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

Tristram Chivers ^{*a} and Risto S. Laitinen ^{*b}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Binary S,N anions, *e.g.*, NSN²⁻ and SSNS⁻, 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 (NO₂⁻), nitrate (NO₃⁻) and peroxyxynitrite (OONO⁻) are simple, fundamentally important species of sulfur and nitrogen, respectively, that are discussed thoroughly in inorganic chemistry textbooks. The conjunction 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 dianion NSN²⁻, 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 HN=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.

^a Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4. Email: chivers@ucalgary.ca

^b Laboratory of Inorganic Chemistry, Environmental and Chemical Engineering, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland. Email: risto.laitinen@oulu.fi

Chart 2 Conjugate acids of binary S,N and ternary S,N,O anions showing geometrical isomers. Only one resonance form has been depicted in each case.

role of nitric oxide as a signaling molecule has been covered comprehensively in a recent *Perspective* by Feelisch *et al.*⁹ 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).¹⁰ 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 (a) the Gmelin test for the analysis of sodium nitroprusside Na₂[Fe(CN)₅NO] solutions (Section 6.2.2)¹¹ and (b) the reaction of a terminal nickel(II) sulfide complex and nitric oxide (Section 6.2.3).¹² In the context of atmospheric chemistry, binary S,N anions have been invoked as chromophores responsible for Jupiter’s Great Red spot.¹³

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).⁶ The combination of flash vacuum photolysis coupled with matrix isolation IR spectroscopy has enabled the identification of monomeric HNSO₂,⁸ as well as the NSO₂ and NSO radicals (Section 2.2).^{14,15} 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).¹⁶

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

Scheme 1 Contributions of different resonance structures in the bonding of cis-HNSO according to Natural Resonance Theory (NRT) calculations.⁶

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.¹⁷

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 *t*-butoxide in ether solvents such as tetrahydrofuran (THF) or boiling dimethoxyethane (DME), as exemplified by the high-yield syntheses of K[NSO] and K₂[NSN] reported by Armitage and Herberhold, respectively;^{1, 2} 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),¹⁸ 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)].¹⁹

Although the sulfur-centred anions, NSO[−] and NSN^{2−} 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 R₄N⁺, 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 nitrite 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).³ Thirty years later Filipovic *et al.* re-investigated this synthesis using K¹⁵NO₂, which allows monitoring the progress of the reaction by ¹⁵N 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 monothionitrate ion SNO₂[−] formed in the first step of the reaction [eqn. (4)].²⁰ Stable salts of SNO₂[−] have not yet been isolated.

The propensity of Ph_3P for cleavage of S–S bonds with the formation of $\text{Ph}_3\text{P}=\text{S}$ can be used to generate a new anion from a sulfur-rich precursor. Thus, Chivers *et al.*, showed that the rapid reaction of Ph_3P with blue solutions of $[\text{PPN}][\text{SSNSS}]$ or $[\text{Ph}_4\text{As}][\text{SSNSS}]$ ²¹ in acetonitrile produces the corresponding salts of the SSNS^- anion, which form orange solutions [eqn (5)].²² Similarly, Seel prepared the monothionitrite ion SNO^- by treatment of SSNO^- with one equivalent of Ph_3P in acetonitrile and isolated it as a PPN^+ salt [eqn (6)].³ However, this simple procedure cannot be used to generate the dithionitrite ion S_2N^- from SSNS^- and the isolation of this important member of the family of binary S–N anions remains elusive (Section 3.3).²²

Although the NSO_2^- ion, isoelectronic with SO_3 , has been generated by the gas-phase reaction of the NH_2^- anion with SO_2F_2 [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 azidosulfite anion SO_2N_3^- , which has been isolated by Christe and co-workers as thermally unstable cesium and tetramethylammonium salts [eqn (8)],²³ is a potential precursor for NSO_2^- via loss of N_2 . However, mild heating of $\text{Cs}[\text{SO}_2\text{N}_3]$ leads directly to the evolution of SO_2 and formation of cesium azide.²³ This transformation is attributed to the remarkably long S–N bond in $\text{M}[\text{SO}_2\text{N}_3]$ salts ($\text{M} = \text{Cs}$, 1.981(12) Å;²³ $\text{M} = \text{Me}_4\text{N}$, 2.005(2) Å).²⁴ Typical S–N bond lengths are given in Table 2. For comparison, the S–N bond in $\text{Cs}[\text{SO}_3\text{N}_3]$ is substantially shorter (by 0.23 Å) as a result of the stronger Lewis acidity of SO_3 compared to that of SO_2 .²³

2.2 The conjugate acids HNSO, HNSNH, HSNO and HNSO₂

The neutral molecules HNSO, HSNO, HNSNH and HNSO_2 are conjugate acids of the anions discussed in the previous section. In the absence of a stabilising cation, however, the synthesis and 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 $\text{K}_2[\text{NSN}]$ with stoichiometric amounts of acetic acid [eqn (9)]; however, characterisation of this thermally labile molecule was limited to variable temperature ^1H NMR spectra, which indicated the presence of two isomers in solution.⁵

Scheme 2 Synthesis of a Lewis acid adduct of *cis*-HNSO.⁶

Monomeric thionylimide HNSO is a gas which, at low temperatures, forms a colourless liquid that quickly polymerises to a brown solid, polythionylimide $[(\text{HNSO})_x]$, at ambient temperature.²⁵ In 2015 Schulz and co-workers invoked adduct formation with $\text{B}(\text{C}_6\text{F}_5)_3$ to stabilise HNSO, which was formed *in situ* by protonation of $\text{K}[\text{NSO}]$ 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 HSNO, a structural isomer of HNSO (Section 5.2), has been suggested to result from the reaction of H_2S with protein S-nitrosothiols. In 2012 Filipovic *et al.* confirmed the existence of HSNO under physiologically relevant conditions by a combination of spectroscopic techniques.⁷ Four years later McCarthy *et al.* showed that HSNO is formed in high concentration when NO and H_2S are mixed at room temperature on metallic surfaces.¹⁰

Similar to the observations for HNSO, the parent N-sulfonylamine HNSO_2 has a tendency to associate in the condensed state and the cyclic trimer $(\text{HNSO}_2)_3$ has been isolated in early work.²⁷ This behaviour mirrors the well-established trimerisation of the isoelectronic molecule sulfur trioxide SO_3 in the solid state. Monomeric HNSO_2 remained elusive until 2016 when Zeng *et al.* used flash vacuum photolysis of methoxysulfonyl azide $\text{CH}_3\text{OS}(\text{O})_2\text{N}_3$ at *ca.* 1000 K to generate this simple N-sulfonylamine 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, HNSO_2 isomerises into the structural isomer N-hydroxysulfinylamine HONSO (Section 5.2).

3. Spectroscopic characterisation

3.1 NMR spectra

Nitrogen has two NMR-active isotopes (^{14}N , $I = 1$, 99.6%; ^{15}N , $I = \frac{1}{2}$, 0.4 %). Although the quadrupolar ^{14}N nucleus gives rise to broad lines, the ^{14}N chemical shift of the simple S,N and S,N,O species described in the previous sections is informative in view

Scheme 3 Formation of $\text{HNSO}_2(\text{g})$ by photolysis of methoxysulfonyl azide.⁸

Fig. 1 ^{15}N NMR spectrum of a solution of $\text{S}_4^{15}\text{N}_4\text{H}_4 + 2\text{KNH}_2$ in liquid ammonia at 25 $^\circ\text{C}$.²⁹

of the broad range of values for this parameter.²⁸ For example, the ^{14}N NMR spectrum of a liquid ammonia solution of *cyclo*- S_7NH containing KNH_2 shows well-separated signals for the acyclic SNSS^- and SSNSS^- anions as well as a singlet for the cyclic anion S_3N_3^- .²⁹

The expense involved in the synthesis of ^{15}N -enriched sulfur-nitrogen compounds, is justified by the advantage offered by ^{15}N -labelled precursors for the characterisation of species with more than one nitrogen environment.^{28a} This benefit is nicely demonstrated by the identification of the acyclic SNSNH^- anion in the ^{15}N NMR spectrum of a liquid ammonia solution of $\text{S}_4^{15}\text{N}_4\text{H}_4$ treated with two equiv. of KNH_2 . This spectrum is comprised of two mutually coupled resonances $^2J(^{15}\text{N}, ^{15}\text{N} = 2 \text{ Hz})$ one of which exhibits a $^1J(^{15}\text{N}, ^1\text{H})$ coupling of 55 Hz (Fig. 1).²⁹

The SNSNH^- anion has not been characterized in the solid state. However, treatment of the cyclic tetraimide $\text{S}_4\text{N}_4\text{H}_4$ with two equivalents of the Wittig reagent $\text{Ph}_3\text{P}=\text{CH}_2$ in THF produces a yellow solid, presumably $[\text{Ph}_3\text{PMe}][\text{S}_2\text{N}_2\text{H}]$, which serves as an *in situ* reagent for the preparation of the homoleptic nickel(II) complex $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$ (Scheme 4).³⁰

In the absence of ^{15}N -labelling, polarisation transfer techniques can be used to enhance the sensitivity of ^{15}N NMR experiments. For example, the ^1H - ^{15}N HMQC (heteronuclear multiple quantum coherence) spectrum of a mixture of the cyclic diimide isomers 1,3-, 1,4-, and 1,5- $\text{S}_6(\text{NH})_2$, together with the triimides 1,3,5- and 1,3,6- $\text{S}_5(\text{NH})_3$, provides well-resolved ^1H and ^{15}N chemical shifts for each component; the $^1J(^{15}\text{N}, ^1\text{H})$ values are in the range 91–94 Hz.³² This technique is also informative in discerning the presence of *cis* and *trans* isomers in a D_8 -toluene solution of the adduct $\text{HNSO}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 3); the distinctive NMR parameters for the two isomers are $\delta(^1\text{H}) = 10.4$ and 10.6 ppm , $\delta(^{15}\text{N}) = -95$ and -106 ppm , and $^1J(^{15}\text{N}, ^1\text{H}) = 65$ and 70 Hz .⁶

Scheme 4 Preparation of $\text{Ni}(\text{S}_2\text{N}_2\text{H})_2$ via the *in situ* reagent $[\text{Ph}_3\text{PMe}][\text{S}_2\text{N}_2\text{H}]$

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 $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ and an aqueous solution of sodium sulfide [Section 6.2.2, eqn (10)].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, $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{S}]^{4-}$ and $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SS}]^{4-}$, 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_{2v}) NSO^- and NSN^{2-} anions give rise to simple IR spectra comprised of asymmetric and symmetric stretching modes (ν_{as} and ν_{s}) and a bending mode (δ). The experimental values are compared with those of the isoelectronic SO_2 molecule in Table 1.¹⁸ The stretching modes (ν_{as} and ν_{s}) for NSN^{2-} occur at lower frequencies (by 150–160 cm^{-1}) than those for SO_2 . The similar values of all three vibrations for NSO^- 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 “ $\text{Cs}[\text{NSO}_2]$ ” from the hydrolysis of $\text{Me}_3\text{NSNSiMe}_3$ with wet CsF ; the identification relied primarily on the field ionisation mass spectrum of “ $[\text{Ph}_4\text{P}][\text{NSO}_2]$ ”.³⁴ A subsequent detailed spectroscopic analysis of a bulk sample of “ $\text{Cs}[\text{NSO}_2]$ ” showed it to be comprised mainly of the NSO^- anion with major IR bands at 1267, 989 and 509 cm^{-1} (*cf.* values for $\text{Cs}[\text{NSO}]$ in Table 1); this conclusion was supported by the ^{14}N NMR chemical shift of a solution of the bulk material.³⁵ The calculated vibrational frequencies for NSO_2^- (g) are 1188 (symmetric stretching), 1049 (asymmetric stretching), 473 (symmetric bending) and 419 cm^{-1} (asymmetric bending).⁴

Table 1 The fundamental vibrations (cm^{-1}) of the isoelectronic species SO_2 , NSO^- and NSN^{2-}

	ν_{as}^a	ν_{s}^a	δ
OSO^{2-}	1360	1151	518
$\text{Na}[\text{NSO}]^{18}$	1283	999	528
$\text{K}[\text{NSO}]^{18}$	1276	994	519
$\text{Rb}[\text{NSO}]^{18}$	1271	986	507
$\text{Cs}[\text{NSO}]^{18}$	1272	992	511
$(\text{Me}_4\text{N})[\text{NSO}]^{33}$	1268	992	496
$\text{K}_2[\text{NSN}]^2$	1198	1001	528

^a The vibrations ν_{as} and ν_{s} are primarily (80 %) S–N and S–O stretching modes, respectively, in the salts of NSO^- .¹⁸

In the absence of an X-ray crystal structure, vibrational spectroscopy of the ^{15}N -labelled SS^*NS^- anion ($^*\text{N} = 30\% \text{ }^{15}\text{N}$) revealed an unbranched structure^{22b} 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^*NS^- 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 SSNS^- anion resembles that of peroxyxynitrite OONO^- rather than the branched structure of the isoelectronic trithiocarbonate dianion CS_3^{2-} . 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 arrangement or a cyclic structure for the triatomic molecule NS_2 .³⁶

3.3 UV-visible spectra

Several S,N and S,N,O anions are highly coloured. Consequently, they exhibit strong, visible absorption bands with characteristic wavelengths, e.g. SSNSS^- (λ_{max} 582 nm),²¹ SSNS^- (λ_{max} 465 nm),²² SSNO^- (λ_{max} 448 nm in acetone, 443 nm in acetonitrile),^{3,12} SNO^- (λ_{max} 334).¹² 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_2^-) of SSNS^- has been proposed on the basis of the observation of absorption bands at λ_{max} 375 nm in acetonitrile or 390 nm in $\text{NH}_3(\text{l})$, respectively.^{37,38} In a second example, the observation of an absorption band at 375 nm upon addition of an ionic nitrite to a solution of elemental sulfur in acetone has been attributed to the initial formation of the labile SNO_2^- anion (Section 2.1).²⁰

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

Chart 3 Conformations and selected structural parameters of the *cis*- SSNO^- ²⁰ and *cis,trans*- SSNSS^- ^{21b} anions in their PPN^+ salts.

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

	Single bond	Example	Double bond	Example
$d(\text{S–N})$	1.7714(4)	H_3NSO_3^a	1.544(2)	$(\text{NSF})_4^b$
$d(\text{S–O})$	1.644(17)	R_1SOR_2^c	1.492(1)	$\text{R}_1\text{R}_2\text{SO}^c$
$d(\text{S–S})$	2.0529(2)	S_8^d	1.908(16)	$(\text{RO})_2\text{SS}^c$

^aJ. W. Bats, P. Coppens and T. F. Koetzle, *Acta Crystallogr., Sect. B*, 1977, **33**, 37–45. ^bD. Gregson, G. Klebe and H. Fuess, *Acta Crystallogr., Sect. C*, 1991, **47**, 1784–1786. ^cThe mean value from several related species from Cambridge Crystallographic Data Base, see Conquest 1.19, Cambridge Crystallographic Data Center, Cambridge 2016. ^dG. Santiso-Quinones, R. Brueckner, C. Knapp, I. Dionne, J. Passmore and I. Krossing, *Angew. Chem. Int. Ed.*, 2009, **48**, 1133–1137.

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 $\text{M}[\text{NSO}]$ (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 $[\text{Me}_4\text{N}][\text{NSO}]$ 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 $[\text{K}(18\text{-crown-6})]^+$ salt for the first structural determination of the NSN^{2-} dianion more than 20

Fig. 2 X-ray structure of $[\text{K}(18\text{-crown-6})]_2[\text{NSN}]$.³⁹ The van der Waals radii of sulfur, nitrogen, and potassium are indicated as transparent spheres.

years after its discovery (Fig. 2).³⁹ In the solid state the NSN²⁻ dianion exhibits modestly longer S–E bond lengths compared to the corresponding distances in the isoelectronic SO₂ molecule (E = N, 1.484(3) Å; E = O, 1.4297(4) Å). The E–N–E bond angle (E = N, 129.9(2)°; E = O, 117.5(1)°) is significantly widened in the dianion, presumably as a result of Coulombic repulsions between the negatively charged N atoms.³⁹

The bulky PPN⁺ cation [(Ph₃P)₂N⁺] 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 (Bu₄N⁺) salt.^{21,40} The acyclic SSNSS⁻ anion in the PPN⁺ and Ph₄As⁺ 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 [K(18-crown-6)]⁺ salt in which it is coordinated to the potassium centre in a κ^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(C₆F₅)₃ confirmed that the HNSO ligand retains the *cis* conformation (Fig. 4),⁶ which was previously found in the gas phase by microwave

Fig. 4 Molecular structure of HNSO•B(C₆F₅)₃.⁶

spectroscopy.⁴¹ The ligand is bonded to the strong Lewis acid B(C₆F₅)₃ through the N atom ($d(\text{B}–\text{N}) = 1.624(3)$ Å). Adduct formation induces a modest perturbation of the bond distances compared to the values for the monomer in the gas phase ($d(\text{S}–\text{N}) = 1.530(2)$ vs 1.5123 Å; $d(\text{S}–\text{O}) = 1.427(2)$ vs. 1.4513 Å) and a significant narrowing of the N–S–O bond angle from 120.41° in the gas phase to 114.3(2)° 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 π -system (Fig. 5).⁶ The two doubly occupied MOs, ψ_{MO1} and ψ_{MO2} , can be viewed essentially as bonding and non-bonding, respectively. The

Fig. 3 Molecular structure of [K(18-crown-6)][SSNO]. Bond lengths: O–N 1.247(2), N–S 1.669(2), S–S 1.9526(9) Å.¹² The van der Waals radii of oxygen and potassium are indicated as transparent spheres.

Fig. 5 MO diagram of the π system in NSO^- .⁶ (Reproduced with permission © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

molecular orbital coefficients indicate that $\psi_{\text{MO}2}$ 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} .⁴²

In a broad-ranging investigation Dixon and co-workers calculated thermodynamic parameters for the structural isomers of the elemental combinations $[\text{HNOS}]$, $[\text{HNO}_2\text{S}]$ and $[\text{HNOS}_2]$.¹⁶ The main findings can be summarised as follows:

- As found experimentally for the combination $[\text{HNOS}]$, the *cis* isomer of HNSO is more stable than the *trans* form (a geometrical isomer) (Section 4),^{6,42} but by only a small amount, *ca.* 12 kJ mol^{-1} . However, the structural isomers NSOH and *cis*- or *trans*- HSNO are *ca.* 164.4 and 161.5 kJ

mol^{-1} higher in energy, respectively, than *cis*- HNSO (Fig. 6a).

- Similarly, as determined experimentally, the most stable isomer of $[\text{HO}_2\text{NS}]$ has the branched structure HNSO_2 (*cf.* SO_3), (Section 2.2),⁸ which is estimated to be more stable than the unbranched isomer HONSO by 76.6 kJ mol^{-1} ;¹⁶ Zeng and co-workers estimate this energy difference to be 44.3 kJ mol^{-1} .⁸ The thionitrate isomer HSNO_2 lies *ca.* 179.9 kJ mol^{-1} above the *N*-sulfonylamine HNSO_2 (Fig. 6b).¹⁶
- In the case of $[\text{HNOS}_2]$ the most stable arrangement is the unbranched isomer HSNSO , which lies *ca.* 64.0 kJ mol^{-1} below the branched linkage isomer HNS(O)S (Fig. 6c).¹⁶

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.¹⁶

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 Feelisch *et al.*⁹ 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_2S as a “crucial intermediate linking H_2S and nitroso chemistries” (Section 2.2),¹⁰ (b) the identification of the intermediates formed in the Gmelin reaction (Section 6.2.2),¹² (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),¹¹ and (d) the formation of SSNO^- from the reaction of persulfides RSSH with nitrite ion NO_2^- .⁴³

Fig. 6 Calculated heats of formation $\Delta H_f(298)$ (kJ mol^{-1}) and bond lengths ($\text{\AA}$) of selected structural isomers of (a) $[\text{HNOS}]$, (b) $[\text{HNO}_2\text{S}]$, and (c) $[\text{HNOS}_2]$.¹⁶

6.1 The gunpowder reaction

Gunpowder (also known as black powder) has been used as an explosive material since the middle ages. It is comprised of a mixture of potassium nitrate, charcoal and sulfur.⁴⁴ 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)].²⁰

6.2 Metal complexes

The formation of metal complexes of S₂N and S₂N₂O 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 S₂N and S₂N₂O anions such as NSO⁻ and NSN²⁻ furnished a straightforward source of coordination complexes of these ligands via metathetical reactions with halides of main group elements or transition metals.¹⁷ In typical examples, *e.g.* Cp₂Ti(NSO)₂, Ph_{3-x}As(NSO)_x (*x* = 1, 2), the NSO⁻ ligand is κ^1 (*N*-bonded) whereas the NSN²⁻ dianion may act as a bridging ligand between two metal centres.¹⁷

Conversely, the discovery of transition-metal complexes has provided the impetus for the synthesis of ion-separated salts of certain S₂N anions. For example, the isolation of a few crystals of the homoleptic nickel(II) complex Ni(S₃N)₂ from the reaction of S₈N₄ with NiCl₂ in methanol⁴⁵ was followed almost 25 years later by the characterisation of the PPN⁺ and Ph₄As⁺ salts of the SSNS⁻ anion [Section 2.1, eqn (5)],²² which have been used as metathetical reagents for the preparation of copper (I) complexes, *e.g.* [PPN][Cu(S₃N)₂], in which the SSNS⁻ ligands are *S,S*-bidentate.⁴⁶ In a similar vein, although the acyclic SNSNH⁻ and SNSN²⁻ anions are frequently encountered in metal complexes,¹⁷ 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).³⁰

6.2.2 Lassaigne's test and the Gmelin reaction. Lassaigne's test is a long-standing mainstay for the qualitative analysis of sulfur in an organic compound. It involves fusion 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)].¹¹

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-workers¹¹ have identified the violet species as the complex ion [Fe(CN)₅N(O)S]⁴⁻ (λ_{max} 542 nm), which is rapidly transformed into the blue tetra-anion [Fe(CN)₅N(O)SS]⁴⁻ (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).¹² The SNO⁻ and SSNO⁻ anions in these iron(II) complexes are both κ^1 (*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⁻ anion⁹ 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)][(L)NiS] (*L* = β -diketiminato) with an excess of nitric oxide, which produced orange crystals of [K(18-crown-6)][SSNO] (Fig. 3) in high yield, in addition to the nitrosyl complex (L)Ni(NO).¹² 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.¹² These findings point to the possible involvement of transition-metal sulfides in the regulation of NO availability *in vivo*.

6.3 Atmospheric chemistry

Binary S₂N anions and ternary S₂N₂O 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 HSNO₂ initially.⁴⁷ However, it should be noted that these two structural isomers are of substantially higher energy (by > 165 kJ mol⁻¹) than *N*-sulfonylamine HNSO₂, which is the most stable arrangement for [HO₂NS] (Fig. 6b).¹⁶

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

Fig. 7 Structures of (a) [Fe(CN)₅N(O)S]⁴⁻ and (b) [Fe(CN)₅N(O)SS]⁴⁻ fully optimised at the B3LYP/6-311G level of theory.¹¹

reaction between NH_3 and H_2S is an important component of the clouds of Jupiter and other giant planets.¹³ In this context Loeffler and co-workers have investigated the irradiation of both natural abundance and ^{15}N -enriched (98 %) NH_4SH using IR and UV-visible spectroscopy.¹³ The IR spectra of irradiated samples exhibit a broad band at 682 cm^{-1} , which is shifted upon ^{15}N -labelling. Consequently, this band is attributed to a sulfur-nitrogen stretching vibration of a binary sulfur-nitrogen anion NS_x^- (x is not specified),^{13a} cf. ν_{sym} (SNS) = 686 cm^{-1} for SSNS^- and 710 cm^{-1} for SSNSS^- in the Raman spectra of sulfur in liquid ammonia solutions.⁴⁸ The IR spectra also exhibit bands at 566 and 491 cm^{-1} attributed to the trisulfur radical anion ($\text{S}_3^{\bullet-}$) and polysulfide anions $\text{S}_x^{2-}/\text{HS}_x^-$, respectively. Irradiation of H_2S is known to produce polysulfanes H_2S_x which will be converted to the polysulfides $\text{S}_x^{2-}/\text{HS}_x^-$ in the presence of NH_3 .^{13a} The formation of the ubiquitous $\text{S}_3^{\bullet-}$ from polysulfides S_x^{2-} via dissociation ($x = 6$) or disproportionation ($x = 4, 5$) is a widespread phenomenon in a variety of settings.⁴⁹

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 SSNSS^- ($\lambda_{\text{max}} 582\text{ nm}$),²¹ SSNS^- ($\lambda_{\text{max}} 465\text{ nm}$)²² and $\text{S}_3^{\bullet-}$ ($\lambda_{\text{max}} 610\text{ nm}$)⁴⁹ (Section 3.3). The UV-visible spectra of irradiated NH_4SH show a strong absorbance near 600 nm , which was attributed to $\text{S}_3^{\bullet-}$,^{13b} however, the binary anion SSNSS^- could also contribute to this absorption. Consequently, the green colour of irradiated NH_4SH may be due to a mixture of $\text{S}_3^{\bullet-}$ and/or SSNSS^- with the yellow polysulfides S_x^{2-} from which the radical anion is generated.

6.4 The H_2S -NO interaction

Nitric oxide (NO) and hydrogen sulfide (H_2S) 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 HSNO is formed when these two gaseous molecules react on metallic surfaces at room temperature (Section 2.2).¹⁰

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 H_2S , react with nitrite to produce NO via polysulfide (S_x^{2-}) and SSNO^- intermediates.⁴³ Specifically, monitoring the reaction of AdSSH with $[\text{Bu}_4\text{N}][\text{NO}_2^-]$ 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 $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (BzCl), provided unequivocal identification of the $\text{S}_3^{\bullet-}$ radical ion and its precursors S_x^{2-} ($x = 3-6$) (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 ^{15}N NMR spectroscopy leading to the reaction pathway depicted in Scheme 5.⁴³

7 Summary and conclusions

Stable salts of the binary sulfur-nitrogen anions NSN^{2-} , SSNS^- and SSNSS^- and the ternary sulfur-nitrogen-oxygen anions NSO^- , SSNO^- and SO_2N_3^- with large cations, e.g. Cs^+ , Me_4N^+ , PPN^+

Scheme 5 Reaction of adamantyl disulfane with nitrite produces NO via polysulfides and SSNO^- ($x < y$).

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 HSNO in aqueous solution under physiological conditions from the treatment of a molecule containing a thiosemicarbazide moiety has been established by high-resolution mass spectrometry.⁵⁰

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. HNSO_2 and the radicals NSO_2 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.¹⁶

Several important binary S,N and ternary S,N,O anions and their protonated derivatives have only been characterized spectroscopically, e.g. NS_2^- (Section 3.3), SNO_2^- (Section 2.1) NSO_2^- (Section 3.2) and HNSNH (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 NSO_2^- 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*-sulfonylamine HNSO_2 (Section 2.2) with a base such as $[\text{Bu}_4\text{N}][\text{OH}]$ or $[\text{PPN}][\text{OH}]$. Since organic thionitrates such as $t\text{BuSNO}_2$ are used in organic synthesis,⁵¹ reaction of the ephemeral thionitrate anion SNO_2^- with an electrophile, e.g. Me_3SiCl or BzCl (Section 6.4), may provide organic derivatives RSNO_2 ($\text{R} = \text{Me}_3\text{Si}, \text{Bz}$).

The binary NS_2^- 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, ONO^- ? 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

- 1 D. A. Armitage and J. C. Brand, *J.C.S., Chem. Comm.*, 1979, 1078-1079.
- 2 M. Herberhold and W. Ehrenreich, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 633-633.
- 3 F. Seel, R. Kuhn, G. Simon and M. Wagner, *Z. Naturforsch.*, 1985, **40b**, 1607-1617.
- 4 N. H. Morgon, H. V. Linnert and J. M. Riveros, *J. Phys. Chem.*, 1995, **99**, 11667-11672.
- 5 M. Herberhold, W. Jellen, W. Bühlmeier, W. Ehrenreich and J. Reiner, *Z. Naturforsch.*, 1985, **40b**, 1229-1232.
- 6 R. Labbow, D. Michalik, F. Reiss, A. Schulz and A. Villinger, *Angew. Chem., Int. Ed.*, 2016, **55**, 7680-7684, and references cited therein.
- 7 M. R. Filipovic, J. Lj. Miljkovic, T. Nauser, M. Royzen, K. Klos, T. Shubina, W. H. Koppenol, S. J. Lippard and I. Ivanović-Burmazović, *J. Am. Chem. Soc.*, 2012, **134**, 12016-12027, and references cited therein.
- 8 G. Deng, Z. Wu, D. Li, R. Linguerri, J. S. Francisco and X. Zeng, *J. Am. Chem. Soc.*, 2016, **138**, 11509-11512, and references cited therein.
- 9 M. N. Cortese-Krott, A. R. Butler, J. D. Woollins and M. Feelisch, *Dalton Trans.*, 2016, **45**, 5908-5919, and references cited therein.
- 10 M. Nava, M-A Martin-Drumel, C. A. Lopez, K. N. Crabtree, C. C. Womack, T. L. Nguyen, S. Thorwirth, C. C. Cummins, J. F. Stanton and M. C. McCarthy, *J. Am. Chem. Soc.*, 2016, **138**, 11441-11444.
- 11 Y. Gao, A. Toubaei, X. Kong and G. Wu, *Chem. Eur. J.*, 2015, **21**, 17172-17177.
- 12 N. J. Hartmann, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2016, **138**, 12352-12355.
- 13 (a) M. J. Loeffler, R. L. Hudson, N. J. Chanover and A. A. Simon, *Icarus*, 2016, **271**, 265-268; (b) M. J. Loeffler, R. L. Hudson, N. J. Chanover and A. A. Simon, *Icarus*, 2016, **258**, 181-191.
- 14 X. Zeng, H. Beckers and H. Willner, *Angew. Chem., Int. Ed.*, 2013, **52**, 7981-7984.
- 15 Z. Wu, D. Li, H. Li, B. Zhu, H. Sun, J. S. Francisco and X. Zeng, *Angew. Chem., Int. Ed.*, 2016, **55**, 1507-1510.
- 16 M. Mendez, J. S. Francisco and D. A. Dixon, *Chem. Eur. J.*, 2014, **20**, 10231-1023.
- 17 T. Chivers, "A Guide to Chalcogen-Nitrogen Chemistry", World Scientific, Singapore, 2005.
- 18 S. Mann and M. Jansen, *Z. Anorg. Chem. Allg. Chem.*, 1995, **621**, 153-158.
- 19 W. Heilemann and R. Mews, *Chem. Ber.*, 1988, **121**, 461-463.
- 20 R. Wedmann, A. Zahl, T. E. Shubina, M. Dürr, F. W. Heinemann, B. E. C. Bugenhagen, P. Burger, I. Ivana-Burmazovic and M. R. Filipovic, *Inorg. Chem.* 2015, **54**, 9367-9380.
- 21 (a) T. Chivers and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1979, 752-753; (b) T. Chivers, W. G. Laidlaw, R. T. Oakley and M. Tric, *J. Am. Chem. Soc.*, 1980, **102**, 5773-5781.
- 22 (a) J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 1980, 1023-1024; (b) The Thio Analogue of Peroxynitrite, (SSNS)-: (b) J. Bojes, T. Chivers, W. G. Laidlaw and M. Trsic, *J. Am. Chem. Soc.*, 1982, **104**, 4837-4841.
- 23 K. O. Christe, J. A. Boatz, M. Gerken, R. Haiges, S. Schneider, T. Schroer, F. D. Tham, A. Vij, V. Vij, R. I. Wagner and W. W. Wilson, *Inorg. Chem.*, 2002, **41**, 4275-4285.
- 24 A. Kornath, O. Blecher and R. Ludwig, *Z. Anorg. Allg. Chem.*, 2002, **628**, 183-190.
- 25 P. W. Schenk, *Chem. Ber.*, 1942, **75**, 94-99.
- 26 G. Hartmann, R. Hoppenheit and R. Mews, *Inorg. Chim. Acta*, 1983, **76**, L201-L202.
- 27 G. Faleschni, E. Nachbaur and F. Belaj, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 1992, **65**, 147-150.
- 28 (a) T. Chivers, R. T. Oakley, O. J. Scherer, and G. Wolmershäuser, *Inorg. Chem.*, 1981, **20**, 914-917; (b) P. S. Belton and J. D. Woollins, *Magn. Reson. Chem.*, 1986, **24**, 1080-1082.
- 29 T. Chivers and K. J. Schmidt, *J. Chem. Soc., Chem Commun.*, 1990, 1342-1344, and references cited therein.
- 30 T. Chivers, F. Edelmann, U. Behrens and R. Drews, *Inorg. Chim. Acta*, 1986, **116**, 145-151.
- 31 T. L. Roemmele, J. Konu, R.T. Boeré and T. Chivers, *Inorg. Chem.*, 2009, **48**, 9454-9462.
- 32 T. Chivers, M. Edwards, D. D. McIntyre, K. J. Schmidt and H. J. Vogel, *Magn. Reson. Chem.*, 1992, **30**, 177-182.
- 33 S. Mann and M. Jansen, *Z. Naturforsch.*, 1994, **49b**, 1503-1506.
- 34 (a) H. W. Roesky, W. Schmieder, W. Isenberg, D. Böhler and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 153, full version published in *Angew. Chem. Suppl.*, 1982, 269-282; (b) H. W. Roesky, W. Schmieder, W. Isenberg, W. S. Sheldrick and G. M. Sheldrick, *Chem. Ber.*, 1982, **115**, 2714-2727.
- 35 T. Chivers, K. J. Schmidt, D. D. McIntyre and H. J. Vogel, *Can. J. Chem.*, 1989, **67**, 1788-1794.
- 36 M. Iraqi, N. Goldberg and H. Schwarz, *Chem. Ber.*, 1994, **127**, 1171-1173.
- 37 T. Chivers and M. Hojo, *Inorg. Chem.*, 1984, **23**, 2738-2742.
- 38 J. P. Lelieur and G. Lepoutre, *Inorg. Chem.*, 1989, **28**, 2489-2491, and references cited therein.
- 39 T. Borrmann, E. Lork, R. Mews, M. M. Shakirov and A. V. Zibarev, *Eur. J. Inorg. Chem.*, 2004, 2452-2458.
- 40 (a) T. Chivers and I. Drummond, *Inorg. Chem.*, 1974, **13**, 1222-1225; (b) N. Burford, T. Chivers, A. W. Cordes, R. T. Oakley, W. T. Pennington and P. N. Swepston, *Inorg. Chem.*, 1981, **20**, 4430-4432.
- 41 (a) W. H. Kirchoff, *J. Am. Chem. Soc.*, 1969, **91**, 2437-2442; (b) M. Carlotti, G. Di Lonardo, G. Galloni and A. Trombetti, *J. Mol. Spectrosc.*, 1980, **84**, 155-161.
- 42 T. Trabelsi, O. Yazidi, J. S. Francisco, R. Longuerri and M. Hochlaf, *J. Chem. Phys.*, 2015, **143**, 164301-164310, and references cited therein.
- 43 T. S. Bailey, H. A. Henthorn and M. D. Pluth, *Inorg. Chem.*, 2016, **55**, 12618-12625.
- 44 For a detailed discussion of the history and chemistry of black powder, see F. Seel, in *Sulfur: Its Significance for Chemistry, for the Geo-, Bio- and Cosmophere and Technology*, ed. A. Müller and B. Krebs, Elsevier, Amsterdam, 1984, pp. 55-66, and references cited therein.
- 45 T. S. Piper, *J. Am. Chem. Soc.*, 1958, **80**, 30-32.
- 46 J. Bojes, T. Chivers and P. W. Coddling, *J.C.S. Chem. Commun.*, 1981, 1171-1173.
- 47 S. M. Resend, *J. Atmos. Chem.* 2007, **56**, 21-32.
- 48 T. Chivers and C. Lau, *Inorg. Chem.*, 1982, **21**, 453-455.
- 49 (a) T. Chivers, *Nature*, 1974, **252**, 32-33; (b) T. Chivers and P. J. W. Elder, *Chem. Soc. Rev.*, 2013, **42**, 5996-6005.
- 50 A. S. M. Islam, R. Bhowmick, K. Pal, A. Katarkar, K. Chaudhuri and M. Ali, *Inorg. Chem.*, 2017, **56**, 4324-4331.

- 51 H. J. Kim and Y. H. Kim, *Tetrahedron Lett.*, 1987, **28**, 1669-1670, and references cited therein.

Tristram Chivers, a native of Bath, England, received his BSc, PhD and DSc degrees all from the University of Durham (UK). He joined the University of Calgary in 1969 and served as Head of the Chemistry Department from 1977 to 1982. He currently holds the title of Faculty Professor and Professor Emeritus of Chemistry. His primary research interests are in the general area of main group element chemistry with emphasis on chalcogen chemistry and inorganic ring systems. He is the author of two books: "A Guide to Chalcogen-Nitrogen Chemistry" and (with I. Manners) "Inorganic Rings and Polymers of the p-Block Elements: From Fundamentals to Applications". He received the Alcan Lecture Award of the Canadian Society for Chemistry (CSC) in 1987, the E.W.R. Steacie Award from the CSC in 2001, and the Royal Society of Chemistry Award (UK) for Main-Group Element Chemistry in 1993. He was elected a Fellow of the Royal Society of Canada in 1991. He received an honorary DSc from the University of Oulu, Finland in 2006. In 2008 he was the recipient of the ASTech Outstanding Leadership in Alberta Science Award.

Risto Laitinen received his PhD from Helsinki University of Technology (Finland). He joined University of Oulu in 1988 as Professor of Inorganic and Analytical chemistry, and was a Head of Chemistry Department in 1993-2013. In 1984-1985 he was an Alexander von Humboldt research fellow in Technische Universität Berlin (Germany). His research interests lie in the chemistry of sulfur, selenium, and tellurium. He has edited a book: "Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials" (with J. D. Woollins) and has long been involved in IUPAC. He is currently secretary in Division of Chemical Nomenclature and Structure Representation).

Table of Contents

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.