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CHEMISTRY OF THIONITROSYL GROUP(NS)

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The present review deals with a comprehensive account of syntheses, physical properties, chemical reactions and the electronic structure of NS, its ions and transition metal complexes.

Beginning with an up-to-date account of the syntheses, the chemical, thermodynamic, spectroscopic properties and the electronic structures of NS and its related compounds, a detailed and an up-to-date description of the ionic and the covalent compounds of NS and their chemical reactions with a variety of reactants along with a description of its non-metallic and metallic adducts has been presented therein.

A till-todate account of thionitrosyl complexes of the transition metal ions has been discussed. The evidence of the different modes of bonding of NS in these complexes as derived essentially from their i.r. spectral studies and X-ray data have been examined critically in the last section of the review.

Keywords : NS Compounds and its Transition Metal Complexes

INTRODUCTION

THIONITROSYL radical with one unpaired electron unlike its homologue, viz., NO, polymerizes so readily that it is not possible to isolate it as a monomer solid or liquid and even in the gaseous phase, it has only a transient existence (Heal, 1972). As a result of this, the studies pertaining to the structure, bonding and the reactivity of thionitrosyl† have always been challenging and despite the large interest in the chemistry of thionitrosyl, the amount of work in this field is relatively much less and fragmentary.

Although several important reviews of the compounds containing sulphur and nitrogen (Heal, 1972; Becke-Goehring, 1957, 1959, 1962, 1970; Becke-Goehring & Schlafer, 1966; Roesky *et al.*, 1967, 1968; MacDiarmid *et al.*, 1976; Padma & Murty, 1976; Banister, 1979; Appel & Kohnke, 1978; Haidue, 1978; and Heal, 1968) covering the chemistry of polymeric sulphur nitrides and those of sulphur-nitrogen-fluorine (Glemser, 1963, 1964, 1969; Glemser & Field, 1967; Glemser & Biermann, 1968; and Glemser & Mews, 1972) have appeared in the literature, but there has been no comprehensive review exclusively on thionitrosyls. In the present review, our main aim has been to provide a comprehensive account up to December 1979 of syntheses, physical properties, chemical reactions and structures of thionitrosyl, its ions and the transition metal thionitrosyl complexes.

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†In this review the term 'Thionitrosyl' is employed as a general name for the compounds of the NS group.

SYNTHESES AND GENERAL PROPERTIES

The thionitrosyl radical, like NO, H, I, NO₂ can ClO₂ and also exist as NS⁺ or NS⁻ formed respectively by loosing or gaining an electron and therefore, most of its properties should be approximately similar to those of NO. The presence of NS was observed for the first time by Fowler and Bakker in 1932 while studying the band spectrum of the emitted light after passing an electric discharge through a mixture of nitrogen and sulphur vapours. They observed a resemblance of the band spectrum with that of NO (Fowler & Bakker, 1932) and concluded the presence of NS in the mixture. A few other methods for its formation have since been developed. These are :—

- (i) The passing on an electric discharge through SF₆ or sulphur vapour and nitrogen (Fowler & Bakker, 1932; Joshi, 1966; and Peyron & Thanmy, 1967).
- (ii) The interaction of sulphur vapour, H₂S or SCl₂ and active nitrogen (Bett & Winkler, 1964; Goudmand & Dessaux, 1967; Pannetier & Goudmand, 1962; and Petropules *et al.*, 1970).
- (iii) Photolysis of a mixture of COS and NF₃ (McGrath & Morrow, 1966).
- (iv) Volatilization of (SN)_n (Teichman & Nixon, 1976).
- (v) Thermal pyrolysis of S₄N₄ over quartz wool and silver wool at a temperature greater than 300 °C (Smith, 1979).

Evidence for the formation of SN⁺ and SN⁻ ions was provided for the first time by Dressler (Dressler, 1955) and O'Hare (O'Hare, 1971) respectively during their spectroscopic studies. Subsequent work by other workers (Glemser *et al.*, 1959 *a, b*; Glemser & Perl, 1961; Glemser & Richert, 1961; Glemser & Wyszomirski, 1961; Glemser & Koch, 1971*a, b*; and Glemser & Wegener, 1971) led to the isolation of a number of ionic salts containing NS⁺ ion which will be discussed at a later stage in the review.

NS bond length (149.7 pm) calculated from its spectroscopic moment of inertia (Zeeman, 1951), is shorter by 24–28 pm than the sum of the single bond covalent radii of nitrogen and oxygen. It suggests the bond order of NS between two and three which is parallel to that of NO because of the similar electronic structures of NS and NO molecules (Three bonding MO fully occupied and an odd electron in the antibonding MO).

The ionization potential for the process, NS (²π) → NS⁺(¹Σ) + e⁻ at 0 °K is 9.85 eV., (O'Hare, 1970). This value is slightly greater or similar to that for NO → NO⁺ + e⁻ (9.8 eV) (Tate & Vaughan, 1935; and Hagstrum & Tate, 1941) and is lesser than that for N₂ → N₂⁺ + e⁻ (15.5–17.2 eV)*, (Angus & Lackie, 1935) or that for O₂ → O₂⁺ + e⁻ (12.2–18.2 eV)* (Bornstein, 1951). The lower value of the ionization potential of NS than that for N₂ or O₂ and similar to that of NO reflects the loss of an

*The range in the value of the ionization potentials of N₂ and O₂ is given. The exact value will depend on the electronic state of the ion (N₂⁺ or O₂⁺).

odd electron from the antibonding MO of NS or NO to produce more stable ion which is isoelectronic to CO or N₂. The ionic character of the NS bond (24%) calculated on the basis of Pauling's criterion (Pauling, 1960) may be compared with that of PS bond (42%). This decrease in the ionicity of the bond parallels the difference between the electronegativities of phosphorus and nitrogen.

THERMODYNAMIC PROPERTIES

The thermodynamic properties of NS, NS⁺ and NS⁻ have been studied both theoretically and from the spectral and thermochemical data by O'Hare (O'Hare, 1970). The data relating to these properties are given in Table I.

TABLE I

Thermodynamic data of NS⁺, NS and NS⁻

(After Moore, 1970; Chiu & Silvers, 1975; Byfleet *et al.*, 1971; Carrington *et al.*, 1968; Amano *et al.*, 1969)

	Total energy hartree	Ionization potential eV	Dissociation energy (<i>D</i>) eV	Dipole moment (μ)	Quadrupole moment $Q \times 10^{-26}$ esu cm ²	ΔH_f eV
NS ⁺	-451.574631	24.32	5.31 \pm 0.31	3.893	0.1611	12.76
NS	-451.932861	9.45	5.2 \pm 0.2	1.732	-0.6734	2.91
NS ⁻	-451.95446	—	4.05 \pm 0.2	0.09	-3.89	—

The dissociation energy of NS molecule was determined using Hildenbrand and Murad relationship (Hildenbrand & Murad, 1969) (4.8 eV) which is in excellent agreement with the one obtained by the method proposed by Gaydon (Gaydon, 1968) (4.79 eV). Equation, $D_0^0(\text{NS}^-) = D_0^0(\text{NS}) + I(\text{S}) - I(\text{NS})$ was subsequently applied to calculate the heat of dissociation of NS⁺ (5.31 eV). Dissociation of NS⁻(³ Σ) to give N(¹S) and S⁻(²P) involves the uncoupling of the same number of electron pairs as those in the dissociation of NO⁻(³ Σ) to N(¹S) and O⁻(²P). Assuming the molecular extra correlation energy, ΔE_{cor} to be the same for both the processes, the dissociation energy, $D(\text{NA})$ and the electron affinity of NA and A (where A is O or S) were related as $D(\text{NA}^-) = D(\text{NA}) + E_a(\text{NA}) - E_a(\text{A})$. Using the data of NO (Berry, 1969; and Clementy *et al.*, 1964), ΔE_{cor} was calculated for NO⁻ which was also assumed to be the same for NS⁻ (0.1333 eV). Combination of the Hartree-Fock energies of N(⁴S), S⁻(²P) and NS⁻, yielded $D(\text{NS})$ from which the value of $D(\text{NS}^-)$ (4.05 \pm 0.2 eV) was calculated after the addition of $\Delta E_{\text{cor}}(\text{NS})$ to $D(\text{NS})$.

$*D_0^0/D_{\text{LBX}}^0 = \frac{5.256}{r_0 I(\text{S}) - E_a(\text{N})_0} + 0.448$, where D_0^0 is the true dissociation energy; D_{LBX}^0 , dissociation energy determined by the Linear Birge-Sponer extrapolation of spectroscopic data method (Hertzberg, 1950); r_0 , equilibrium internuclear distance (1.4957 Å for NS); $I(\text{S})$, ionization energy of sulphur (10.36 eV); and $E_a(\text{N})$, electron affinity of nitrogen (0.04 eV) (Beckett & Cassidy, 1969).

Using similar relationship, O'Hare has calculated the heat of formation of NS and NS⁺ (Table I). O'Hare's value of $\Delta H_f(\text{NS}^+)$ was slightly higher than that obtained by Shenkel *et al.* (1963) (10.9 eV). He ascribed this difference between the two values to the incorrect assumptions made by Shenkel *et al.* (1963) in their calculations.

Ab initio calculations for NS, NS⁺ and NS⁻ based on the Hartree-Folk Roothan approach by various workers (Roothan, 1951; Salahub & Messmer, 1976*a, b*; Jafri *et al.*, 1977; Deutsch & Curtiss, 1977; and Karpfen *et al.*, 1978) yielded the values of the ionization potential, and the dissociation energy in excellent agreement with the ones obtained by the experimental data.

It is interesting to note the $D(\text{NS})$ is less than that of $D(\text{NS}^+)$. Since NS⁺ has one less antibonding electron than in NS, the lower value of $D(\text{NS})$ is not unexpected. This type of lowering in the values of dissociation energies of the singly +vely charged species was also observed in other diatomic molecules which are isoelectronic with NS e.g., SiF, PO, CCl, etc. The same trend is also observed in the values of this ionization potentials of NS and NS⁺.

ELECTRONIC STRUCTURE OF NS AND RELATED COMPOUNDS

It is interesting that in contrast to its homologue, NO, having the same number of valence electrons, thionitrosyl molecule has only a transient existence in the gaseous phase. In solid or liquid phase it polymerizes too readily into S₂N₂, S₄N₄ and (SN)_x and is therefore not possible to isolate it. Further, S₂N₂, unlike N₂O₂, a colourless crysial-line solid, is highly explosive if not pure and undergoes polymerization into (NS)_x *via* S₄N₄. The geometries of these molecules are summarized in Table II. Several attempts (Peyron & Thanmy 1967; Bett & Winkler, 1964; Goudmand & Dessaux, 1967; Chiu & Silvers, 1975; and Silvers & Chiu, 1974) have been made to understand the electronic factors which lead to such a behaviour of NS.

TABLE II
Geometries of SN, S₂N₂ and S₄N₄

		r_{SN}	SNS	N
SN	$C_{\infty v}$	1.495	—	—
S ₂ N ₂	D_{2h}	1.620	95	85
S ₄ N ₄	D_{2d}	1.616	113	105

Monomer NS is a paramagnetic molecule having a doublet ${}^2\pi_{1/2}$ ground state with the lowest excited state ${}^2\pi_{3/2}$ lying 223 cm⁻¹ above the ground level. A calculated electronic configuration of the ground state of NS is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$, where the valence electrons of only nitrogen and sulphur are considered. In the molecular orbital description of NO $3\sigma^2$ and $1\pi^4$ levels are reversed, although the energy distance between them ($3\sigma^2$ and $1\pi^4$) is small in both the molecules. The calculations indicate that the sulphur *d*-orbital participation in the bond formation of NS is small (< 10%). With the result its effect on orbital energies is less than 0.3

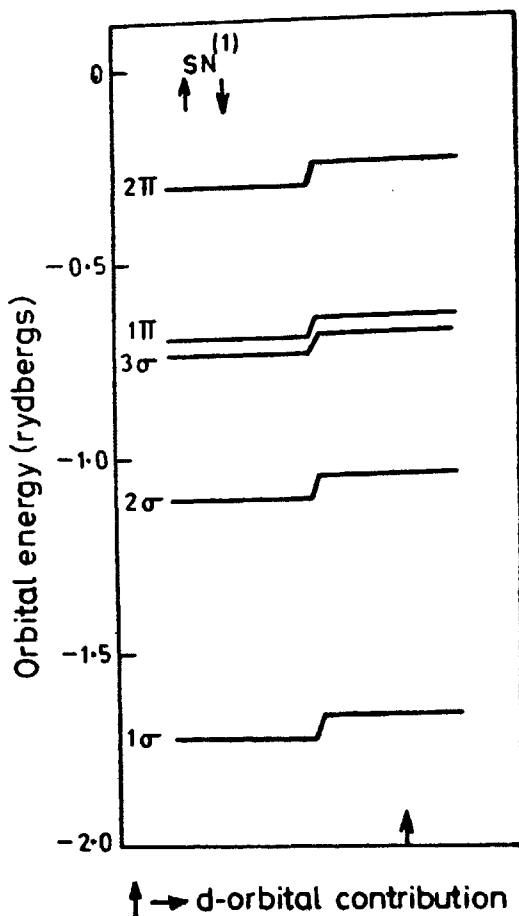


FIG. 1. Orbital energies for the molecular orbitals of NS.

eV. (Fig. 1). However, for S_2N_2 the extent of d -orbital participation is relatively larger though still of minor importance. A charge distribution analysis in each of the MO as well as the total charges on sulphur and nitrogen in SN shows that the charges in the sulphur and nitrogen spheres are within a few per cent of each other for all the molecular orbitals. Consequently, since the number of valence electrons on atomic sulphur is one more than that on atomic nitrogen, a net charge transfer (equivalent to approximately 0.5 electron) takes place from sulphur to nitrogen, which is in conformity with the electronegativity values of sulphur (2.5) and nitrogen (3.0). It will, thus, lead to a high value of the dipole moment of $SN(S^{\delta+} - N^{\delta-})$ (Experimental value of dipole moment of SN is $1.86D$). The situation in NO is just opposite to that of NS. The charge distribution in nitrogen and oxygen spheres in NO is less even and the calculated value of charge transfer is approximately equivalent to 0.32 electrons. This will result in a lower value of dipole moment of $N^{\delta-} - O^{\delta+}$ (the observed value of dipole moment of NO is $0.16D$). The direction of dipole moment of HO is opposite to what one would expect on the basis of the

electronegativity values of nitrogen (3.0) and oxygen (3.5). Hartree and Folk calculations (Neumann, 1970; and Green, 1972) predicted that the dipole moment of NO will be small and of opposite sign to that predicted by methods which include correlation effects. Thus, the dipole moment of NO depends on the detailed behaviour of electrons rather than on the net electronic charge in a somewhat arbitrary volume around each nucleus.

The structure of S_2N_2 (a square planar with alternating sulphur and nitrogen atoms and a bond distance of 1.65 Å) could be due to aligning of two $S^{\delta+} - N^{\delta-}$ molecules in such a way that the two dipoles interact in an electrostatically favourable manner. This type of alignment will not be stable in case of N_2O_2 which is actually a loosely bonded trapezoidal arrangement of N and O with the shortest distance (2.18 Å) between two nitrogen atoms (Green, 1973; Dulmager *et al.*, 1953; Lipscomb *et al.*, 1961; Lipscomb, 1971; Dinerman & Euring, 1970, 1971; Bragin & Evans, 1969; Warm & Chapmann, 1966; and MacDiarmid *et al.*, 1976). Despite the chemical binding in S_2N_2 is more complex than the simple dipolar interaction, it seems that one of the main factors controlling the relative geometry of S_2N_2 and N_2O_2 is electrostatic in nature. A charge distribution study in S_2N_2 shows a charge transfer of 0.48 electron per atom from S to N. A CNDO/2 localized MO study of S_2N_2 leads to the conclusion that the molecule is formed from σ electrons in three center bonds and four unshared pairs of electrons superimposed on a square planar (D_{2h} symmetry) σ bond structure. The physical and chemical properties of disulphur dinitride have been the subject of several studies (Walatka *et al.*, 1973; Green *et al.*, 1975a, b; Bright *et al.*, 1975; Rajan & Falicov, 1975; Zunger, 1975; Ley, 1975; Rudge & Grant, 1975; Mengel *et al.*, 1975; Patton & Roymond, 1969; Salahub & Messmer, 1976a, b; Messmer & Salahub, 1976; Collins & Duke, 1975; Torok *et al.*, 1974; Banister, 1975; Jolly, 1972; Cavallone & Clementi, 1975; Kertesz *et al.*, 1976; Baughman *et al.*, 1976; and Becke-Goehring & Zirker, 1956a, b).

A considerable amount of work (both theoretical and experimental) has been done on the structure of S_4N_4 , (Lippincott & Tobin, 1953; Sharma & Jonhue 1963; Brateman, 1965; Turner, 1966; Mason, 1969; Gopinathan & Whitehead, 1975; Slater, 1973; Goddard & Ladner, 1971; Hunt *et al.*, 1972; Chapman *et al.*, 1962; Clark, 1952; Griffith & Rutt, 1968; Lu & Donobue, 1944; Meinzer *et al.*, 1969; and Rogers & Gross, 1952). It is now generally agreed that S_4N_4 has a structure with four coplanar nitrogen atoms and four sulphur atoms alternatively above and below the plane. However, the question of the electronic structure and the nature of bonding are still open. Various workers, (Goddard & Ladner, 1971; and Hunt *et al.*, 1972) have found a different net charge transfer from sulphur to nitrogen (0.328–0.56 electron). All the methods indicate substantial S-S orbital overlap and little or practically no N-N bonding interaction. All the studies relating to sulphur nitrides and their structure lead to polar bonds in them. Further, it appears that in the polymerization process of SN to $(SN)_x$ bond dipolar forces determine the geometry of the dimer, S_2N_2 which is then thermally excited to a low lying high spin state and the chain propagation takes place as a result of interaction of these excited species followed by their rearrangements to yield $(SN)_x$ structure.

SPECTROSCOPIC PROPERTIES OF NS

A large number of papers related to the microwave spectra of NS have appeared in the literature, (Narsimham & Srikameswaran, 1962, 1963; Narasimhan & Bala Subramanian, 1971, 1974; Patel, 1963; Pannetier *et al.*, 1964, 1965; Young *et al.*, 1964; Carrington & Levy, 1966; Joshi, 1966; Torok *et al.*, 1974; Lovas & Tiemann, 1974; Johnson *et al.*, 1975; Gottlieb *et al.*, 1975; Kuiper *et al.*, 1975; Jenouvrier & Daumont, 1976; Vervloet & Jenouvrier, 1976; Varshalovich, 1977; Raghuveer, 1978; Murai *et al.*, 1979). In 1932, Fowler and Bakker had discovered the A_x and C_x systems of NS radical in the light emitted by an electric discharge through a mixture of nitrogen and sulphur vapour. Subsequently, there have been a number of other investigations in the course of which the excited valence states $B^2\pi$, $A^2\Delta$, $G^2\Sigma^-$, $H^2\pi$ and $I^2\Sigma^+$ have been identified besides the ground $X^2\pi$. Rosen has compiled all the spectroscopic data of NS molecule upto 1969 in the book "*Spectroscopic Data relative to Diatomic Molecules.*" Furthermore, a low lying $2\Sigma^+$ has also been reported which has been named as β -state. The observed states, X , B , A , G , H and I are associated respectively with the theoretical states $2\pi(1)$, $2\pi(2)$, $2\Delta(1)$, $2\Sigma^-(1)$, $2\pi(3)$ and $2\Sigma^+(2)$.

The electronic emission spectrum of NS has been discussed by Joshi (1966). The electronic states of NO and NS are shown in Fig. 2.

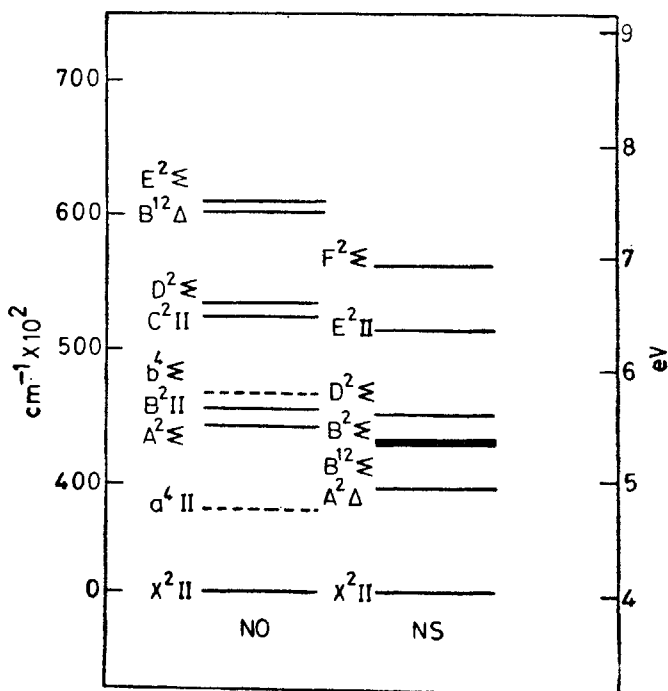


FIG. 2. Electronic states for NO and NS molecules.

The IR spectra of NS radical showed a very weak band at 1225 cm^{-1} (Teichman & Nixon, 1976) the vibration frequency of the gaseous NS molecule (Chapman *et al.*, 1964; and Nickless, 1968) is given as 1204.1 cm^{-1} .

Very little information is available in the literature concerning the ionic state of NS, the only ionic state to be even partially characterized is the ground state, Σ^+ . The band associated with the first ionization potential of the NS molecule corresponding to the ionization $\text{NS}^+(\text{X}^1\Sigma^+) \leftarrow \text{NS}(\text{X}^2\pi)$ has been observed by photoelectron spectroscopy using HeI and NeI photon sources (Dyne *et al.*, 1977). The vertical ionization of this band has been measured as $8.87 \pm 0.01\text{ eV}$ and the position of three vibration components associated with this band leads to $\text{We} = (1415 \pm 20)\text{cm}^{-1}$ and $\text{We Xe} = (15 \pm 10)\text{cm}^{-1}$ for the $\text{NS}^+(\text{X}^1\Sigma^+)$ state. The increased value of We compared with the neutral molecule value of 1219cm^{-1} (Jenouvrier & Pascot, 1973) is, as expected, consistent with the removal of an electron from an antibonding orbital and is directly analogous to the corresponding increase in vibrational frequency on going from $\text{NO}(\text{X}^2\pi)$ to $\text{NO}^+(\text{X}^1\Sigma^+)$.

The potential energy diagram (Fig. 3) has been constructed by using all the $\text{NS}^+(\text{X}^1\Sigma^+)$ parameters (Duke *et al.*, 1975). An average of the parameters of the $\text{X}^2\pi_{1/2}$ and $\text{X}^2\pi_{3/2}$ states has been taken in drawing this diagram. Also values of the dissociation energy and first ionization potential of $\text{S}(^3\text{P})$ have been taken as $(4.87 \pm 0.25)\text{eV}$ (Zeeman, 1951) and 10.357 eV (Moore, 1970) respectively.

ELECTRON PARAMAGNETIC RESONANCE

Carrington and Levy (1967) first observed the electron paramagnetic resonance spectrum of NS obtained by the action of nitrogen atoms with hydrogen sulphide in a spectrophotometer cavity and by reacting N-atoms with S_2Cl_2 (Carrington *et al.*, 1968). Uehara & Morino (1969) have detected an intense electron paramagnetic resonance spectrum of NS in the gas phase by passing a mixture of N_2 and SCL_2 through a microwave discharge cavity and then through a spectrometer cavity. The electron paramagnetic resonance spectrum of NS consists of three triplets and the position of the centre of the spectrum indicates a g factor close to 0.8 (the value expected for a molecule in a $^2\pi_{3/2}$ state in the lowest rotational level with $J = \frac{3}{2}$). The analyses of ultraviolet spectrum of NS shows that the ground state is actually $2\pi_{1/2}$ state. The electron spin g factor g_e of NS lies probably between the free spin g factor and the electron spin g factors for O_2 , for SO (Uehara, 1969) NS radical would be expected to have an electronic structure similar to that of NO and molecular parameters for the two species are compared in Table III (Fig. 4).

IONIC COMPOUNDS

Glemser & Koch (1971 *a, b*) for the first time obtained the ionic compound of NS^+ by the reaction of NSF with AsF_5 . A number of other methods for the syntheses of such saltlike compounds have since then been developed. The best results are achieved

*The dipole moments of NS^- and NS^+ are $0.09D$ (O'Hare, 1971) and $3.893D$ respectively. The change of dipole moments of NS from $1.84D$ (theoretical $1.73D$) to $0.09D$ for NS^- is consistent with the addition of one electron primarily at the sulphur end of the molecule.

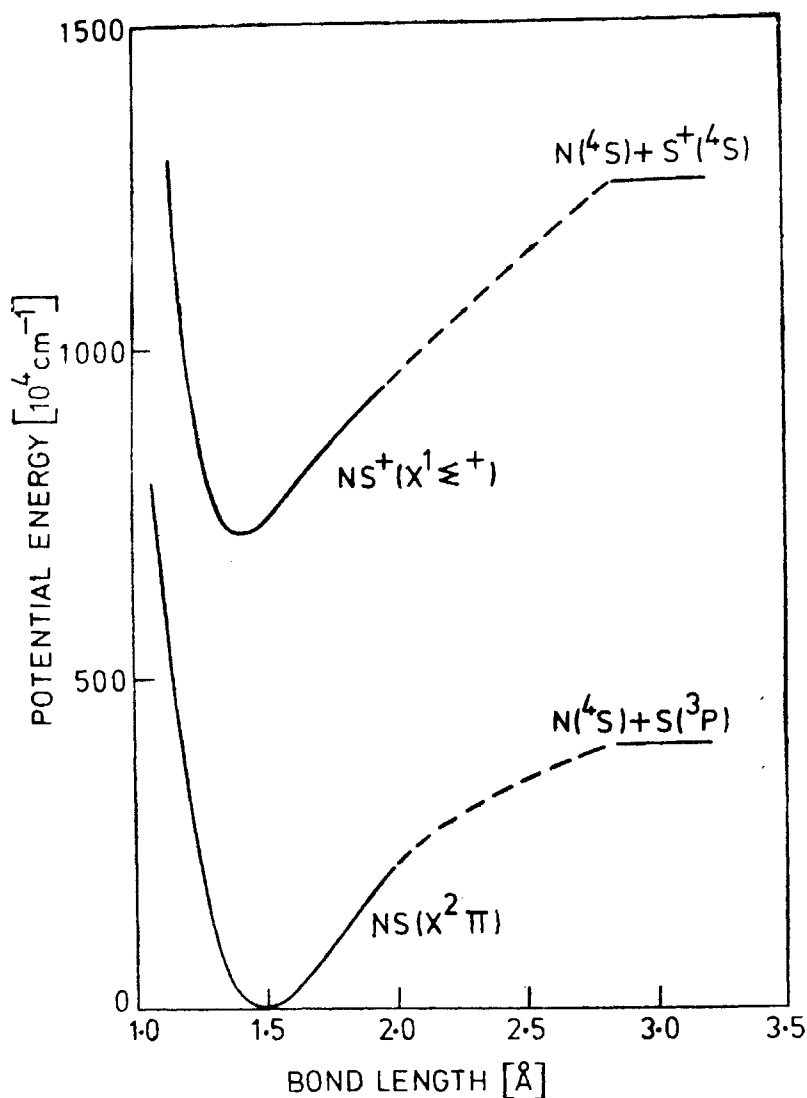


FIG. 3. Potential energy diagram

TABLE III

Molecular parameters for NS and NO

	NS	NO
Rotational constant B_0	0.7724 cm^{-1}	1.6957 cm^{-1}
Fine structure constant A	$223.0(3) \text{ cm}^{-1}$	$123.160 \pm 0.02 \text{ cm}^{-1}$
Hyperfine constant h	$56.8 \pm 0.5 \text{ MHz}$	$75.81 \pm 0.24 \text{ MHz}$
Quadrupole coupling constant Q	$3.1 \pm 0.5 \text{ MHz}$	$1.8 \pm 0.3 \text{ MHz}$
Dipole moment μ	$1.732 D$	$0.158 \pm 0.005 D$

by reacting NSF with the Lewis acids, MF_5 ($M = As$ or Sb or BF_3) in the gaseous phase at reduced pressure (Glemser *et al.*, 1959*a, b*, 1961*a, b*; and Mews, 1976*a, b*). For preparative purposes these salts could best be synthesized by the reaction of NSF with MF_5 in liquid SO_2 . A yield upto 90–100 per cent can be attained by this method.

The thionitrosyl compounds, $NS^+ AsF_6^-$, $NS^+ SbF_6^-$ or $NS^+ BF_6^-$, were also obtained by the action of tri or tetramer of NSF with an excess of AsF_5 , SbF_5 or BF_5 respectively (Mews *et al.*, 1975).

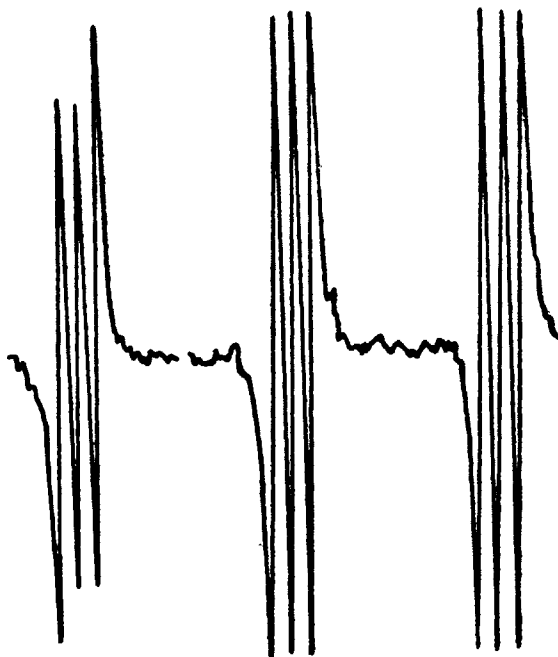
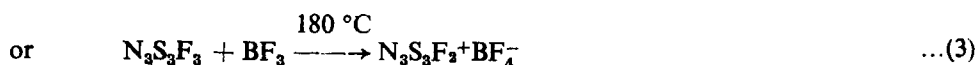
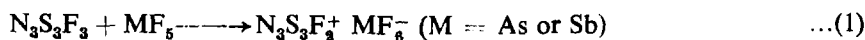
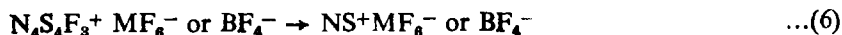


FIG. 4. EPR spectrum of NS.



Purification of $\text{NS}^+\text{AsF}_6^-$ can be affected by subliming the crude product at 40°C under reduced pressure whereby a stable colourless waxy solid which can be kept without decomposition for years in dry glass vessel, was obtained. The purification of $\text{NS}^+\text{SbF}_6^-$ was accomplished by heating it at 100°C and the residue, thus left, is crystallized either from liquid SO_2 or from SO_2ClF . Tetrafluoro derivative is not stable even at low temperatures and it could, therefore, not be purified by recrystallization.

The ionic nature of these compounds was confirmed by the following experimental techniques.

(a) *Raman Spectra*

The Raman spectra of all these salts showed one band in the region 1435 cm^{-1} which was assigned to $\nu_{(\text{NS})}$. This band appeared in the spectrum of NSF at a lower frequency (1372 cm^{-1}). From these band positions, the valence field force constants** of the NS and its bond order were calculated. The results indicate a considerable strengthening of NS bond in NS^+ salt like compounds, which further confirms the ionic nature of the salts. The frequencies of some of the compounds are shown in Table IV.

TABLE IV
Thionitrosyl cations

	m.p. $^\circ\text{C}$	Colour	Raman frequency $\nu_{(\text{NS})}\text{cm}^{-1}$	Reference
$\text{NS}^+\text{AsF}_6^-$	—	Colourless	1437	(Glemser <i>et al.</i> , 1971)
$\text{NS}^+\text{SbF}_6^-$	—	Colourless	1448	(Mews, 1976a, b)
NS^+BF_6^-	—	Colourless	—	(Glemser <i>et al.</i> , 1959a, b, 1961)
$\text{NS}^+\text{CF}_3\text{SO}_3^-$	120	Colourless	1443	(Mews, 1976a, b)
$\text{NS}^+\text{AlCl}_4^-$	—	—	—	(Banister & Clarke, 1972)
$\text{NS}^+\text{FeCl}_4^-$	—	—	—	—
$\text{NS}^+\text{GaCl}_4^-$	—	—	—	—

(b) *NMR Spectra*

There appeared no signal of F^{19} between $+350$ to -440 ppm, characteristic to SF. It has, therefore, been assumed that there is no bond between sulphur and fluorine.

(c) *Exchange Reactions*

The lack of exchange of F^{19} between the anions of these compounds and (AsF_6^-) further confirm the ionic nature of the compounds.

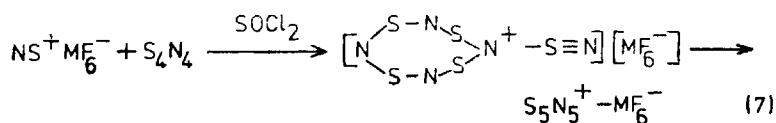
** $f(\text{S}^+)$ Nin $\text{NS}^+\text{AsF}_6^- = 11.85$ Dynes/ \AA $f(\text{NS})$ in NSF = 10.71 Dynes/ \AA
Bond order, $\eta(\text{NS}^+) = 2.6$ Bond order of NS; $\eta\text{NS} = 2.4$

Since attempts to obtain a single crystal of these compounds failed, no single crystal X-ray structural studies was thus far reported in the literature.

Thionitrosyl salts have been used to introduce thionitrosyl group into other molecules. Synthetic possibilities by these ionic compounds include reactions with anions, nucleophiles and with compounds having polar bonds. Thus,

(i) *Reaction of Thionitrosyl Cation with Anions*: The reaction of $\text{NS}^+\text{AsF}_6^-$ with $\text{NO}^+(\text{CF}_3\text{SO}_3)^-$ in liquid sulphurdioxide yielded a colourless product, $\text{NS}^+\text{CF}_3\text{SO}_3^-$ (m.p. 120°C) which was purified by sublimation ($30^\circ\text{C}/0.01$ torr). It was extremely hygroscopic and sensitive to hydrolysis. The ease of sublimation was taken as an indication for its being monomer at least in the gaseous phase. The presence of a band in its Raman spectrum due to ν_{NS^+} at 1443 cm^{-1} is in support of its being an ionic compound.

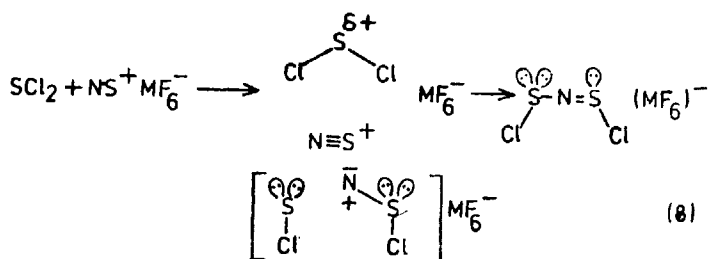
(ii) *Reaction of Thionitrosyl Cation with Nucleophiles*: Insertion of NS unit into S_4N_4 gives yellow pentathiazyl salts in the yields of about 80 per cent. Thus,



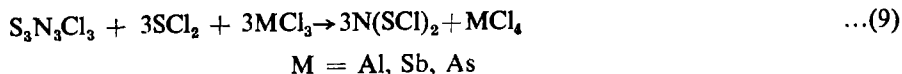
M = As (Yellow solid m.p. 267°C) or Sb (yellow solid, m.p. 175°C).

The formulation of the intermediate product in these reactions is quite arbitrary because both are simply addition of the nucleophile, S_4N_4 , to sulphur of NS: to form either linear cationic thiazenes or a cyclo addition product of NS: to S_4N_4 . When the same reaction was carried out in liquid SO_2 , the reaction product was a black solid, $(\text{S}_5\text{N}_5)^+\text{AsF}_6^-$ (dec. 110°C) together with other unidentified substances. The i.r. spectrum of $\text{S}_5\text{N}_5^+\text{AsF}_6^-$ showed a strong band at 700 cm^{-1} characteristic of AsF_6^- group and a broad band at 850 cm^{-1} indicating its polymeric nature. The ratio of NS: AsF_6^- in the black compound can be varied by changing the stoichiometry of the reacting species. A drop in this ratio (increase in charges of the polymer) was associated with shift of position of ν_{NS} band towards higher wave numbers.

(iii) *Reaction of the Thionitrosyl Cation with Polar Bonds*: The reaction of S_2Cl_2 with NS^+MF_6^- gave $\text{N}(\text{S}_2\text{Cl}_2)^+\text{MF}_6^-$ (M = As or Sb) according to the following reaction:



The synthesis of the cation, $[\text{N}(\overline{\text{SCl}}_2)]^+$ (Glemser, 1969) was first accomplished as tetrachloroborate from the reaction of NSF_3 and BCl_3 . It can also be obtained from SCl_2 , $(\text{NSCl})_3$ and MCl_3 (Glemser *et al.*, 1971; and Alange *et al.*, 1979). Thus,



The compound $[\text{3N}(\text{SCl}_2)_2][\text{MF}_6]^-$ which can be regarded as derivative of : $\text{CISN}=\text{SCl}_2$ or $\text{CISN} = \text{SClF}$, decomposes on reacting with NOCl .

The reaction of NS^+MF_6^- with SCl_2 can be generalized for sulphanyl chloride. Thus, the salts $[\text{CF}_3\text{SN}(\text{SCl})]^+\text{MF}_6^-$ and $[(\text{CF}_3)_2\text{C}=\text{N}-\text{SN}(\text{SCl})]^+\text{MF}_6^-$ were prepared by reacting NS^+MF_6^- with CF_3SCl and $(\text{CF}_3)_2\text{C}=\text{N}-\text{SCl}$ respectively.

COVALENT COMPOUNDS

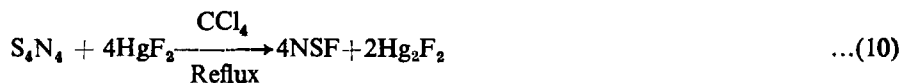
The chemistry of the compounds containing nitrogen sulphur and halide (halide = Cl or F) is mainly concerned with the covalent compounds of thionitrosyl. There are three principal covalent compounds of NS viz., NSF , NSF_3 and NSCl which we shall discuss here.

THIONITROSYL FLUORIDE NSF

The literature methods of synthesizing this compound are :

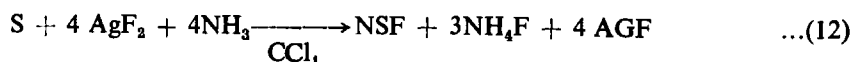
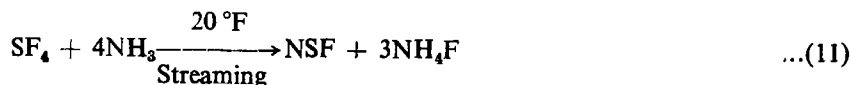
Fluorination of Compounds containing NS Bonds

AgF_2 (Glemser *et al.*, 1960, 1961), COF_2 and HgF_2 (Glemser, 1964) can fluorinate S_4N_4 producing NSF .



Other compounds used as fluorinating agents are SeF_4 , F_2 (Cohen *et al.*, 1965), SF_4 (Cohen & MacDiarmid, 1965), IF_5 and SbF_5 . The latter two agents give first adducts, viz., $(\text{NSF})_4\text{S}_4\text{N}_4$ or $\text{S}_4\text{N}_4(\text{SbF}_5)_4$ which gave NSF when they are thermally decomposed (Cohen *et al.*, 1966).

Reaction of SF_4 with NH_3



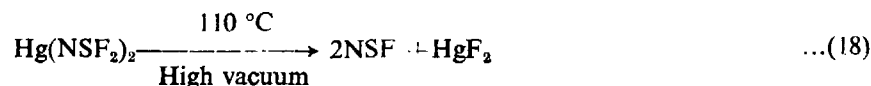
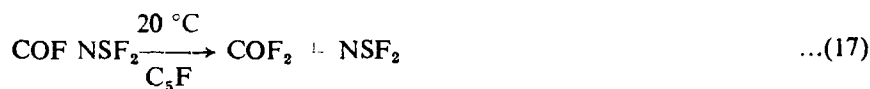
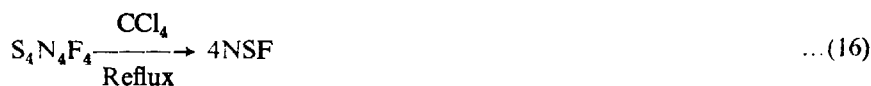
*Reaction of NF_3 with Sulphur or Metal Sulphide (after Glemser *et al.*, 1965 1967; and, McGrath & Morrow, 1966)*





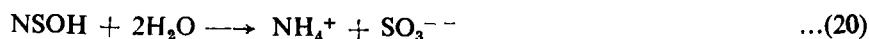
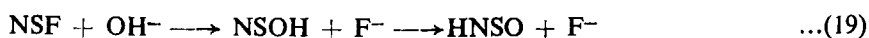
In the course of these reactions other by-products difficult to separate were also obtained. Maximum yield was found to be 20–30 per cent.

Decomposition of Compounds containing NSF Group (after Glemser et al., 1961; Clifford et al., 1964; Ruff, 1966)

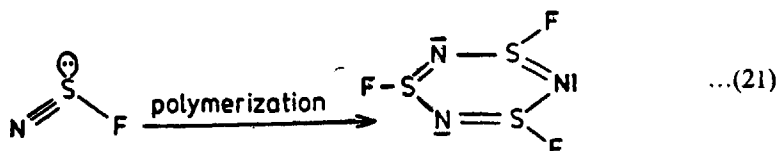


The last reaction is suitable for the preparation of NSF in large quantities.

Thionitrosyl flouride (m.p. -89°C , b.p. 0.4°C) is a pungent smelling and pale yellow liquid. It is hydrolysed with water to give NH_3 , sulphite and fluoride ion probably *via* unstable intermediate, thionylimide (Roesky et al., 1968).

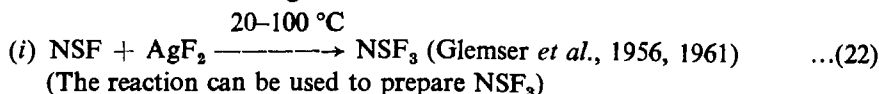


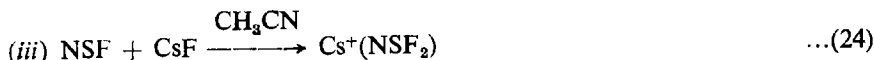
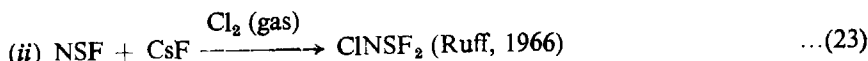
The hydrolysis of NSF with dilute NaOH yielded first a yellow precipitate which was dissolved rapidly. It cannot be stored at room temperature in glass vessels owing to its decomposition into N_2 , SOF_2 , SiF_4 and $(\text{NSF})_3$. In teflon or copper containers it is relatively stable in liquid state but there trimerization also occurs slowly.



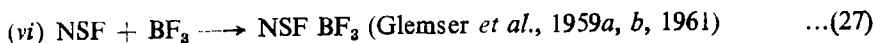
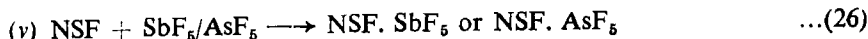
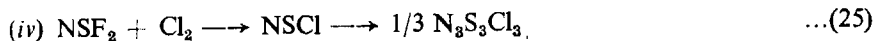
In gaseous state at reduced pressure S_4N_4 or $\text{S}_3\text{N}_2\text{F}_2$ are the products of decomposition (Glemser et al., 1957, 1959b).

Other reactions of NSF are given below :





Reactions (ii) and (iii) illustrate the transformation of NSF into NSF₂.



Reactions (v) and (vi) are used in the preparation of ionic compounds of NS⁺ (see section of Ionic compounds)

(vii) The thionitrosylfluoride (NSF) is decomposed by HF



(viii) The thionitrosylfluoride loses F⁻ and goes over to thiazyl cation



(ix) γ-irradiation of NSF in SF₆ gives probably NSF₂ and FNSF radicals (Boate & Preston, 1978).

Kirchhoff and Wilson (1963) determined the molecular parameters from IR, NMR, microwave studies and proposed structure (I). It was further confirmed by LCAOMO *ab initio* studies (Collins & Duke, 1978) and CNDO/2 calculations (Gonbeau & Pfister Gnillouzo, 1976). These results do not agree with the structure (II) and (III) proposed by Glemser, *et al.* (1960) from their studies and supported by Rogowski (1961) on the basis of electron diffraction studies. (Duke Collins & Duke, 1978) recently observed that NSF is more stable than SNF. The observed S—F distance is 1.585Å in SOCl₂, 1.53Å in sulphonyl fluoride (Lide *et al.*, 1957), 1.58Å in SF₆, 1.50Å in S₂F₁₀ and N—S distance 1.416Å in NSF₃. It is evident from these results that S—F and N—S distances in thionitrosylfluoride are significantly larger than the ordinary single and triple bonds.

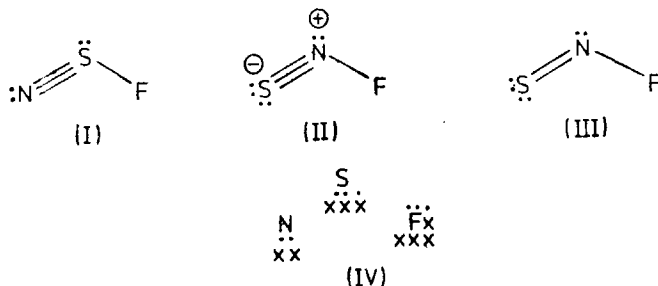


FIG. 5

The NS force constant $f(\text{NS})$ calculated from microwave and IR data has a value 10.7 mdyne/\AA (Richert & Glemser, 1961; Mirri & Guarhieri, 1967; and Cook & Kirchhoff, 1967) from which a bond order of 2.4 was calculated (Siebert 1953). For NSCl having similar structure, $f(\text{NS})$ is found to be 10.0 mdyne/\AA and bond order, 2.2 (Muller *et al.*, 1967). Thus, NS bond order depends upon the electronegativity of the element attached to sulphur which therefore suggests $d\pi - p\pi$ bonding between N and S. Since then structure IV was proposed based on the hypothesis of Linnett (1961). This structure is thought to be the most stable configuration of NSF in the ground state as the doublet quartet of electrons (O'Hare, 1970). The 'dots' represent the electrons with spin quantum number of $+1/2$ and the 'crosses', the electrons with spin quantum number of $-1/2$ or vice versa. Both the spin sets of nine electrons favour a bent configuration. The two sets of four electrons around each nucleus can be treated as being uncorrelated and spatially related to one another. The electrostatic repulsion and the pauli-principal effect cancel one another as far as the spatial correlation of the two sets is concerned. The electrons are widely separated in structure (IV) than they are in other structures.

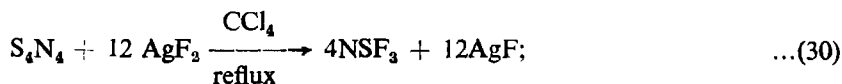
The enthalpy of formation $\Delta H_f(\text{NSF, gas, } 298\text{--}15^\circ\text{K}) 41 \pm 2 \text{ kcal mole}^{-1}$ (O'Hare, 1970) is derived from $\Delta H_f(\text{NSF}_3, \text{ gas, } 298.15^\circ\text{K})$ and the mass spectro-metric appearance potentials (Glemser & Biermann 1968; and Glemser *et al.*, 1968). The dissociation energy $D_{\text{NS}}(\text{NSF}) = 71 \pm 5 \text{ kcal mole}^{-1}$ (O'Hare, 1970) dipole moment $1.902D$ (Cook & Kirchhoff, 1967). NMR and electronic spectral studies of NSF (Barrow *et al.*, 1969) have also been carried out.

THIONITROSYL TRIFLUORIDE NSF_3

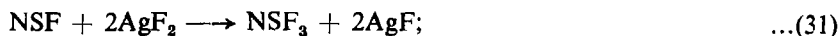
NSF_3 is the first compound with N—S triple bond and in which nitrogen and fluorine together share six covalent bonds with sulphur.

NSF_3 can be synthesized (a) by fluorination of N—S compounds containing sulphur in +4 or lower oxidation states and (b) by the reaction of $\text{S}^{+6} - \text{F}$ compounds with excess of ammonia. It can thus be obtained :

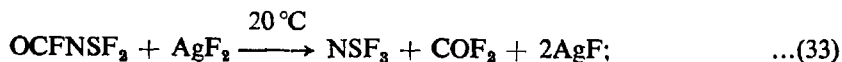
(a₁) by refluxing tetrasulphurtetranitride with silver difluoride in carbon tetrachloride (Glemser *et al.*, 1957; Glemser & Richert, 1961; and Glemser *et al.*, 1964)



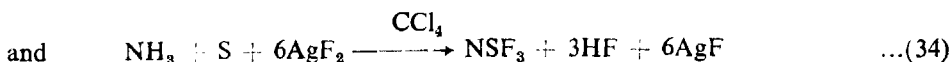
(a₂) by fluorination of thionitrosyl fluoride with the silver difluoride (Glemser *et al.*, 1957; Glemser & Richert, 1961; and Glemser *et al.*, 1964; and Clifford & Thompson, 1966)



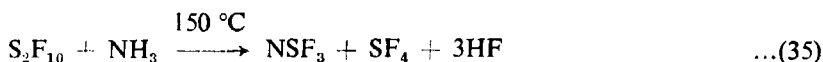
(a₃) by the reaction of COFNSF_2 with AgF_2 ... (32)



(b₁) by passing ammonia into a suspension of sulphur and AgF₂ in CCl₄



(b₂) by reducing S₂F₁₀ with excess of ammonia (Clifford *et al.*, 1966; and Cohen *et al.*, 1965)

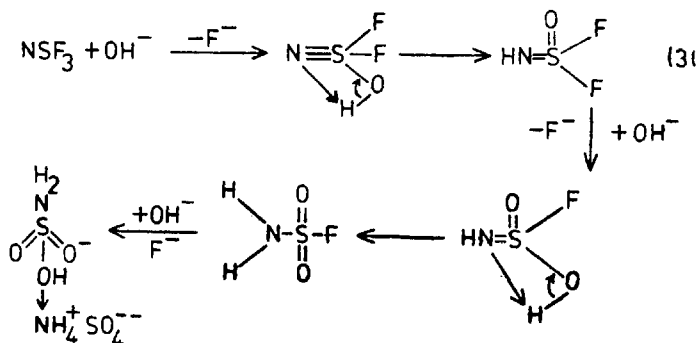


The last method of synthesizing NTS₃ is in particular not very much employed because of high toxicity of S₂F₁₀ and of the low yield.

Thionitrosyltrifluoride is a colourless, pungent smelling gas (m. p. $-72.6^\circ \pm 0.5$, b.p. $-27.1^\circ \pm 0.1^\circ$). Its enthalpy of formation and dissociation energy, $D(\text{NA})$, are 85 kcal mole⁻¹ and 93 ± 2 kcal mole⁻¹ respectively (Mews *et al.*, 1975). It is thermally and chemically very stable because of which its use as dielectric has been suggested elsewhere. It decomposes only above 500 °C in glass vessels to give sulphur, SO₂, nitrogen, SiF₄ and metallic fluorides as decomposition products (Glemser *et al.*, 1961). It is unaffected by metallic sodium upto 300 °C and unlike NSF it is not hydrolysed by dilute mineral acids.

The important reactions of NSF₃ are as follows :

(a) It is hydrolysed by strong alkali. In this reaction proton migration is suggested if a sulphur oxygen double bond can form at the expense of a sulphur-nitrogen multiple bond (Roesky *et al.*, 1967).

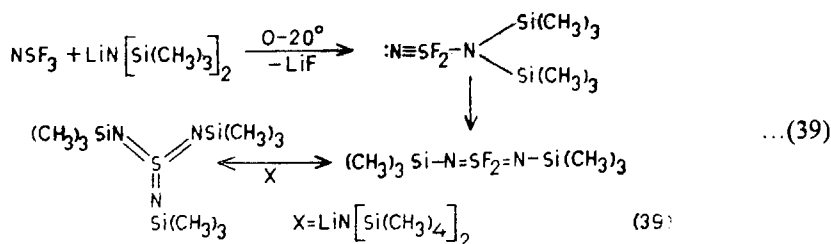


(b) It forms adducts with Lewis acids, like BF₃, MF₅ (M = AS, Sb) (Glemser *et al.*, 1959a,b; and Muller *et al.*, 1966)

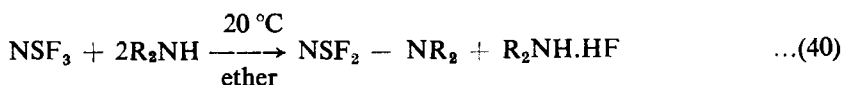


In gaseous phase these adducts dissociate into their components. Their IR spectra show a shift in the position of $\nu_{(\text{NS})}$ towards higher wave numbers by about 200 cm⁻¹ which is due to the increase in the N—S bond order from 2.7 to 2.9.

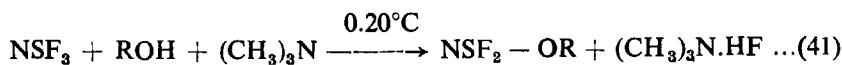
(c) It reacts with $\text{LiN}[\text{Si}(\text{CH}_3)_3]_2$ to yield $(\text{CH}_3)_3\text{Si}-\text{N}=\text{SF}_2=\text{N}-\text{Si}(\text{CH}_3)_3$ (Glemser & Wegener, 1970) which further reacts with one more molecule of $\text{LiN}[\text{Si}(\text{CH}_3)_3]_2$ resulting in the splitting of two fluorine atoms attached to sulfur and the formation of the aza analogue of SO_3 .



(d) The fluorine atom of NSF_3 can be exchanged with $-\text{NR}_2$ or $-\text{OR}$ group while retaining its $\text{N}-\text{S}$ bond (Glemser *et al.*, 1968)



$\text{R} = \text{C}_2\text{H}_5$, piperidine

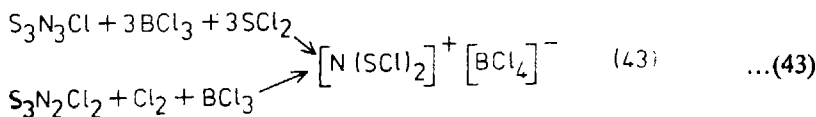


$\text{R} = \text{C}_6\text{H}_5$.

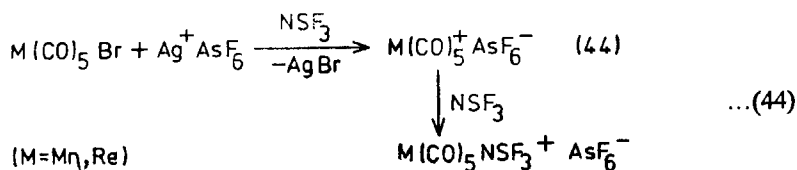
(e) Boron trichloride reacts with NSF_3 with the formation of an ionic compound, $[\text{N}(\text{SCl})_2]^+ [\text{BCl}_4]^-$

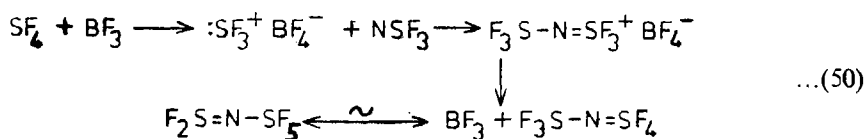


Although this reaction is not well understood mechanistically, but possibly it proceeds *via* an adduct formation followed by $\text{F}-\text{Cl}$ exchange on sulphur and reduction of NSF_3 to NSCl . The following syntheses of this compound support the reaction path



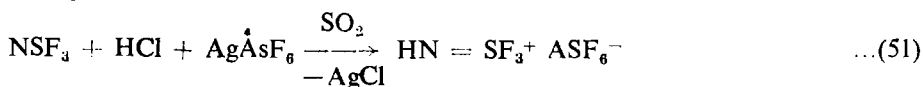
(f) Coordinatively unsaturated transition metal complexes react as Lewis acids and add electrophilically (Mews *et al.*, 1975)





The primary cation, thus formed should be unstable under the reaction conditions and it therefore takes F^- ion from the anion to form neutral $\text{F}_3\text{S}-\text{N}=\text{SF}_4$. Disproportionation then leads to $\text{SF}_5-\text{N}=\text{SF}_2$.

(h) The nitrogen of the thionitrosyltrifluoride is protonated by HCl in the presence of AgAsF_6



(i) $\text{LiN}(\text{SiMe}_3)$ (CMe_3) reacts with NSF_3 to give $\text{S}(\text{NSiMe}_3)$ ($:\text{NCMe}_3$)₂ and $\text{S}(:\text{NCMe}_3)$ ₃ (Tesky, 1979).

Structure

The structure of NSF_3 (Fig. 6) has been determined from the IR (Richert & Glemser, 1961; and Rakaswamy *et al.*, 1962), Raman (Muller *et al.*, 1969), NMR (Richert & Glemser, 1961) and microwave spectra (Kirchnoff & Wilson 1962).

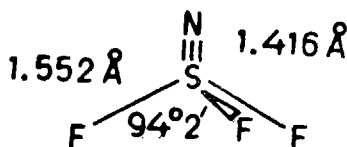


FIG. 6.

The NMR absorption of NSF_3 (Richert & Glemser, 1961) lies in the same region as that in the spectrum of SF_6 suggesting all the fluorine atoms to be equivalent and bound to the sulfur atom. The molecule has, therefore, C_{3v} symmetry. This symmetry is further confirmed by IR spectrum which is similar to OPF_3 . As regards the number and the shape of the bands, calculation of the $\text{S}-\text{N}$ bond strength from the force constants (Richert & Glemser, 1961; Rakaswamy *et al.*, 1962; and Muller *et al.*, 1969) $f_{\text{NS}}(\text{NSF}_3)$ (12.4 mdyne/Å) and $f_{\text{SF}}(5.6 \text{ mdyne/Å})$ gives the bond order of $\text{N}-\text{S}$; 2.7. These results were confirmed by the microwave spectrum of NSF_3 (Kirchoff & Wilson, 1962). It has a dipole moment of 1.91 Debye. The very short $\text{S}-\text{N}$ bond distance indicates considerable amount of $\text{P}(\text{N})-\text{d}(\text{S})$ overlap (bond order 2.7). The electronic spectra of NSF_3 has been discussed (Muller *et al.*, 1969).

THIONITROSYL CHLORIDE

The preparation of thionitrosyl chloride can be effected by any one of the following methods :

(a) the action of chlorine on gaseous thionitrosylfluoride



(b) by the action of S_2Cl_2 with ammonium chloride;

(c) by thermal fission of $S_3N_2Cl_2$;

(d) by the action of chlorine upon $S_3N_2Cl_2$ (Maguire *et al.*, 1963; and Jolly & Maguire, 1967)



(e) by reacting S_2Cl_2 vapour and active nitrogen (Maguire *et al.*, 1963)



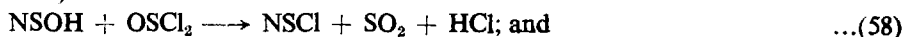
(f) by the thermal decomposition of trithiazyltrifluoride $N_3S_3Cl_3$ (Glemser *et al.*, 1961; and Lipp & Jolly, 1971)



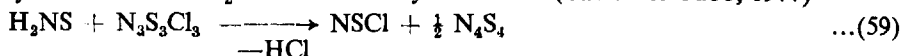
(g) by chlorination of tetrasulphurtetranitride (Vincent & Monteil, 1978)



(h) by the reaction of thionylchloride with thionylimide (Dekock & Hadad, 1977)

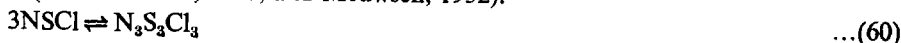


(i) by the reaction of H_2NS with trithiazyltrichloride (Barton & Bubb, 1977)

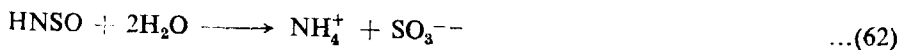


Properties

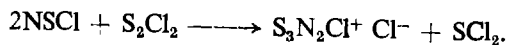
Thionitrosyl chloride, a greenish yellow gas, readily polymerizes to form a stable trimer (Glemser *et al.*, 1961; and Meuwesen, 1932).



It is moisture sensitive and readily hydrolysed by water to form $HNSO$, NH_4^+ and SO_3^{--} (Dekock & Haddad, 1977)



The values of the enthalpy and entropy change in the formation of $NSCl$ from trithiazyltrichloride are $\Delta H = 21.9 \pm 3.0$ kcal/mole and $\Delta S^\circ(NSCl) = 77.5 \pm 9.4$ cal/deg/mole respectively. $NSCl$ is known to react with S_2Cl_2 (Maguire *et al.*, 1963) according to the equation



The absolute entropy of $NSCl(g)$ has been calculated from spectroscopic data (O'Hare, *et al.*, 1966) as 63.66 cal deg $^{-1}$ mole $^{-1}$.

The pressure of $NSCl$ vapour in equilibrium with solid $N_3S_3Cl_3$ is measured in a static system at 31 to 60 °C (Patton & Jolly, 1970). A plot of $\log p_{NSCl}$ vs. $\frac{1}{T}$ gives a straight line (Fig. 7) through the points corresponds to the equation

$P_{\text{NSCl}} = 12.321 - \frac{3360}{T}$. From this $\Delta H_f(\text{NSCl}) = 46.2 \pm 1.5$ kcal/mole and $\Delta S(\text{NSCl}) = 129.6 \pm 4.8$ cal deg⁻¹ mole⁻¹ were calculated for the reactions

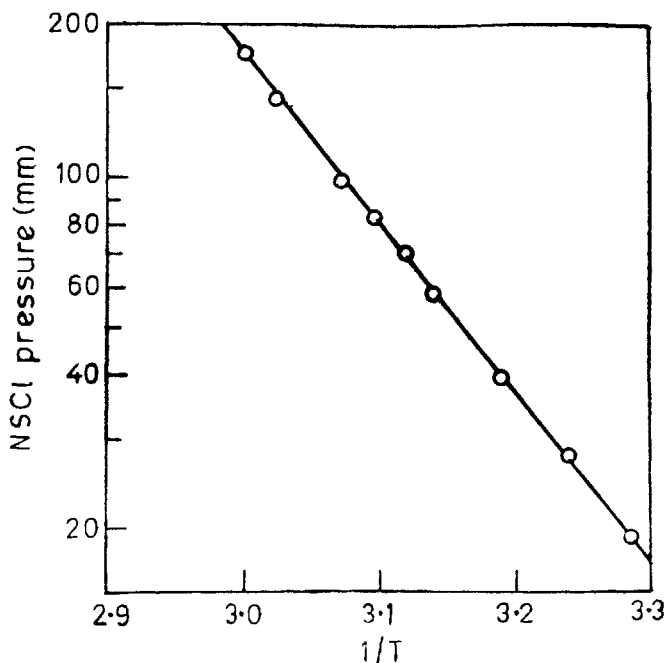
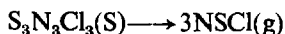


FIG. 7. Plot of $\log P_{\text{NSCl}}$ VS. $1/T$.

The RI spectrum of NSCl (Glemser *et al.*, 1961; Becke-Goehring & Schlafer, 1966; Muller *et al.*, 1976; and Siebert, 1966) shows absorption bands due to $\nu_{(\text{NS})}$, $\nu_{(\text{SCl})}$ and $\nu_{(\text{NSCl})}$ at 1320 cm⁻¹, 412 cm⁻¹, and 269 cm⁻¹ respectively.

Structure

NSCl should be nonlinear according to Walsh rule (Walsh, 1953) with C_s point group. Accordingly, its IR or Raman spectrum shows three allowed bands. From the positions of these bands (1320, 412 and 269 cm⁻¹), force constants were calculated by neglecting the cross terms in the potential function (Table VI). Because of the very high force constant ($f_{\text{NS}} = 10.02$ mdyne/Å) (Sanyal *et al.*, 1976) and bond order ($\text{NS}_1 = 2.3$) values structure (I) and valence bond structures (II & III) and not the SNCl are proposed for thionitrosylchloride (Siebert, 1966).

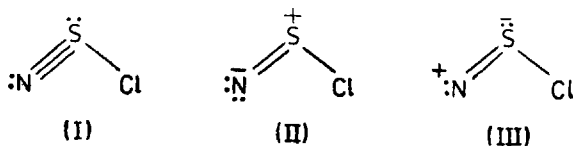


FIG. 8.

TABLE VI

Vibrational frequencies (in cm⁻¹) and force constants (m dyne/Å) for NSCl

Vibration	Frequency	Fundamentals	Force constants
ν_N	1333.0(R) 1323.8(Q) 1316.0(P)	1324.5	$10.04 \pm 0.07 (F_{11})$
ν_{S-Cl}	423.9(R) 414.4(Q) 405.6(P)	414.8	$1.49 \pm 0.23 (F_{22})$
δ_{NSCl}	281.5(R) 275.2(Q) 261.7(P)	271.6	$0.83 \pm 0.02 (F_{33})$

These structures are similar to those of thionitrosyl-fluoride. The structures of thionitrosylhalides are different from those of nitrosyl halides, NO_x where halide atom is attached to the nitrogen atom and not with the oxygen (Ketellar & Palmer, 1937; Burns & Bernstein, 1950; Stephensen & Jones, 1952; Beppu *et al.*, 1970; Cook, 1965; and Weatherly & Williams, 1956). Microwave spectrum (Millen & Pannel, 1961) of the NSCl was observed by pumping the products of thermally decomposing $N_3S_3Cl_3$ continuously through the cell. The rotation constants were obtained for $N^{14}S^{32}Cl^{35}$, $N^{14}S^{32}Cl^{37}$, and $N^{15}S^{32}Cl^{35}$ in ground vibrational state and from there the molecular dimensions were determined. These are summarised in Table VII.

TABLE VII

Molecular dimension of NSCl

Compound	$N^{14}S^{32}Cl^{35}$	$N^{14}S^{32}Cl^{37}$	$N^{15}S^{32}Cl^{35}$
NS	1.450	1.458	1.448
SCI	2.163	2.157	2.164
NSCl	$117^\circ, 48'$	$118^\circ, 8'$	$117^\circ, 45'$

The S-Cl bond length of NSCl is longer than the sum of Pauling's covalent radii ($1.04 + 0.99 = 2.03 \text{ \AA}$). This anomaly in the bond length seems consistent with the fact that the quadrupole coupling constant of the Cl nucleus is smaller than the average value for many ordinary molecules. This indicates the weak ionic nature of S-Cl bond in the thionitrosyl molecule.

Structural Correlations

Various attempts have been made to establish a relationship between the N-S bond distance (r_{NS}) and the bond order η_{NS} (Fig. 9) in order to characterize the N-S bond in NSF, NSF₃ and NSCl. As a result of this a relationship between r_{NS} and f_{NS} has been found which takes the form $f_{NS} = 1.45 r_{NS}^{-7.00}$. However, this linear dependence of r_{NS} and η_{NS} (Glemser 1963; Griffith & Rutt, 1968; and Banister *et al.*, 1967) shall be considered only as an approximation. Table VIII shows physical properties and Table IX shows force constants, bond distances, bond orders, bond energies and IR frequencies for NSF, NSF₃ and NSCl. The frequency

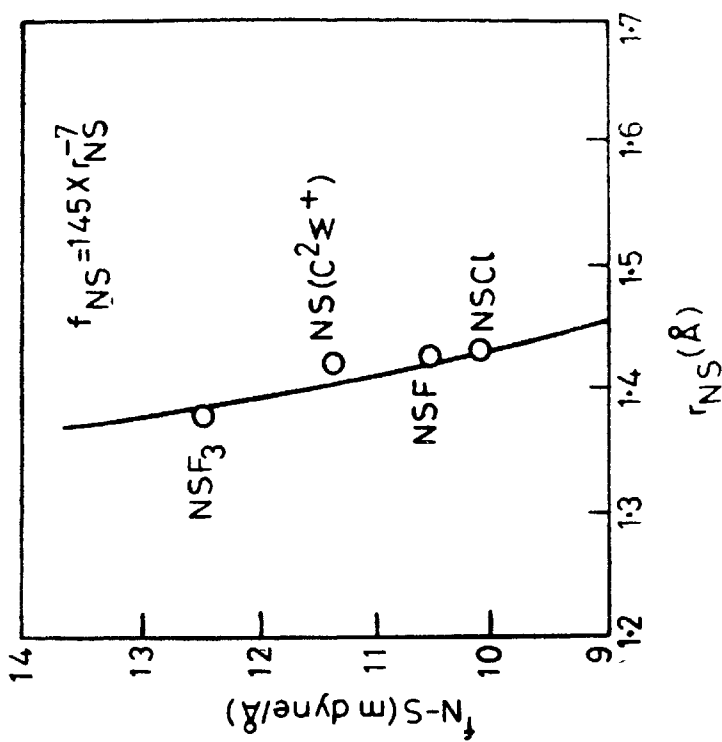


FIG. 9. Correlation of force constants and bond lengths.

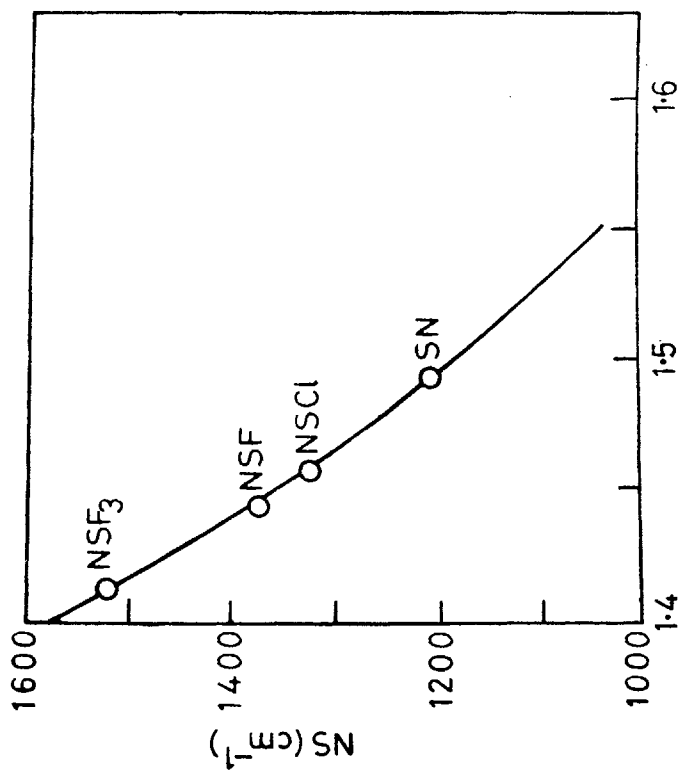


FIG. 10. Correlation of S-N stretching frequencies and bond lengths.

observed for NSF (1372 cm^{-1}) suggests that its bond order is less than that in NSF_3 (1515 cm^{-1}) and greater than that in NSCl (1320 cm^{-1}) (Fig. 10).

METALLIC AND NON-METALLIC ADDUCTS AND COMPOUNDS OF SULPHUR NITRIDE

Many reactions of S_4N_4 or S_2N_2 with the compounds of the transition metals, post transition metals and with Lewis acids give rise to compounds in which (i) there are S—N ligands or (ii) there are adducts of molecule of S_4N_4 . These have been well reviewed (Becke-Goehring & Schlafer, 1968; and Heal, 1972) and only the main results will be described here (Table X).

Two types of structures have been found for S_4N_4 adducts complexes. X-ray structure determination of $\text{S}_4\text{N}_4\text{SbCl}_5$ and $\text{S}_4\text{N}_4\text{BF}_3$ (Drew *et al.*, 1967) show that in the solid state they are covalent with donor nitrogen and unidentate S_4N_4 . Conductance measurements have established (Paul *et al.*, 1971) that in solution some compounds are ionized. Several other structures are possible in the solid state and in solution, for instances, I (Weiss & Thewalt, 1966), II and especially for 'soft' Lewis acids, structures which include donor sulphur.

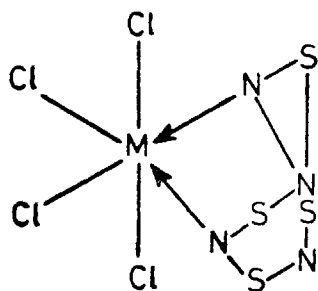
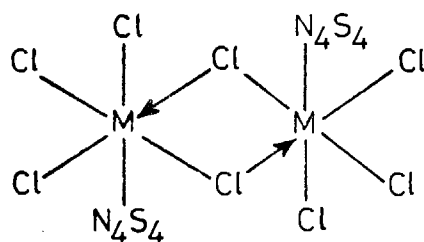


FIG. 11.

TABLE VIII

Physical properties of NSF, NSF₃ and NSCl

Compound	NSF	NSF ₃	NSCl
Molecular weight	65.01	103.01	81.46
Colour	pale yellow	colourless	greenish yellow
m. p.	-89	-72.6±0.5	—
b. p.	+0.4±2.0	-27.1±0.1	—
Density	—	1.92	—
Molar heat of volatilisation (cal)	6052±30	5526±50	—
Enthalpy of formation ΔH_f	41±2 kcal/mole	-85 kcal/mole	21.9±3.0 kcal/mole
Trouton's constant	22.1	22.5	—

TABLE IX

Force constant, bond distance, bond order and IR frequencies for NSF, NSF₃ and NSCl

Compound	r_{NS} (Å°)	f_{NS} (mdyne/Å)	η_{NS}	Bond energy d_{NS}	IR ** (cm ⁻¹)
NSF	1.446	10.71	2.4	71	1372 640
NSF ₃	1.416	12.55	2.7	93	366 1515 (ν_{NS}) 811 775] ν_{SF}
NSCl	1.46	10.02	2.2	—	1320 412 273

TABLE X

Compounds of S₄N₄ and S₃N₃ and their melting point and colour

Sl. No.	Compound	Colour (m.p.)	References
(1)	(2)	(3)	(4)
1	S ₄ N ₄ TiCl ₄	(RBr, 132)	(Wolbling, 1908; Becke-Goehring & Magin, 1965; and Ashley & Torrible, 1969)
2	S ₄ N ₄ 2TiCl ₄	(RBr, —)	-do-
3	S ₄ N ₄ TiBr ₄	(DBr, 138)	(Ashley & Torrible, 1969 and Alange & Banister 1978)
4	S ₄ N ₄ TiF ₄	(O, 120)	(Alange & Banister 1978)
5	S ₄ N ₄ TiI ₄	(B, 100)	-do-

(Table X continued on p. 42)

** The frequencies are written in order ν_{NS} , ν_{SX} and δ_{NSX}

Sl. No.	Compound	Colour (m.p.)	References
(1)	(2)	(3)	(4)
6	$S_4N_4VCl_4$	(Br, 190)	(Weiss & Thawalt, 1966; and Ashley & Torrible, 1969)
7	$S_4N_42FeCl_2$	(RBr, 80)	(Alange & Banister, 1978)
8	$Fe(NS)_4$	(B, —)	(Becke-Goehring & Zirker, 1956 <i>a, b</i> ; Becke-Goehring & Voight, 1956; and Fluck <i>et al.</i> , 1956)
9	$Co(NS)_4$	(DV, —)	(Daum <i>et al.</i> , 1955; Becke-Goehring <i>et al.</i> , 1955 <i>a, b</i> ; and Fluck <i>et al.</i> , 1956)
10	$Ni(NS)_4$	(DV, —)	(Becke-Goehring 1953, Becke-Goehring <i>et al.</i> , 1955 <i>a, b</i> ; and Fluck <i>et al.</i> , 1956)
11	$Cu(NS)_2$	(Br, —)	(Thewalt, 1976)
12	$(CuNS)_4$	(B, —)	-do-
13	$Cu(NS)_2Cl_2$	(B, —)	-do-
14	S_4N_4CuCl	(B, —)	(Becke-Goehring <i>et al.</i> , 1955 <i>a, b</i>)
15	S_4N_4CuBr	(B, —)	-do-
16	$S_4N_4CuCl_2$	(B, —)	-do-
17	$S_4N_4ZrCl_4$	(RO, 260)	(Ashley & Torrible 1969; and Alange & Banister, 1978)
18	$S_4N_4NbCl_5$	(GBr, 180)	(Ashley & Torrible, 1969)
19	$S_4N_4MoCl_5$	(Bl, —)	(Davis, 1906)
20	$Ag(NS)_2$	(RBr, —)	(Thewalt, 1976)
21	$S_4N_4HfCl_4$	(R, 140)	(Alange & Banister, 1978)
22	$S_4N_4TaCl_5$	(R, 180)	(Ashley & Torrible, 1969; and Alange & Banister, 1978)
23	$S_4N_4WCl_4$	(Br, —)	(Becke-Goehring <i>et al.</i> , 1955 <i>a, b</i> ; and Alange & Banister, 1978)
24	$S_4N_4WBr_4$	(DaBr, 251)	-do-
25	$S_4N_4WOCl_4$	(DaBr, —)	-do-
26	$Pt(N_4S_4)(PPh_3)_2$		(Bhattacharya <i>et al.</i> , 1979)
27	$Pt(N_2S_2)(PPh_3)_2$		-do-
28	$Pt(NS)_4$	(DaBr, 144)	(Fluck <i>et al.</i> , 1956)
29	$Pt(N_2S_4)(PPh_3)_2$		(Bhattacharya <i>et al.</i> , 1979)
30	$Hg(SN)_2$		(Meuwsen <i>et al.</i> , 1953; and Becke-Goehring & Zirker, 1956 <i>a, b</i> ; and Becke-Goehring & Voight, 1956)
31	$Hg(SN)_2$		-do-
32	$S_4N_4Bf_5$	(DaR, 14–147)	(Glemser & Ludemann, 1958; and Wynne & Jolly, 1967)
33	$S_4N_4BCl_3$	(OR, 138)	(Paul & Banister, 1971; Ashley & Torrible, 1969; and Wynne & Jolly, 1967)
34	$S_4N_42BCl_3$	(OBr, —)	
35	$S_4N_4BBr_3$		(Wynne & Jolly, 1967)
36	$S_4N_4AlCl_3$	(DaR, —)	(Chan & Olsen, 1972)
37	$S_4N_4AlBr_3$	(O, 122 °C)	-do-
38	$S_4N_42AlBr_3$	(OBr, 144)	(Wolbling, 1908)
39	$S_4N_42GaCl_3$	(DR, 100)	(Alange <i>et al.</i> , 1978)
40	$S_4N_42InCl_3$	(RBr, 100)	-do-
41	$S_4N_4\frac{1}{2}SnCl_4$	(DR, 200–202)	(Ashley & Torrible, 1969; and Davis, 1906)
42	$S_4N_4\frac{1}{2}SnBr_4$	(DBr, 198–200)	(Banister & Younger, 1970)

(Table X contd. on p. 95)

Sl. No.	Compound	Colour (m. p.)	References
(1)	(2)	(3)	(4)
43	$S_4N_42SbF_5$		(Cohen <i>et al.</i> , 1965, 1966 and Cohen & MacDiarmid, 1965)
44	$S_4N_44SbF_6$	(g, 145)	-do-
45	$S_4N_4SbCl_5$	(DR, 160-162)	(Paul <i>et al.</i> , 1971; Ashley & Torrible, 1969; and Wynne & Jolly, 1967)
46	$S_4N_42SbCl_6$		-do-
47	$S_4N_42SbBr_3$		(Rotgers, 1907)
48	$S_4N_42SbI_3$		-do-
49	$S_4N_4SO_3$		(Becke-Goehring <i>et al.</i> , 1954)
50	$S_4N_42SO_3$		-do-
51	$S_4N_44SO_3$		-do-
52	$S_4N_4SeCl_4$	(Y, 127-129)	(Paul, <i>et al.</i> , 1971)
53	$S_4N_4Se2Cl_4$	(Y, —)	(Wolbling, 1908)
54	$S_1N_4SeCl_4SO_3$		(Ashley & Torrible, 1969)
55	$S_4N_4TeCl_4$	(DR, 140 °C)	(Paul <i>et al.</i> , 1971)
56	$S_4N_4TeB_4$		(Aynsley & Campbell, 1957)
57	$S_4N_4TeCl_4BCl_3$		(Ashley & Torrible, 1969)
58	$S_4N_4TeCl_4SbCl_5$		-do-
59	$S_4N_4TeCl_4SO_3$		-do-
60	$S_4N_4SnCl_4POCl_3$		(Banister <i>et al.</i> , 1976)
61	$S_4N_2CF_3CON$	(Y, —)	(Studel <i>et al.</i> , 1977)
62	$S_4N_4AsPh_3$		(Holt <i>et al.</i> , 1977)

Letters within parentheses indicate the following colours and the numbers for melting point in °C : B = black; Bl = Blue; Br = Brown; D = deep; Da = dark; G = green; O = orange; R = red; V = violet; Y = yellow.

The chemistry of $N_2S_2^+$ (Bali & Malhotra, 1976), $S_3N_3^-$ (Bojes & Chivers, 1977, 1978

a, b), $S_4N_3^+$ (Meuwsen, 1932, Meuwsen *et al.*, 1953; Becke-Goehring, 1962; Becke-Goehring *et al.*, 1953; MacDiarmid, 1956; Glemser *et al.*, 1961; Kruh *et al.*, 1961; Weiss, 1962, 1964; Cordes *et al.*, 1965; Paul *et al.*, 1968, 1976, 1977; Harcourt, 1977; and Banister & Durrant, 1978), $S_4N_4^-$ (Chapman *et al.*, 1962; Gillespie *et al.*, 1977; Banister & Durrant, 1978; and Ballard *et al.*, 1978), $S_4N_5^-$ (Bojes *et al.*, 1978; Scherer & Wolmerschaler, 1977; and Chivers & Proctor, 1979), $(S_5N_5)^+$ (Banister *et al.*, 1969; Banister & Durrant, 1978; and Bartetzko & Gleiter, 1978) and $S_5N_6^-$ (Chivers & Proctor, 1979) have also been studied.

TRANSITION METAL THIONITROSYL COMPLEXES

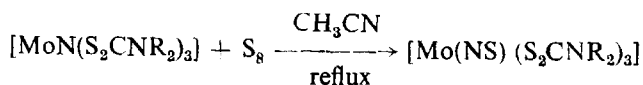
Recently, there has been a considerable upsurge in the study of transition metal thionitrosyl complexes. This is partly due to the increase in the understanding of the way in which NS binds to a metal. Similar to nitrosyl complexes, there are three principal bonding modes in thionitrosyl complexes: (a) terminal, linear M—N—S

groups; (b) terminal, bent M—N—S groups; and (c) bridging NS groups. In case (a) the thionitrosyl ligand can be represented as coordinated “NS⁺” and in (b), as coordinated “NS⁻”.

It is convenient to classify MNS complexes by the number of *d* type electrons present in the complex. Thus, MNS complex with *n* number of *d* electrons of *M* plus the number of electrons in the π^* orbitals of NS (or more conveniently, *n* is the number of *d* electrons if the thionitrosyl is regarded as being coordinated as NS⁺) would be written as (MNS)^{*n*}. This classification scheme will be used throughout the remainder of this review.

Seven Coordination

The compounds [Mo(NS)(S₂CNR₂)₃], [R₂ = Me₂, Et₂, (CH₂)₄] have been shown to be seven coordinated (Chatt & Dilworth, 1974; and Bishop & Chatt, 1979). These were prepared by treating dioxo complex [MoO₂(S₂CNR₂)₂] with trimethylsilylazide in acetonitrile under reflux. It seemed likely that this reaction proceeds *via* intermediate formation of a nitrido complex and subsequently the nitrido complex [MoN(S₂CNR₂)₃] reacts with elemental sulphur in refluxing acetonitrile to give the thionitrosyl complexes.



(yield could be improved by using propylene sulphide).

These complexes are yellow, stable in air, diamagnetic and nonconducting in 1,2-dichloroethane solution. The ¹H NMR spectrum of [Mo(NS)(S₂CNMe₂)₃] in nitrobenzene at room temperature shows a 1:2:3 triplet due to the dithiocarbonate methyl group. The structure of [Mo(NS)(S₂CNMe₂)₃] has been described as pentagonal bipyramid with the thionitrosyl group in one of the apical positions. The M—N—S angle for this (MNS)⁴ complex is 172.0(7) (Hursthouse & Motevalli, 1979). The structure is shown schematically in Fig. 12.

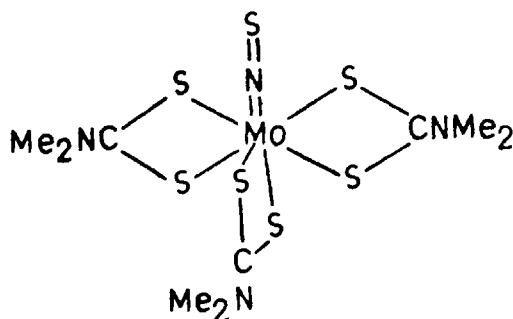


Fig. 12.

In the thionitrosyl complex the Mo—N bond length (1.74Å) is longer than in the nitride (1.64Å), as would be expected specially, if the thionitrosyl ligand behaves in a manner analogous to the NO⁺ ligand, as the almost linear Mo—N—S system

implies. A comparison between thionitrosyl complex and the analogous molecule Mo(NO) (S₂CNBU₂)₃ is summarized in Table XI.

TABLE XI

Bond distance of Mo-N and bond angle Mo-N-X in molybdenum thionitrosyls

Complex	Mo-N distance	Mo-N-X
Mo(NS) (S ₂ CNMe ₂) ₃	1.73 Å	173.2°
Mo(NO) (S ₂ CNBU ₂) ₃	1.74 Å	172.0(7)

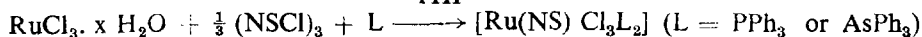
The Mo-N bond distance and M-N-X angle are equal, within the limit of experimental error. Thus it would seem that the NS and NO ligands are quite similar. The N-S distance in the free NS ligand or the value calculated from the sums of covalent radii for an NS double bond or even values found in a variety of compounds purporting to contain N=S partially multiple bonds is smaller than the N-S distance (1.59 Å) in the [Mo(NS) (S₂CNMe₂)₃] which is consistent with a considerable degree of M-NS π back bonding.

The thionitrosyl sulphur in these complexes can be alkylated with triphenylmethyl tetrafluoroborate to give [Mo(NSCP₃) (S₂CNR₂)₃] BF₄ (Bishop & Chatt, 1979; and Pandey & Agarwala, 1980*a, b*).

Six Coordination

Ruthenium Complexes — Only a few thionitrosyl complexes of ruthenium with triphenylphosphine and triphenylarsine have so far been prepared. [Ru(NS)Cl₃L₂] (L = PPh₃ and AsPh₃) were prepared by the reaction of RuCl₃ · x H₂O with (NSCl)₃ in THF or in CCl₄-CHCl₃ mixture in presence of triphenylphosphine and triphenylarsine (Pandey & Agarwala, 1980*a, b*).

THF

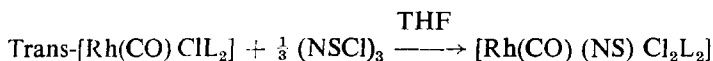


IR spectra of these complexes showed a strong sharp absorption band in the region 1290–1295 cm⁻¹ assigned to ν_{NS+}. The X-ray crystal structure of [Ru(NS)Cl₃(AsPh₃)₂] (Pandey, & Agarwala 1981). Showed Ru-N-S angle, 179° suggesting NS ligand to be functioning as a three electron donor. [RuCl₂(PPh₃)₃] Reacted with trithiazyltrichloride in THF at room temperature to give the first dithionitrosyl complex which on recrystallization from solvent-hexane (solvent = CH₂Cl₂, CHCl₃ or CHBr₃) gave a stable, diamagnetic solvated complex [Ru(NS)₂Cl₂(PPh₃)₂] solvent (Jain *et al.*, 1981*a, b*). IR spectrum of the complex showed absorption bands at 1300 cm⁻¹ and 1120 cm⁻¹, assigned to coordinated NS⁺ and NS⁻ groups respectively. Reactions of [Ru(NS)₂Cl₂(PPh₃)₂] CH₂Cl₂ with NOX (X = Cl, Br or Br₃) gave a diamagnetic, nonconducting nitrosylthionitrosyl complex [Ru(NO)(NS)ClX(PPh₃)₂] (X = Cl or Br) whose IR spectrum showed the replacement of the band at 1120 cm⁻¹ by a new one at 1880 cm⁻¹ characteristic of ν_{NO+}. The position of the second band due to ν_(NS+) remained practically constant (1320 cm⁻¹). On refluxing dithio or mononitrosyl monothionitrosyl dihalide complex with an excess of NOCl, NOBr, NOBr₃

ruthenium nitrosyl complexes of the type $[\text{-u(NO) ClX}_2(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$ or Br) have been obtained.

Reactions of $[\text{RuBr}_3(\text{AsPh}_3)_3]$ and $(\text{RuH}(\text{CO})\text{Cl}(\text{PPh}_3)_3)$ with trithiazyltrichloride in THF (Jain *et al.*, 1981*a,b*) yielded $[\text{RuBrCl}_2(\text{NS})(\text{AsPh}_3)_2]$ and $[\text{Ru}(\text{CO})(\text{NS})\text{Cl}(\text{PPh}_3)_2] \cdot \text{CH}_2\text{Cl}_2$ respectively.

Rhodium Complexes — Six coordinate complexes of the type $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2\text{L}_2]$ ($\text{L} = \text{PPh}_3$ or AsPh_3) have recently been reported (Pandey & Agarwala, 1980*a b*; and Jain *et al.*, 1980). Trithiazyltrichloride reacts with *trans* $[\text{Rh}(\text{CO})\text{ClL}_2]$ in tetrahydrofuran to produce the diamagnetic, non-electrolyte, $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2\text{L}_2]$ complexes.



The reaction of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ with $(\text{NSCl})_3$ in carbon tetrachloride-chloroform mixture gives a deep green chlorobridged complex, $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ which on reaction with excess triphenylphosphine or triphenylarsine in dichloromethane yields yellowish orange complexes $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2\text{L}_2] \cdot 0.8\text{CH}_2\text{Cl}_2$ ($\text{L} = \text{PPh}_3$ or AsPh_3) as a result of cleavage of chloro bridge. Their infrared spectra showed absorption bands in the range $2100\text{--}2110\text{ cm}^{-1}$ (ν_{CO}), $1118\text{--}1120\text{ cm}^{-1}$ (ν_{NS}) and 330 cm^{-1} (terminal $\nu_{\text{Rh-C}}$). In the spectrum of the green complex a band appeared at 260 cm^{-1} which is assigned to bridged $\nu_{\text{Rh-Cl}}$. The diamagnetism of complexes indicate the oxidation state of rhodium as either $+1$ or $+3$. The high ν_{CO} frequency ($\nu_{\text{CO}}, 2100\text{ cm}^{-1}$) in these complexes as compared to that in the original compound ($\nu_{\text{CO}}, 1960\text{ cm}^{-1}$) suggested $+3$ oxidation state of the rhodium. The shifting of the ν_{CO} band towards higher wave numbers may possibly be due to the strong σ -bonding *trans* effect of the *trans* NS^- group. Thus, these six coordinated, bent, $(\text{RhNS})^8$ complexes have been regarded as complexes between $\text{Rh}(\text{III})$ and NS^- . The probable structures of $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ (I) and $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2\text{L}_2]$ (II) are

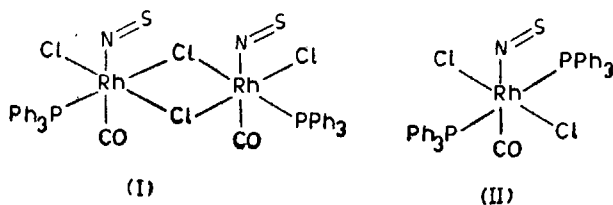
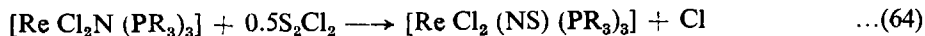


FIG. 13.

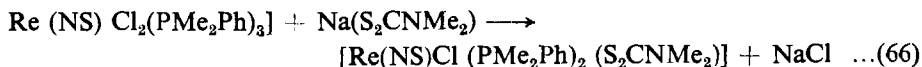
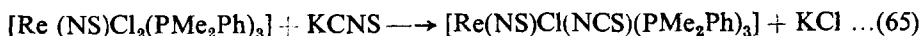
The reaction of compounds $[\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2\text{L}_2]$ with NOCl in CH_2Cl_2 afforded corresponding nitrosyl complexes $\text{Rh}(\text{CO})(\text{NO})\text{Cl}_2\text{L}_2$ ($\text{L} = \text{PPh}_3$ or AsPh_3).

Rhenium Complexes — Reactions of S_2Cl_2 with $[\text{ReCl}_2\text{N}(\text{PRPh}_2)_2]$ ($\text{R} = \text{Ph}$ or Pr^n) give thionitrosyl complexes, $[\text{ReCl}_3(\text{NS})(\text{PRPh}_2)_2]$. The complexes $[\text{ReX}_2\text{N}(\text{PR}_3)_3]$, ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, PEt_2Ph or PMePh_2 ; $\text{X} = \text{Cl}$ or Br) react with half an equivalent of S_2Cl_2 to give the thionitrosyl $[\text{ReClX}(\text{NS})(\text{PR}_3)_3]$. Reaction of nitrido complex $[\text{ReCl}_2\text{N}(\text{PR}_3)_3]$ with an excess of S_2Cl_2 or SCl_2 gave the derivatives $[\text{ReCl}_3(\text{NS})(\text{PR}_3)_2]$.

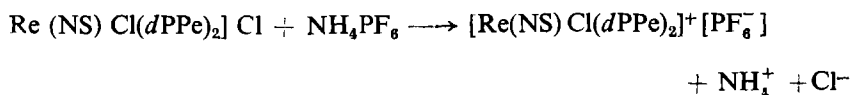
The formation of thionitrosyl from nitrido and S_2Cl_2 is possibly according to the scheme given in equation (64) (Bishop & Chatt, 1979; and Bishop *et al.*, 1975).



$[Re (NS) Cl_2 (PMe_2Ph)_3]$ reacts with $K(CNS)$ or $Na(S_2NCMe_2)$ as



Reaction of S_2Cl_2 with $[ReCl(N)(dPPE)_2] Cl$ ($dPPE = Ph_2PCH_2CH_2PPh_2$) yields $[Re(NS)Cl(dPPE)_2]Cl$ which reacts with $FeCl_3$ or NH_4PF_6 to give $FeCl_4^-$ or PF_6^- salts according to equations



The salt $[Re(NS) Cl(dPPE)_2 (S_2CNET_2)]$ is prepared by the reaction of $[ReCl(N)(dPPE)_2] Cl$ and $Na(S_2CNET_2)$. $[Re(NS) Cl(dPPE)_2] L$ ($L = Cl, FeCl_4$ or PF_6) are yellow and have conductivities in nitrobenzene typical of 1:1 electrolytes. In the infrared, a single strong peak observed in the region $1167-1185 \text{ cm}^{-1}$ confirms the presence of the NS^+ group in these compounds.

The proton NMR spectrum of $[ReNSCl_2 (PMe_2Ph)_3]$ shows two triplets and a doublet in the tertiary phosphine alkyl group region, indicating a meridional configuration for the phosphine ligands with the NS group trans to Cl . An X-ray crystal structure analysis of the analogous nitrosyl complex $[Re(NO) Cl_2 (PMe_2Ph)_3]$ shows the $M - N - O$ system to be essentially linear with $Re - N - O$ $178.8 (1.4)^\circ$ (Muir, *et al.*, 1981, *Unpublished*). It is therefore extremely likely that the thionitrosyl analogues are isostructural with linear NS groups.

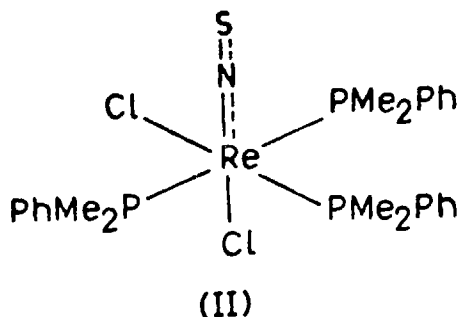


FIG. 14.

The 1H n.m.r. spectrum of $[Re(NS) Cl(S_2CNMe_2) (PMe_2Ph)]$ shows a singlet in the dithiocarbamate methyl region and a pair of doublets in the tertiary phosphine alkyl group region, indicating configuration (III).

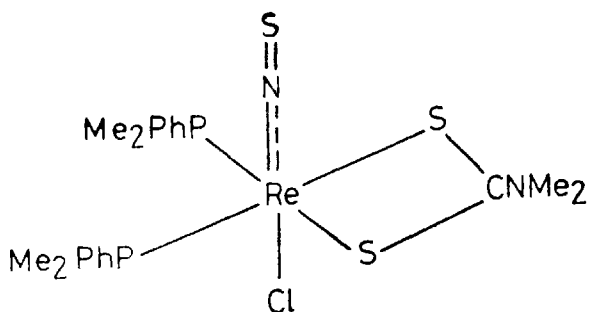
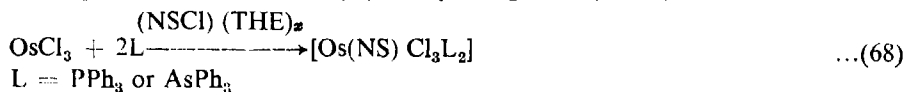


FIG. 15.

The complexes, $[\text{Re}(\text{NS})\text{Cl}_3(\text{PR}_3)_2]$ are paramagnetic with magnetic moments in the range 1.84–2.01 B.M. These values are close to that found for the analogous complex $[\text{Re}(\text{NO})\text{Cl}_3(\text{PMe}_2\text{Ph})]$.

Osmium Complexes — Green complexes of osmium have been reported as a result of reactions of $[\text{OsX}_3\text{NL}_2]$ ($\text{L} = \text{AsPh}_3, \text{PMe}_2\text{Ph}$, or $\frac{1}{2}$ bipy) with half an equivalent of S_2Cl_2 . Addition of pyridine (Py) to a methylene chloride solution of the product formed by reaction of salt $[(\text{NBU}_4)] [\text{OsCl}_4\text{N}]$ with S_2Cl_2 , gives green $[\text{Os}(\text{NS})\text{Cl}_3(\text{Py})_2]$ (Bishop & Chatt, 1979). The osmium thionitrosyl complexes, $[\text{Os}(\text{NS})\text{Cl}_3\text{L}_2]$ ($\text{L} = \text{PPh}_3$ or AsPh_3) were prepared by the action of trithiazyltrichloride in THF with osmium trichloride in presence of triphenylphosphine or triphenylarsine respectively (Pandey & Agarwala, 1980).



These complexes are diamagnetic and non-electrolyte. In their infrared spectra, a strong band is observed in the range 1270–1282 cm^{-1} indicating that the thionitrosyl groups coordinated as NS^+ . The ^1H NMR spectrum of $[\text{Os}(\text{NS})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$ shows a triplet due to the tertiaryphosphine methyl groups. This is consistent with Fig. 16 having virtually coupled phosphorus ligands.

(III)

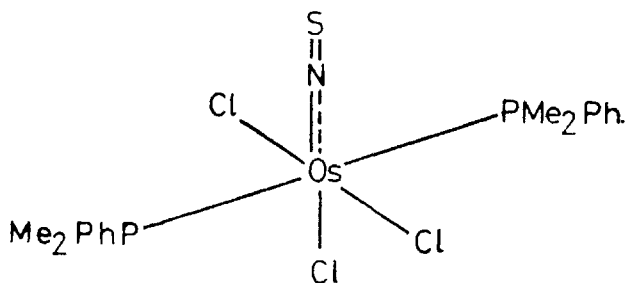


FIG. 16.

Iridium Complex — Until recently only one thionitrosyl complex of iridium $[\text{Ir}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_3]$ is known (Pandey & Agarwala, 1981). It is prepared by the reaction of $(\text{NSCl})_3$ in THF with $[\text{IrH}(\text{CO})(\text{PPh}_3)_3]$ at room temperature in argon atmosphere. It is reddish brown, diamagnetic and non electrolyte amorphous solid. Its IR spectrum shows absorption bands at 2050 cm^{-1} (ν_{CO}) and 1110 cm^{-1} (ν_{NS}). The high frequency of ν_{CO} at 2050 cm^{-1} in $[\text{Ir}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2]$ is reasonable for iridium(III) system and is probably influenced by the strong primarily σ -bonding trans effect of the trans NS^- group. This $(\text{IrNS})^8$ complex has been regarded as complex between Ir(III) and NS^- .

Reaction of $(\text{NSCl})_3$ with $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in oxygen atmosphere gives a bright green compound $[\text{Ir}(\text{CO})(\text{NSO})\text{Cl}_2(\text{PPh}_3)_2]$ which was until recently, the first complex containing thionitrite group. The same compound was also prepared by the reaction of $[\text{Ir}(\text{CO})\text{Cl}(\text{O}_2)(\text{PPh}_3)_2]$ with $(\text{NSCl})_3$ in THF. This indicates

TABLE XII
Six coordinate thionitrosyl complexes

Compound	Colour	N-S stretching frequencies cm^{-1}	References
(1)	(2)	(3)	(4)
$\text{Ru}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2$	red brown	1300	(Pandey & Agarwala, 1980 a, b,)
$\text{Ru}(\text{NS})\text{Cl}_2(\text{AsPh}_3)_2$	red brown	1995	-do-
$\text{Ru}(\text{NS})_2\text{Cl}_2(\text{PPh}_3)_2, \text{S}$	yellowish brown	1300, 1120	(Jain <i>et al.</i> , 1981a, b)
(S = CH_2Cl_2 , CHCl_3 , CHBr_3)			
$\text{Ru}(\text{NO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2$	brownish orange	1315	-do-
$\text{Ru}(\text{CO})(\text{NS})\text{Cl}(\text{PPh}_3)_2, 2. \text{CH}_2\text{Cl}_2$	brown	1120	-do-
$\text{Ru}(\text{NS})\text{Cl}_2\text{Br}(\text{AsPh}_3)_2$	brown	1290	-do-
$\text{Ru}(\text{CO})(\text{NS})(\text{Cl}_2\text{PPh}_3)_2$	green	1118	(Pandey & Agarwala, 1980 a, b)
$\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2(\text{PPh}_3)_2, 0.5\text{CH}_2\text{Cl}_2$	orange red	1120	(Pandey & Agarwala, 1980a,b; and Jain <i>et al.</i> , 1980)
$\text{Rh}(\text{CO})(\text{NS})\text{Cl}_2(\text{AsPh}_3)_2, 0.5\text{CH}_2\text{Cl}_2$	orange red	1120	(Jain <i>et al.</i> , 1980)
$\text{Re}(\text{NS})\text{Cl}_2(\text{PMe}_2\text{Ph})_2$	pink	1180	(Bishop & Chatt, 1979)
$\text{Re}(\text{NS})\text{Cl}_2(\text{PEt}_2\text{Ph})_2$	pink	1167	-do-
$\text{Re}(\text{NS})\text{Cl}_2(\text{PMePh}_2)_2$	pink	1172	-do-
$\text{Re}(\text{NS})\text{ClBr}(\text{PEt}_2\text{Ph})_2$	pink	1168	-do-

(Contd. Table XII on p. 50)

Compound (1)	Colour (2)	N—S stretching frequencies cm ⁻¹ (3)	References (4)
Re(NS) Cl(SCN) (PMe ₂ Ph) ₃	red pink	1177	(Bishop & Chatt, 1979)
Re(NS) Cl(S ₂ CNMe ₂) (PMe ₂ Ph) ₃	yellow brown	1150	-do-
Re(NS) Cl(dppe) ₂ Cl	yellow	1185	-do-
Re(NS) Cl(dpps) ₂ PF ₆	yellow	1177	-do-
Re(NS) Cl(dppe) ₂ FeCl ₄	yellow	1173	-do-
Re(NS) Cl(dppe) ₂ S ₂ CNEt ₂	yellow	1183	-do-
Re(NS) Cl ₃ (PMe ₂ Ph) ₂	purple	1228	-do-
Re(NS) Cl ₃ (PEt ₂ Ph) ₂	purple	1230	-do-
Re(NS) Cl ₃ (PMePh ₂) ₂	purple	1220	-do-
Re(NS) Cl ₃ (PPh ₃) ₂	purple	1214	do-
Re(NS) Cl ₃ (PPr ⁿ -Ph) ₂	purple	1226	-do-
Os(NS) Cl ₃ (PPh ₃) ₂	green	1285	-do-
Os(NS) Cl ₃ (AsPh ₃) ₂	green	1282	(Bishop & Chatt, 1979; and Pandey & Agarwala, 1980a, b)
Os(NS) Cl ₃ (PMe ₂ Ph) ₂	green	1285	(Bishop & Chatt, 1979)
Os(NS) Cl ₃ (bipy)	green	1282	-do-
Os(NS) Cl ₃ (P ₄) ₃	yellow green	1284	-do-
Os(NS) ClBr ₂ (AsPh ₃) ₂	green	1270	-do-
Os(NS) ClBr ₂ (bipy)	green	1280	-do-
Ir(CO) (NS) Cl ₂ (PPh ₂) ₂	orange	1120	-do-

that the Vaska's complex in solution takes up oxygen from the atmosphere to form oxygen complex which on reaction with (NSCl)₃ forms thionitritoiridium complex.

Five Coordination

These thionitrosyl complexes are amongst a few examples of five coordination, which are the derivatives of rhodium and iridium triphenylphosphine of general formula. M(NS) ClX(PPh₃)₂ (X = Cl, Br; M = Rh, Ir) (Raju, 1980; and Jain *et al.*, 1981a,b). Rh(NS) ClX(PPh₃)₂ and similar complexes were prepared by the action of Rh(X) (PPh₃)₃ with trithiazyltrichloride in THF as red brown amorphous solid. Rh(NS) Cl₂(PPh₃)₂ was also prepared by the action of Rh(NS) (PPh₃)₃ with chlorine gas (Pandey & Agarwala, 1980a,b). By a similar method IrHCl₂(PPh₃)₃ on reaction with trithiazyl trichloride in THF gave Ir(NS)Cl₂ (PPh₃)₂. Ir spectra of these complexes showed an absorption band in the region 1117–1120 cm⁻¹ which was assigned to ν_{NS-}. By analogy with nitrosyl complexes [Rh(NO) Cl₂(PPh₃)₂] and [Ir(NO) Cl₂(PPh₃)₂] the structures of the corresponding thionitrosyl complexes M(NS) Cl₂(Ph₃)₂ (M = Rh or Ir) have been assigned (Fig. 17).

They were found to be non-conducting in nature, soluble in benzene, chloroform and dichloromethane.

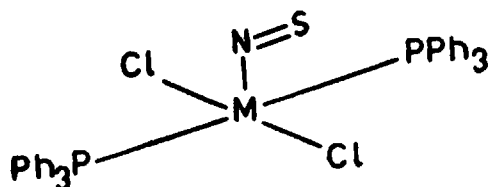
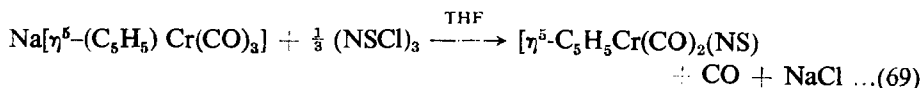


FIG. 17.

Four Coordination

There are two compounds in this class, one each of chromium and rhodium. The action of trithiazyltrichloride on $\text{Na}[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]$ in tetrahydrofuran gave di-carbonyl (η^5 -cyclopentadienyl) thionitrosylchromium (I) $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NS})]$ as dark red violet, diamagnetic solid (Kolthammer & Legzdins, 1978; and Greenhough *et al.*, 1978, 1979).



Its IR spectrum shows three strong bands attributable to terminal CO and NS group.

The structure of $[\eta^5\text{-(C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NS})]$ has been determined by X-ray crystallography (Greenhough *et al.*, 1978, 1979) and is shown schematically in (Fig. 18). Its molecular geometry is similar to that exhibited by molecules $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ (Berndt & Marsh, 1963) and $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2(\text{NO})]$ and the Cr—C—(cp), Cr—C—(O) and C—O bond lengths are comparable to those found in other cyclopentadienyl chromium carbonyls (Maltio, 1981—Personal commn.). The Cr—N—S angle is $176.8(2)$ (Table XIII & Table XIV) suggesting that the thionitrosyl ligand coordinates essentially linearly to the metal *via* the nitrogen atom. Hence the thionitrosyl group can be considered to be bonded as NS^+ , a mode of coordination that is directly analogous to metal-thiocarbonyl bonding. A comparison of the spectroscopic properties of the compounds $[\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})(\text{NX})(\text{X} = \text{O}, \text{S})]$ suggests that the NS ligand is more effective in removing electron density from the central atom than the NO ligand.

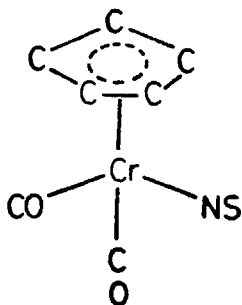
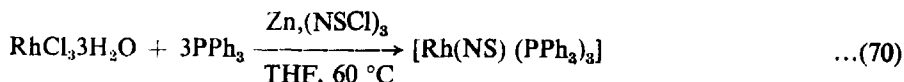


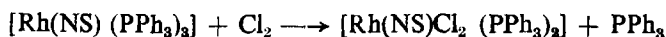
FIG. 18.

The reaction of $([\eta^5\text{-C}_5\text{H}_5] \text{Cr}(\text{CO})_2(\text{NS}))$ with NOCl and NOPF_6 gave the nitrosyl complex $([\eta^5\text{-C}_5\text{H}_5] \text{Cr}(\text{NO})_2\text{Cl})$ and a water sensitive, green black solid, $([\eta^5\text{-C}_5\text{H}_5] \text{Cr}(\text{CO})(\text{NO})(\text{NS})\text{PF}_6]$.

The rhodium thionitrosyl, $\text{Rh}(\text{NS})(\text{PPh}_3)_3$ is prepared by action of trithiazyl-trichloride in THF with hydrated rhodium trichloride in the presence of excess of triphenylphosphine and granulated zinc (Pandey & Agarwala, 1981).



Reaction of $(\text{Rh}(\text{NS})(\text{PPh}_3)_3)$ with chlorine gas afforded a reddish brown compound $\text{Rh}(\text{NS})\text{Cl}_2(\text{PPh}_3)_2$:



It is pink coloured, diamagnetic and nonconducting crystal. Its IR spectrum showed a strong absorption band at 1120 cm^{-1} which is assigned to ν_{NS} .

TABLE XIII

Four coordinate thionitrosyl complexes

Complex	Colour	m.p. (°C)	IR frequencies		
$(\eta^5\text{-C}_5\text{H}_5) \text{Cr}(\text{CO})_2(\text{NS})$	red violet	68-69	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\nu_{\text{NS}}(\text{cm}^{-1})$	$\nu_{\text{NO}}(\text{cm}^{-1})$
$(\eta^5\text{-C}_5\text{H}_5) \text{Cr}(\text{CO})(\text{NO})(\text{NS})\text{PF}_6$	green black	—	2033, 1962	1180	—
$\text{Rh}(\text{NS})(\text{PPh}_3)_3$	pink	155	2122	1243	1790
			—	1120	—

TABLE XIV

Crystallographic data on $(\eta^5\text{-C}_5\text{H}_5)\text{-Cr}(\text{Co})_2 \text{NS}$

Bonds and angles	Values A or degrees
Cr-N	1.694 (3)
Cr-C(O)	1.883 (3)
C-O	1.131 (3)
N-S	1.551 (3)
LCr-N-S	176.8 (2)
LCr-C-O	178.1 (2)
LC(O)-Cr-C(O)	92.4 (2)
LC(O)-Cr-N	94.8 (1)

Bridged Thionitrosyl Complex

The reaction of carbon tetrachloride solution of $(\text{NSCl})_3$ with $[\text{Rh}(\text{NO})\text{Cl}_2(\text{PPh}_3)_2]$ in CHCl_3 under argon atmosphere produces a thionitrosyl bridged complex

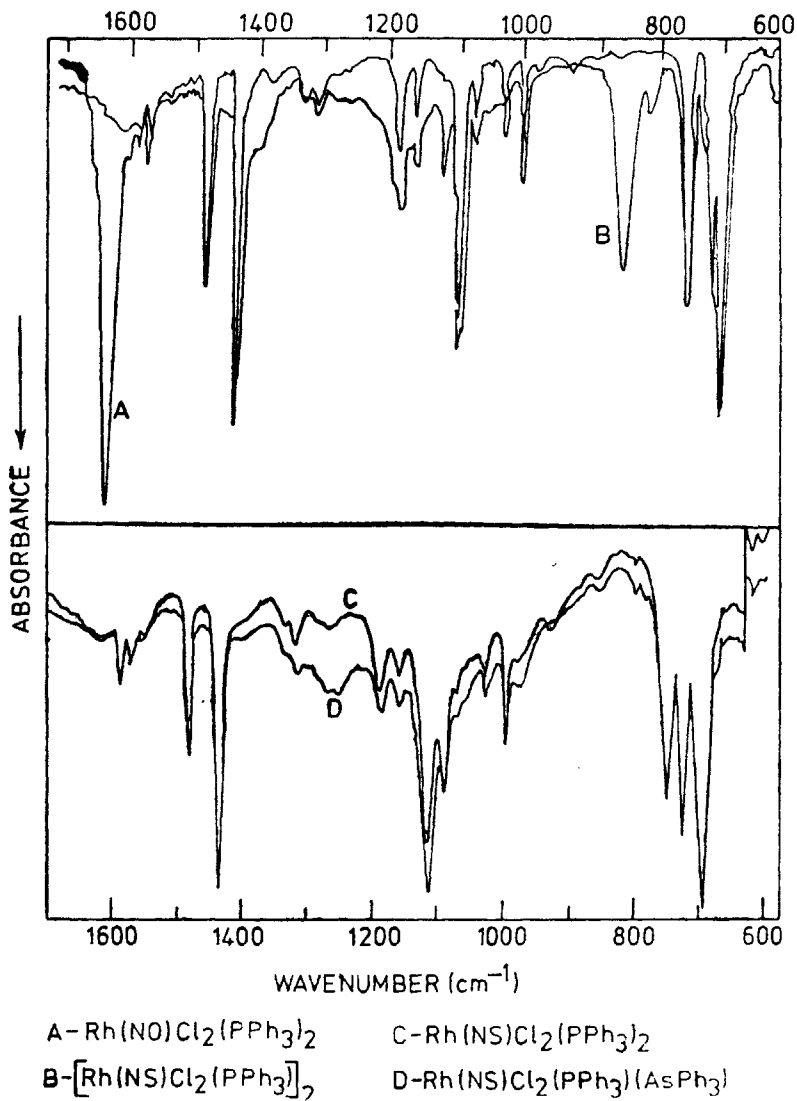
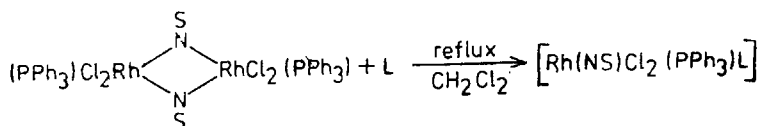


FIG. 19.

[Rh(NS)Cl₂(PPh₃)₂] (Pandey *et al.*, 1981) which is air stable diamagnetic and non-electrolyte in solution. Its IR spectrum (Fig. 19) did not show any band due to $\nu(\text{NO})$ at 1630 cm⁻¹ but a new slightly broad band at 840 cm⁻¹ appeared which was attributed to the bridging thionitrosyl group. These results were interpreted as the replacement of NO group in the compound by the NS. The broadening of the 840 cm⁻¹ band was suggested to be due to the two NS bands $\nu_{\text{as}}(\text{NS})$ and $\nu_{\text{sy}}(\text{NS})$ appearing close together. NS bridge in the compound were further proved by reacting it with PPh₃ and AsPh₃ which resulted in the NS bridge cleavage.



L = PPh₃ brown m.p. 150°C

L = AsPh₃ red brown m.p. 160°C

The IR spectrum of [Rh(NS)Cl₂(PPh₃)L] (L = PPh₃ or AsPh₃) showed a characteristic band of terminal NS group at 1120 cm⁻¹ which further conforms to the fact that the band at 840 cm⁻¹ in the complex, [Rh(NS)Cl₂(PPh₃)₂] is a characteristic band bridging thionitrosyl group.

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