuperscript{−} molecule in Table 1.\textsuperscript{18} The stretching modes (\(\nu_{as}\) and \(\nu_{s}\)) for NSO\textsuperscript{2−} occur at lower frequencies (by 150-160 cm\(^{-1}\)) than those for SO\textsuperscript{−}. The similar values of all three vibrations for NSO\textsuperscript{−} salts indicate only minor interactions with the cation in the solid state.

Infrared spectroscopy proved to be decisive in the rebuttal of the claim for the isolation of \("\text{Cs}_2\text{[NSO}_2\text{]}\"\) from the hydrolysis of Me\textsubscript{3}NSNSiMe\textsubscript{3} with wet CsF; the identification relied primarily on the field ionisation mass spectrum of \("[\text{Ph}_3\text{P}][\text{NSO}_2]\"\).\textsuperscript{34} A subsequent detailed spectroscopic analysis of a bulk sample of \("\text{Cs}_2\text{[NSO}_2\text{]}\"\) showed it to be comprised mainly of the NSO\textsuperscript{−} anion with major IR bands at 1267, 989 and 509 cm\(^{-1}\) (cf. values for Cs[NSO\textsuperscript{−}] in Table 1); this conclusion was supported by the \(^{14}N\) NMR chemical shift of a solution of the bulk material.\textsuperscript{35} The calculated vibrational frequencies for NSO\textsuperscript{−} (g) are 1188 (symmetric stretching), 1049 (asymmetric stretching), 473 (symmetric bending) and 419 cm\(^{-1}\) (asymmetric bending).\textsuperscript{4}

<table>
<thead>
<tr>
<th>(\nu_{as}) (\text{cm}^{-1})</th>
<th>(\nu_{s}) (\text{cm}^{-1})</th>
<th>(\delta) (\text{cm}^{-1})</th>
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<tbody>
<tr>
<td>1360</td>
<td>1151</td>
<td>518</td>
</tr>
<tr>
<td>1283</td>
<td>999</td>
<td>528</td>
</tr>
<tr>
<td>1276</td>
<td>994</td>
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<td>1198</td>
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<td>528</td>
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</table>

\(\nu_{as}\) and \(\nu_{s}\) are primarily (80\%) S–N and S–O stretching modes, respectively, in the salts of NSO\textsuperscript{−}.\textsuperscript{18}

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\(\delta\) and \(\nu\) values are primarily (80\%) S–N and S–O stretching modes, respectively, in the salts of NSO\textsuperscript{−}.\textsuperscript{18}
In the absence of an X-ray crystal structure, vibrational spectroscopy of the $^{15}$N-labelled SS*N-anion ($^{15}$N = 30 % $^{15}$N) revealed an unbranched structure$^{22}$ by comparison with that of SS*NSS for which the linear cis,trans arrangement was established by X-ray crystallography (Section 4).$^{21}$ The latter anion exhibits two strong bands at 595 and 570 cm$^{-1}$ in the Raman spectra assigned to the two S=S stretching vibrations for the different S−S bond lengths (Chart 3). The Raman spectrum of SS*NSS has a prominent band at 574 cm$^{-1}$, which is readily attributable to an S=S bond consistent with an unbranched structure. In both anions the N=S stretching modes occur at higher frequencies and are easily identified by the presence of $^{15}$N satellites. Thus the structure of the SS*N-anion resembles that of peroxinitrite OONO$^{-}$ rather than the branched structure of the isoelectronic trihydrocarbodiimide CS$_3$.$^{36}$ The technique of neutralisation-reionisation and charge reversal mass spectrometry supports a S=S−N=S connectivity for neutral and ionic NS$_3$ species in the gas phase; however, this methodology was not able to distinguish between an unsymmetrical N=S−S=O arrangement or a cyclic structure for the triatomic molecule SS$_2$.$^{36}$

### 3.3 UV-visible spectra

Several S,N and S,O,N anions are highly coloured. Consequently, they exhibit strong, visible absorption bands with characteristic wavelengths, e.g. SSNS ($\lambda_{max}$ 582 nm)$^{22}$. SSNS ($\lambda_{max}$ 465 nm)$^{21}$ SSN$^{-}$ ($\lambda_{max}$ 448 nm in acetonitrile, 443 nm in acetonitrile) and SNO$^{-}$ ($\lambda_{max}$ 334). In common with $^{15}$N NMR spectroscopy, the technique of UV-visible spectroscopy can be used to monitor the course of reactions involving the formation of S,N and S,N,O anions and, in some cases, to detect new species. For example, the formation of NS$_2^-$ from the electrochemical or chemical reduction (with NH$_3$) of SS$^-$ has been proposed on the basis of the observation and absorption bands at $\lambda_{max}$ 375 nm in acetonitrile or 390 nm in NH$_3$ solution$^{24}$, respectively.$^{37}$ In a second example, the observation of an absorption band at 375 nm upon addition of an aminonitrite to a solution of elemental sulfur in acetonitrile has been attributed to the formation of NS$_2^-$ (Section 2.1).$^{20}$

UV-visible spectra have also been used to monitor the rapid formation of a bright yellow solution of [TAS][NSO] in acetonitrile with elemental sulfur to give a red intermediate, $\lambda_{max}$ 501 nm, cf. 448 nm for SSN$^{-}$. The red solution slowly becomes purple and subsequently turns dark blue owing to the formation of SSNSS ($\lambda_{max}$ 582 nm), which was also identified by $^{14}$N NMR spectroscopy.$^{35}$ The new red species was tentatively identified as “SSSSO”, which undergoes disproportionation to give the blue SSNSS$^{-}$ anion and unidentified sulfur-oxygen species.

### Table 2 Typical S=N, S=O and S=S bond lengths in Å

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Single bond</th>
<th>Example</th>
<th>Double bond</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(S=O)</td>
<td>1.7714(4)</td>
<td>H$_2$NSO$_3^-$</td>
<td>1.544(2)</td>
<td>(NSF)$_2$</td>
</tr>
<tr>
<td>d(S=O)</td>
<td>1.644(17)</td>
<td>R$_2$SOR$_2^-$</td>
<td>1.492(1)</td>
<td>R$_2$S$_2^-$</td>
</tr>
<tr>
<td>d(S=S)</td>
<td>2.0529(2)</td>
<td>Ss$^d$</td>
<td>1.908(16)</td>
<td>(RO):SS$^c$</td>
</tr>
</tbody>
</table>


### 4 Molecular structures

The solid-state molecular structures of salts of many of the anions discussed above have been established by X-ray crystallography. For the purpose of comparison, benchmark values of S−E (E = N, O) and S=S single and double bond lengths are given in Table 2. The structures of two alkali-metal salts M[NSO] (M = K, Rb) have been determined by X-ray powder diffraction analysis,$^{18}$ however the use of a large counter-cation is often necessary in order to enhance solubility and improve the stability of salts of S,N or S,N,O anions so that single crystals for X-ray analysis can be obtained. For example, single crystals of the tetramethylammonium salt [Me$_4$N][NSO] have been procured; however, the X-ray structural parameters are unreliable because the O and N atoms could not be distinguished.$^{33}$

As a cogent example of the protective influence of large cations, Mews et al. used the [K(18-crown-6)]$^+$ salt for the first structural determination of the NSN$^2$ dianion more than 20 years ago.$^{28}$

![Fig. 2 X-ray structure of [K(18-crown-6)][NSO]. The van der Waals radii of sulfur, nitrogen, and potassium are indicated as transparent spheres.](image-url)
years after its discovery (Fig. 2).\(^{39}\) In the solid state the NSN\(^2-\)
dianion exhibits modestly longer S–E bond lengths compared to
the corresponding distances in the isoelectronic SO\(_2\) molecule
(E = N, 1.484(3) Å; E = O, 1.4297(4) Å). The E–N–E bond angle (E
= N, 129.9(2)\(^\circ\); E = O, 117.5(1)\(^\circ\)) is significantly
widened in the dianion, presumably as a result of Coulombic repulsions
between the negatively charged N atoms.\(^{39}\)

The bulky PPN\(^+\) cation \((\text{[PPN]}\]N\(^+\)) has been particularly
effective in providing structural data for S,N and S,N,O anions.
For example, Chivers et al. employed the PPN\(^+\) cation to
determine the structure of the SSNSS\(^-\) anion after unsuccessful
attempts to crystallise the tetrabutylammonium \((\text{Bu}_4\text{N})^+\) salt.\(^{21,40}\) The acyclic SSNSS anion in the PPN\(^+\) and Ph\(_3\)As\(^+\) salts
adopts a sickle-shaped (cis,trans) conformation in the solid
state with a “short-long” sequence of S–N bond distances
associated with significantly different S–S bond lengths (Chart 3).
These investigations also revealed the likelihood of
rotational disorder in salts of small S,N or S,N,O anions with
bulky cations.\(^{40b}\)

Seel et al. also used the PPN\(^+\) cation to obtain single crystals
salts of the red SSNO\(^-\) anion and the thionitrite SNO\(^-\) anion and
determined their X-ray structures.\(^3\) Thirty years later Filipovic et
al. isolated small amounts of yellow crystals of [PPN][SSNO] in
addition to the usual red crystals; however, the structural
parameters for both crystal forms were identical within
experimental error.\(^{20}\) The bond lengths and bond angles of cis-
SSNO and cis,trans SSNSS are compared in Chart 3. The S–S and
S–N bond lengths are both significantly longer in SSNO than the
mean values of the corresponding bonds in SSNSS.

The SSNO\(^-\) anion has also been isolated as the \([\text{K}(18\text{-crown}-6)]\] salt in which it is coordinated to the potassium centre in a
\(\chi^2\) (S,O-bonded) fashion; however, the bond lengths in the anion are similar to those in [PPN][SSNO] (Fig. 3).\(^{12}\)

The X-ray structure of the adduct HNSO•B(C\(_6\)F\(_3\))\(_2\) confirmed
that the HNSO ligand retains the cis conformation (Fig. 4),\(^6\)
which was previously found in the gas phase by microwave
spectroscopy.\(^{41}\) The ligand is bonded to the strong Lewis acid
B(C\(_6\)F\(_3\))\(_2\) through the N atom (d(B–N) = 1.624(3) Å). Adduct
formation induces a modest perturbation of the bond distances
compared to the values for the monomer in the gas phase (d(S–N
= 1.530(2) vs 1.5123 Å; d(S–O) = 1.427(2) vs. 1.4513 Å) and a
significant narrowing of the N–S–O bond angle from 120.41\(^\circ\) in
the gas phase to 114.3(2)\(^\circ\) in the adduct.\(^{6,41}\)

The bond lengths of the structural isomer HSNO are of
particular interest in connection with the predisposition of this
molecule to undergo S–N bond cleavage and, hence, serve as a
source of NO in biological signaling pathways.\(^9\) A recent
investigation employing Fourier-Transform microwave
spectroscopy in conjunction with quantum chemical calculations
furnished exceptionally long S–N distances of 1.834(2) and 1.852(2) Å for cis and trans isomers (cf. Table 1),
respectively; consistently, the estimated bond dissociation
energy of 127.2 kJ mol\(^{-1}\) evinces an unusually weak S–N bond.\(^{10}\)

5 Computational studies

Quantum chemical computational investigations provide
important insights into the electronic structures of S,N and
S,N,O anions and their protonated precursors, as well as the
relative energies of structural isomers. In this section selected
examples chosen primarily from recent studies that have
employed high-level quantum chemical methodology will be
described to illustrate the understanding of the chemistry of
these species that can be gained by the application of
theoretical methods.

5.1 Electronic structures

Molecular orbital (MO) calculations for the 18-electron NSO-
anion reveal a four-electron three-centre $\pi$-system (Fig. 5).\(^6\) The
double occupied MOs, $\psi_{\text{MO1}}$ and $\psi_{\text{MO2}}$, can be viewed
essentially as bonding and non-bonding, respectively. The
molecular orbital coefficients indicate that $\psi_{MO2}$ is in fact weakly bonding with respect to the NS bond and weakly antibonding regarding the SO bond.

5.2 Structural isomers

Simple triatomic species may exist as structural isomers that differ in the identity of the central atom, e.g. OCN (cyanate) and CNO (fulminate); such isomers often have significantly disparate stabilities. In the case of S_N,O anions this phenomenon pertains to the anions NSO and SNO with either sulfur or nitrogen as the central atom. In the case of the tetraatomic NSO$_2$ anion, the number of possible structural isomers is considerably greater. In this section the insights provided by theoretical calculations regarding the relative energies of structural isomers of S_N,O anions and their conjugate acids, as well as their interconversion energies, will be discussed in the context of experimental findings.

During the past 30 years there have been several calculations of the relative stabilities of the structural isomers NSO- and SNO- in the gas phase with very diverse conclusions depending on the methodology employed. A recent study using accurate ab initio approaches and large atomic basis sets concludes that NSO- is more stable than SNO- by ca. 96 kJ mol$^{-1}$. The calculated barrier to intramolecular isomerisation involving oxygen transfer, possibly via a cyclic transition state, is estimated to be ca. 464 kJ mol$^{-1}$.

In a broad-ranging investigation Dixon and co-workers calculated thermodynamic parameters for the structural isomers of the elemental combinations [HNOS], [HNO$_2$S] and [HNOS$_2$]. The main findings can be summarised as follows:

(a) As found experimentally for the combination [HNOS], the cis isomer of HNSO is more stable than the trans form (a geometrical isomer) (Section 4), but by only a small amount, ca. 12 kJ mol$^{-1}$. However, the structural isomers NSOH and cis- or trans-HNSO are ca. 164.4 and 161.5 kJ mol$^{-1}$ higher in energy, respectively, than cis-HNSO (Fig. 6a).

(b) Similarly, as determined experimentally, the most stable isomer of [HO$_2$NS] has the branched structure HNSO$_2$ (cf. SO$_3$), (Section 2.2), which is estimated to be more stable than the unbranched isomer HNSO by 76.6 kJ mol$^{-1}$.

Zeng and co-workers estimate this energy difference to be 44.3 kJ mol$^{-1}$. The thionitrate isomer HSNO$_2$ lies ca. 179.9 kJ mol$^{-1}$ above the N-sulfonlamine HNSO$_2$ (Fig. 6b).

(c) In the case of [HNOS]$_2$ the most stable arrangement is the unbranched isomer HSNO$_2$, which lies ca.64.0 kJ mol$^{-1}$ below the branched linkage isomer HNSO$_2$(O)S (Fig. 6c).

Taken together, these findings for the heats of formation of the conjugate acids of S,N,O anions point to some important conclusions regarding the stability of these species. Firstly, molecules that incorporate the NSO unit are thermochemically more stable than those with the SNO arrangement. Secondly, consideration of calculated bond energies indicate there is a preference to maintain the S=O rather than the N=O bond upon dissociation.

6 Significance in various settings

This final section draws attention to the established and potential relevance of S,N and S,N,O anions in a variety of environments. As mentioned in Section 1, the controversial role of the anions SNO and SSNO and their conjugate acids in biological signaling involving nitric oxide has been addressed thoroughly in a recent Perspective by Feilisch et al.

Consequently, the coverage of that topic in this Tutorial Review is limited to contributions which have appeared since the publication of the Perspective. Specifically, readers are referred to (a) the characterisation of HSNO from the reaction of NO and H$_2$S as a “crucial intermediate linking H$_2$S and nitroso chemistries” (Section 2.2), (b) the identification of the intermediates formed in the Gmelin reaction (Section 6.2.2), (c) investigations of transition-metal complexes of the SSNO- anion in connection with the role of transition-metal sulfides in this chemistry (Sections 6.2.3), and (d) the formation of SSNO- from the reaction of persulfides RSSH with nitrite ion NO$_2^-$.

![Fig. 5 MO diagram of the n system in NSO (Reproduced with permission © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) ](image)

![Fig. 6 Calculated heats of formation $\Delta H(298)$ (kJ mol$^{-1}$) and bond lengths (Å) of selected structural isomers of (a) [HNOS], (b) [HNO$_2$S], and (c) [HNOS$_2$].](image)
6.1 The gunpowder reaction

Gunpowder (also known as black powder) has been used as an explosive material since the middle ages. It comprises of a mixture of potassium nitrate, charcoal and sulfur. The role of charcoal is to reduce the nitrate to nitrite, which reacts with sulfur to produce a combustible material that undergoes a highly exothermic decomposition with the release of various gases including CO₂ and N₂O as well as oxo-anions of sulfur. Seel’s discovery of the SSNO⁻ anion emanated from efforts to understand the chemistry of the gunpowder reaction through studies of the nitrite-sulfur interaction in solution (Section 2.1). The spectroscopic identification of the initial product of this reaction, the monothionitrate anion SNO₂⁻, has only been achieved very recently [eqn (4)].

6.2 Metal complexes

The formation of metal complexes of S, N and S,N,O anions discussed in this section has significance for understanding the coordination behaviour (bonding modes) of these potentially ambidentate ligands, as well as in certain analytical applications and in the elucidation of the role of NO in biological settings.

6.2.1 Metathetical reactions. The availability of direct syntheses of salts of simple S, N and S,N,O anions such as NO⁻ and NSO⁻ furnished a straightforward source of coordination complexes of these ligands via metathetical reactions with halides of main group elements or transition metals. In typical examples, e.g. Cp₂Ti(ONO)₂, Ph₃As(NSO)₃ (x = 1, 2), the NSO⁻ ligand is κ¹ (N-bonded) whereas the NSO²⁻ dianion may act as a bridging ligand between two metal centres.

Conversely, the discovery of transition-metal complexes has provided the impetus for the synthesis of ion-separated salts of certain S,N anions. For example, the isolation of a few crystals of the homoleptic nickel(II) complex Ni(S,Si)Cl₃ from the reaction of S₄Cl₂ with NiCl₂ in methanol was followed almost 25 years later by the characterisation of the PPN⁺ and Ph₃As⁺ salts of the SSNS⁻ anion [Section 2.1, eqn (5)], which have been used as metathetical reagents for the preparation of copper (II) complexes, e.g. [PPN][Cu(S,Si)Cl]₃, in which the SSNS⁻ ligands are S,S-bidentate. In a similar vein, although the acyclic SNSNH⁻ and SSNS²⁻ anions are frequently encountered in metal complexes, they have not been characterised as ion-separated salts; however, the in situ reagent [Ph₃MeP][SNSNH] has been used for the preparation of the homoleptic nickel (II) complex Ni(SNSNH)₂ (Scheme 4).

6.2.2 Lasaigne’s test and the Gmelin reaction. Lasaigne’s test is a long-standing mainstay for the qualitative analysis of sulfur in an organic compound. It involves fusing of the sample with sodium metal (to produce sodium sulfide) followed by treatment of the aqueous solution with sodium nitroprusside to give a deep violet colour, which is usually attributed to an “iron-NOS” complex. Conversely, the Gmelin reaction is used for the quantitative determination of sodium nitroprusside by treatment with a sodium sulfide solution [eqn (10)].

Na₂S + Na₂[Fe(CN)₅NO] → Na₄[Fe(CN)₅S₂] (10)

In a recent enlightening study of the Gmelin reaction using a combination of multinuclear (¹⁷O, ¹⁵N, ¹³C) NMR (Section 3.1), UV-visible, and IR spectroscopic techniques supported by quantum chemical computations, Wu and co-workers have identified the violet species as the complex ion [Fe(CN)₄N(O)S]⁺ (λ_max 542 nm), which is rapidly transformed into the blue tetra-anion [Fe(CN)₄N(O)SS]³⁻ (λ_max 570 nm) in aqueous solution. In the absence of crystal structure determinations, the geometries of these two complexes were determined by quantum chemical calculations (three water molecules were added to each of the models in order to mimic the solvent environment) (Fig. 7). The SNO⁻ and SSNO⁻ anions in these iron(II) complexes are both κ² (N-bonded) with structural parameters that resemble those found for their PPN⁺ salts (Section 4, Chart 3).

6.2.3 Biological signaling. Current interest in the biological role of the SSNO⁻ anion has also prompted an interest in transition-metal complexes of this anion. In this context Hayton and co-workers investigated the reaction of the terminal nickel(II) sulfide complex [K(18-crown-6)][LiNiS] (L = β-diketiminate) with an excess of nitric oxide, which produced orange crystals of [K(18-crown-6)][SSNO] in high yield, in addition to the nitrosyl complex [LiNi(NO)]⁻. This transformation likely involves the initial production of [K(18-crown-6)][SNO] followed by oxidation of SNO⁻ to SSNO⁻ by the excess of NO. In a separate experiment it was observed that [PPN][SSNO] is produced when a solution of [PPN][SNO] in acetonitrile is exposed to NO gas. These findings point to the possible involvement of transition-metal sulfides in the regulation of NO availability in vivo.

6.3 Atmospheric chemistry

Binary S,N anions and ternary S,N,O anions or their conjugate acids are thought to play a role in the chemistry of the atmosphere. For example, it has been suggested that the reaction between HS radicals and NO₂ could generate species such as HSONO and HSNO, initially. However, it should be noted that these two structural isomers are of substantially higher energy (by > 165 kJ mol⁻¹) than N-sulfonylamine HNSO, which is the most stable arrangement for [HO₂NS] (Fig 6b). The identity of the chromophore(s) responsible for Jupiter’s Great Red spot remains an enigma. It has been predicted that ammonium hydrosulfide NH₄SH (formed from a thermal reaction between ammonia and hydrogen sulfide) would have a prominent absorbance at 570 nm in aqueous solution.

Fig. 7 Structures of (a) [Fe(CN)₄N(O)S]⁺ and (b) [Fe(CN)₄N(O)SS]³⁻ fully optimised at the B3LYP/6-311G level of theory.
reaction between NH₃ and H₂S) is an important component of the clouds of Jupiter and other giant planets. In this context Loeffler and co-workers have investigated the irradiation of both natural abundance and ²³⁵N-enriched (98 %) NH₄SH using IR and UV-visible spectroscopy. The IR spectra of irradiated samples exhibit a broad band at 682 cm⁻¹, which is shifted upon ²³⁵N-labelling. Consequently, this band is attributed to a sulfur-nitrogen stretching vibration of a binary sulfur-nitrogen anion NS⁺ (x is not specified), cf. ν.sym (SNS) = 686 cm⁻¹ for SSNS and 710 cm⁻¹ for SSSNS in the Raman spectra of sulfur in liquid ammonia solutions. The IR spectra also exhibit bands at 566 and 491 cm⁻¹ attributed to the trisulfur radical anion (S₃⁺) and polysulfide anions Sₓ⁺/HSₓ⁻, respectively. Irradiation of H₂S is known to produce polysulfides HₓSₙ, which will be converted to the polysulfides Sₓ⁺/HSₓ⁻ in the presence of NH₃. The formation of the ubiquitous S₃⁺ from polysulfides Sₓ⁺ via dissociation (x = 6) or disproportionation (x = 4, 5) is a widespread phenomenon in a variety of settings.

UV-visible spectroscopy (Section 3.3) is a potentially useful technique for identifying the chromophores responsible for the Jovian red spot in view of the intense colours of the sulfur-nitrogen anions SSNS (λ.max 582 nm), SSNS (λ.max 465 nm) and S₃⁺ (λ.max 610 nm) (Section 3.3). The UV-visible spectra of irradiated NH₄SH show a strong absorbance near 600 nm, which was attributed to S₃⁺; however, the binary anion SSSNS could also contribute to this absorption. Consequently, the green colour of irradiated NH₄SH may be due to a mixture of Sₓ⁺ and/or SSNS with the yellow polysulfides Sₓ⁺ from which the radical anion is generated.

6.4 The H₃S-NO interaction
Nitric oxide (NO) and hydrogen sulfide (H₂S) both act as blood pressure mediators. Their similar biological profiles have led to investigations of the nature of the interaction (“cross-talk”) between these species. Recently, it has been shown that HSO⁻ is formed when these two gaseous molecules react on metallic surfaces at room temperature (Section 2.2).

In an informative, detailed study of this topic Pluth and co-workers have demonstrated that certain persulfides RSSH, which are formed by biological oxidation of H₂S, react with nitrite to produce NO via polysulfide (Sₓ⁻) and SSNO⁻ intermediates. Specifically, monitoring the reaction of AdSSH with [Bu₂N][NO₃] in THF by EPR and UV-visible spectroscopy, in combination with the identification of products formed upon treatment of the reaction mixture with the electrophiles C₆H₅CH₂Cl (BzCl), provided unequivocal identification of the Sₓ⁻ radical ion and its precursors Sₓ⁺ (x = 3-6) (see Section 6.3). In addition to the UV-visible absorption band at 446 nm (Section 3.3), the subsequent formation of SSNO⁻ was confirmed by ¹⁵N NMR spectroscopy leading to the reaction pathway depicted in Scheme 5.

7 Summary and conclusions
Stable salts of the binary sulfur-nitrogen anions NSN⁺, SSNS and SSNSS and the ternary sulfur-nitrogen-oxygen anions NO⁻ SNO⁺, SSNO⁻ and SO₃N⁺ with large cations, e.g. Cs⁺, Me₃N⁺, PPN⁺, or TAS⁺, have been isolated and (with the exception of SSNS⁻) structurally characterised in the solid state by single-crystal X-ray crystallography. In addition to their application as metathetical reagents for the preparation of metal complexes, these anionic species are of interest for their role in environments ranging from atmospheric chemistry to cell biology. In particular, the controversial function of the SNO⁻ and SSNO⁻ anions (and their conjugate acids) in biological signaling will continue to be an area of intense investigation. Indeed, very recently, the formation of HSNOS in aqueous solution under physiological conditions from the treatment of a molecule containing a thiosemicarbamide moiety has been established by high-resolution mass spectrometry.

In the absence of stabilising counter-cations, the conjugate acids of these anions are labile species that have been identified either by the formation of either main-group element or transition-metal complexes, e.g. HNSO (Section 2.2, Scheme 2), or by a combination of matrix isolation and IR spectroscopy, e.g. HNSO₂ and the radicals NO and NSO (Section 2.2, Scheme 3).

The ternary S,N,O anions and, especially, their conjugate acids can form a large number of structural isomers. Quantum chemical computational studies based on the calculated heats of formation and bond dissociation energies of the neutral molecules indicate those that incorporate the NSO unit are thermochemically more stable than species with the SNO arrangement owing to the ability of the central sulfur atom to expand its valency and, hence, facilitate the formation of S=O and S=N double bonds.

Several important binary S,N and ternary S,N,O anions and their protonated derivatives have only been characterized spectroscopically, e.g. NSO⁺ (Section 3.3), SNO⁺ (Section 2.1) NSO₂⁻ (Section 3.2) and HNSNO (Section 2.2). In the light of the foregoing overview, these species represent feasible targets for synthetic chemists. For example, the strategy of adduct formation used for the characterisation of HNSO (Scheme 2) can likely be applied to the parent sulfur diimide HNSNH. The elusive NSO₂⁻ anion, which has only been identified in the gaseous state [eqn (7)], is probably accessible as a stable salt with a bulky counter-cation (Section 4) from the deprotonation of N-sulfonlamidine HNSO₂ (Section 2.2) with a base such as [Bu₂N][OH] or [PPN][OH]. Since organic nitronates such as 'BuSNO₂ are used in organic synthesis, reaction of the epimeral thionitrate anion SNO⁺ with an electrophile, e.g. Me₅SiCl or BzCl (Section 6.4), may provide organic derivatives RSO₂ (R = Me₅Si, Bz).

The binary NSO⁻ anion is of considerable interest from both theoretical and experimental standpoints. Does it have an unsymmetrical structure like the isoelectronic neutral molecule disulfur oxide SSO or a symmetrical structure similar to the isolobal nitrite anion, NO⁻? High level quantum chemical
calculations are needed to answer this question and to provide an incentive for the synthesis.

Acknowledgements

Financial support from NSERC (Canada) and Academy of Finland is gratefully acknowledged. The authors are grateful to Prof. Axel Schulz (Univ. of Rostock, Germany) for helpful advice.

References
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Fundamental chemistry of binary S,N and ternary S,N,O Anions: analogues of sulfur oxides and nitrogen oxido-anions

Tristram Chivers* and R. S. Laitinen*

The fundamental chemistry and significance of S,N and S,N,O anions and their conjugate acids in a variety of settings are discussed.