ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 26

TRANSITION-METAL THIONITROSYL AND RELATED COMPLEXES

H. W. ROESKY and K. K. PANDEY

Anorganisch-Chemisches Institut der Universität Göttingen, Göttingen, Federal Republic of Germany

I. Introduction

Nitrosyl complexes of transition metals have created considerable interest for many years. Attempts have been made to understand the

ISBN 0-12-023626-5

nature of the bond formed between metal ions and the nitrosyl group (*21, 36, 41*). However, similar molecules containing the isoelectronic thionitrosyl ligand (NS) have only been discovered since 1974 (*17*). One of the reasons for the relatively late development of the chemistry of transition-metal thionitrosyl complexes is undoubtedly the instability of NS compared to NO and the present lack of reagents that can be utilized to introduce the thionitrosyl group into the transition-metal complexes.

The presence of the thionitrosyl monomer NS was observed for the first time by Fowler and Bakker in 1932, while studying the band spectrum of emitted light after passing an electric discharge through a mixture of nitrogen and sulfur vapor (*22*). A review article by Glemser and Mews (*23*) has described the preparation and physical properties of ionic compounds of composition $NS^+MF_6^-$ (M = As, Sb) and $NS^+BF_4^-$, as well as covalent compounds like NSF, NSF_3, and NSCl. Herberhold has reported metal complexes with thionitrosyl ligands (*28*).

A. THE THIONITROSYL RADICAL

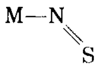
The thionitrosyl radical with one unpaired electron, unlike its homolog NO, polymerizes so readily that it is not possible to isolate it as a monomer, solid, or liquid, and even in the gas phase ·NS has only a transient existence (*27*). Like NO, it can also exist as NS^+ or NS^-, respectively, by losing or gaining an electron (*19, 45*), and, therefore, most of its properties should be approximately similar to those of NO. It has a low ionization potential (*44*) of 9.85 eV and a high dipole moment (*14*), 1.83 ± 0.03 D. It is a paramagnetic molecule having a doublet $^2\pi_{1/2}$ ground state with the lowest excited state, $^2\pi_{3/2}$, lying about 223 cm^{-1} above the ground-state level. A large number of papers related to the microwave spectrum of NS have appeared in the literature (*20, 35, 55*), and the excited valence states $B^2\pi$, $A^2\Delta$, $G^2\Sigma^-$, $H^2\pi$, and $I^2\Sigma^+$ have been identified in addition to the ground state $X^2\pi$. The vibration frequency of the gaseous NS molecule is 1204.1 cm^{-1} (*16, 65*). The ESR spectrum of the NS radical has also been studied (*15, 69*); it consists of three triplets. The *g* factor is consistent with the value expected for a molecule in a $^2\pi_{3/2}$ state in the lowest rotational level with $J = \frac{3}{2}$.

B. BONDING MODES IN METAL COMPLEXES

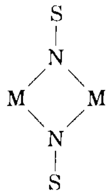
It is evident that NS can be stabilized by coordination to many transition metals, and well over 50 thionitrosyl complexes have been reported. Although the majority of metal thionitrosyl complexes contain terminal NS ligands, there are a few examples of bridging thionitrosyl groups. Similar to nitrosyl complexes, there are three principal bonding modes in thionitrosyl complexes:

M—N≡S

(a)



(b)



(c)

In case **a** the thionitrosyl ligand can be represented as coordinated "NS^+" and in **b** as coordinated "NS^-."

Because of the isoelectronic nature of NO and NS, there has been considerable interest in the comparative bonding properties of these ligands. The molecular orbitals for NO and NS are compared in Fig. 1 (*59*). The 7σ donor orbital of NS is at higher energy than the 5σ donor orbital of NO, whereas the 3π (π^*) acceptor level of NS is at lower energy than the 2π (π^*) acceptor level of NO. There is weaker $p\pi$–$p\pi$

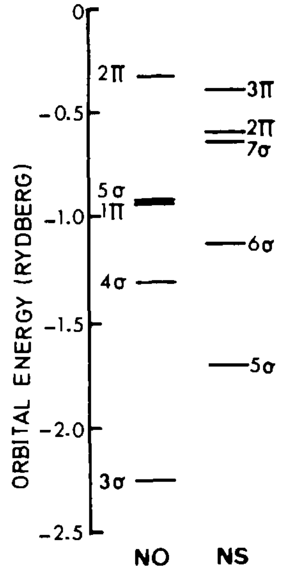


FIG. 1. Molecular orbital diagrams for NO and NS ground-state configurations: (NO) $1\sigma^2$, $2\sigma^2$, $3\sigma^2$, $4\sigma^2$, $1\pi^4$, $5\sigma^2$, $2\pi^1$; (NS) $1\sigma^2$, $2\sigma^2$, $3\sigma^2$, $4\sigma^2$, $1\pi^4$, $5\sigma^2$, $6\sigma^2$, $7\sigma^2$, $2\pi^4$, $3\pi^1$.

bonding for sulfur compared to oxygen. It should also be mentioned that the 7σ level of NS is significantly antibonding in character. These results lead one to expect that M—NS bonds should be stronger than M—NO bonds. Comparison of the spectroscopic properties and the electronic structures of M—NX complexes have indicated that NS is a better σ-donor and π-acceptor ligand than NO.

There has been no comprehensive review of transition-metal thionitrosyl complexes; only a brief introduction has appeared in the literature (*18, 23, 28, 42*). The objectives of this account are (1) to illustrate the currently available synthetic routes to metal thionitrosyl complexes and (2) to give a brief review of the physicochemical properties of these new classes of complexes. Because many metal nitrosyls have been used as reagents in organic synthesis and as homogeneous catalysts in industrial reactions, it is anticipated that some metal thionitrosyls may well find similar uses in the future.

II. Preparation of Thionitrosyl Complexes

In general, metal nitrosyl complexes are readily available by reactions of metal salts or metal complexes with NO gas. In view of the instability of NS, this approach could not be applied to the synthesis of metal thionitrosyl complexes.

As yet, there is no general synthetic route to metal thionitrosyl complexes. However there are a few limited preparative methods known which are discussed here.

1. Reactions of nitride complexes with elemental sulfur or with sulfur halides
2. Reaction of trithiazyltrichloride [$(NSCl)_3$] with transition-metal complexes
3. Elimination of fluoride from NSF metal complexes
4. Generation of NS^+ salts and its reaction with metal complexes

A. CHROMIUM

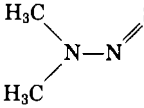
In a preliminary communication, Kolthammer and Legzdins (*24, 38*) reported that $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$ was found to react with trithiazyltrichloride in tetrahydrofuran (THF) to yield the first organometallic thionitrosyl complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ by the reaction

$$Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3] + \tfrac{1}{3}(NSCl)_3 \xrightarrow{THF} (\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) + CO + NaCl$$

Herberhold and Haumaier (*29*) showed that the reaction of $NS^+PF_6^-$, obtained *in situ* from $(NSCl)_3$ and $AgPF_6$ (1 : 3), with benzene tricarbonyl chromium in acetonitrile solution yields the cationic thionitrosyl complex $[Cr(NS)(NCMe)_5](PF_6)_2$. In the presence of *t*-butyl isocyanide and zinc powder this complex is reduced to $[Cr(NS)(CNCMe_3)_5]PF_6$.

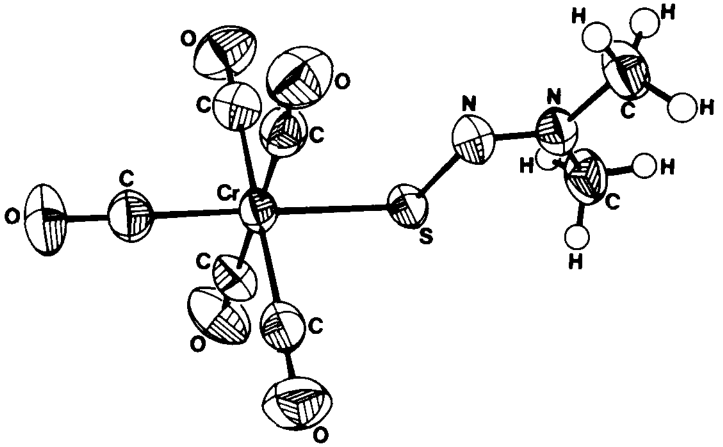
B. Thionitrosoamine Complexes

The unstable dimethyl(thionitroso)amine, prepared from dimethylhydrazine and elemental sulfur, reacts in THF with $(CO)_5Cr \cdot THF$ to yield the 1 : 1 complex:



$$+ (CO)_5Cr \cdot THF \rightarrow (CH_3)_2N_2SCr(CO)_5 + THF$$

The structure was investigated by X-ray analysis. The dimethyl(thionitroso)amine ligand coordinates via the sulfur atom to the metal atom. The Cr—C bond distance [184.6(2) pm] of the CO group in the trans position to the sulfur atom is shortened in comparison to the average value of the remaining CO ligands [190.3(5)] (*58*):



C. Molybdenum

The complexes $Mo(NS)(S_2CNR_2)_3$ [$R_2 = Me_2, Et_2$, or $(CH_2)_4$] (*11, 12*) were prepared by treating the dioxo complex $MoO_2(S_2CNR_2)_3$ with trimethylsilylazide in acetonitrile under reflux. This reaction proceeds via intermediate formation of a nitrido complex and, subsequently, the nitrido complex $MoN(S_2CNR_2)_3$ reacts with elemental sulfur in refluxing acetonitrile to give the appropriate thionitrosyl complex.

$$MoN(S_2CNR_2)_3 + \tfrac{1}{8}S_8 \xrightarrow[\text{reflux}]{CH_3CN} Mo(NS)(S_2CNR_2)_3$$

D. RHENIUM

Reactions of S_2Cl_2 with $ReNCl_2(PRPh_2)$ (R = Ph or *n*-Pr) yield the thionitrosyl complexes $Re(NS)Cl_3(PRPh_2)_2$ (*12*). The complexes $ReNX_2(PR_3)_3$ (PR_3 = PMe_2Ph, PEt_2Ph, or $PMePh_2$; X = Cl or Br) react with half an equivalent of S_2Cl_2 to give the complexes of composition $Re(NS)ClX(PR_3)_3$. Reaction of the nitrido complex $ReNCl_2(PR_3)_3$ with an excess of S_2Cl_2 or SCl_2 affords the derivatives $Re(NS)Cl_3(PR_3)_2$. Similarly, the reaction of S_2Cl_2 with $[ReNCl(dppe)_2]Cl$ (dppe = $Ph_2PCH_2CH_2PPh_2$) results in the formation of $[Re(NS)Cl(dppe)_2]Cl$. In the IR spectra of these rhenium complexes, a single strong peak observed in the region 1167–1185 cm^{-1} confirms the presence of the NS^+ cation. The $[Re(CO)_5NS]^{2+}$ cation is prepared from the reaction of $Re(CO)_5Br$ and $NS^+SbF_6^-$ and also by elimination of a fluoride ion of $[Re(CO)_5(NSF)]^+$, by means of AsF_5 (*43*).

E. RUTHENIUM

The ruthenium thionitrosyl complexes $Ru(NS)Cl_3L_2$ (L = PPh_3, $AsPh_3$) are prepared by the reaction of $RuCl_3 \cdot H_2O$ with $(NSCl)_3$ in THF in the presence of triphenylphosphine or triphenylarsine (*51*). Reaction of $RuCl_2(PPh_3)_3$ with $NSCl(THF)_x$ results in the formation of the dithionitrosyl complex, which, on recrystallization with different solvents, gives solvated complexes of composition $Ru(NS)_2Cl_2(PPh_3)_2 \cdot X$ (X = CH_2Cl_2, $CHCl_3$, or $CHBr_3$). The IR spectra of these complexes show absorption bands at 1300 cm^{-1}, which suggest the presence of a coordinated NS^+ ligand, and at 1120 cm^{-1}, due to coordination of an NS^- ligand (*33*). An X-ray crystal-structure analysis of the analogous nitrosyl complex $Ru(NO)Cl_3(PPh_3)_2$ showed the Ru—NO system is essentially linear with angle Ru—N—O equal to 180° (*26*). It is therefore extremely likely that thionitrosyl analogs have a linear RuNS group.

F. OSMIUM

Green thionitrosyl complexes of osmium have been reported as a result of reactions of $OsNX_3L_2$ [X = Cl or Br, L = $AsPh_3$, PMe_2Ph or $\frac{1}{2}$ (2,2'bipyridyl)] with half an equivalent of S_2Cl_2. Addition of pyridine (py) to a methylene chloride solution of the product formed by reaction of $(Bu_4N)OsNCl_4$ with S_2Cl_2, gives $Os(NS)Cl_3(py)_2$. The osmium thionitrosyl complexes of composition $Os(NS)Cl_3L_2$ (L = PPh_3 or $AsPh_3$) are obtained by the reaction of $(NSCl)_3$ in THF with $OsCl_3$ in the presence of PPh_3 or $AsPh_3$, respectively (*12, 51*).

G. COBALT

Reaction of $(NSCl)_3$ in THF with $CoH[P(OPh)_3]_4$ results in the formation of the five-coordinated air-sensitive intermediate thionitrosyl complex $Co(NS)Cl_2[P(OPh)_3]_2$ (ν_{NS} = 1113 cm^{-1}) (*66*), which, on reaction with air or oxygen, is converted to the thionitro complex $Co(NSO)Cl_2[P(OPh)_3]_2$. The IR spectrum of the thionitro complex exhibits absorption bands at 1540 and 990 cm^{-1}, which are assigned to ν_{NO} and ν_{NS}, respectively, of the NSO group.

H. RHODIUM

Trithiazyltrichloride reacts with $Rh(CO)Cl(PPh_3)_2$ to yield the green complex $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ (*34, 53*), which is also prepared by treating $RhH(CO)(PPh_3)_3$ with a solution of trithiazyltrichloride in THF.

$$2Rh(CO)Cl(PPh_3)_2 + \tfrac{2}{3}(NSCl)_3 \xrightarrow{THF} [Rh(CO)(NS)Cl_2(PPh_3)]_2 + 2PPh_3$$

The reactions of $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ with (L = PPh_3 or $AsPh_3$) result in the formation of red-brown complexes of composition $Rh(CO)(NS)Cl_2L_2$. The products of these reactions strongly depend on the refluxing time. Similarly, the reaction of $NSCl(THF)_x$ with $Rh(CO)Cl(AsPh_3)_2$ results in the formation of a yellow-green complex $[Rh(CO)(NS)Cl_2(AsPh_3)]_2$, which reacts with $AsPh_3$ to give $Rh(CO)(NS)Cl_2(AsPh_3)_2$ (*54*).

The IR spectrum of $Rh(CO)(NS)(PPh_3)_2$ shows absorption bands at 1970 cm^{-1} (due to ν_{CO}) and at 1122 cm^{-1} (due to ν_{NS}). $Rh(NS)(PPh_3)_3$ is also obtained by treating $NSCl(THF)_x$ with $RhCl(PPh_3)_3$ in the presence of PPh_3 and zinc. Its IR spectrum shows an absorption band at 1100 cm^{-1}, due to ν_{NS}. $(NSCl)_3$ reacts with $RhX(PPh_3)_3$ (X = Cl or Br) and with $RhH(PPh_3)_4$ to yield the brown complex $[Rh(NS)ClX(PPh_3)]_2$, which on reaction with triphenylphosphine or triphenylarsine results in the formation of the complex $Rh(NS)ClX(PPh_3)_2$ and $Rh(NS)ClX(PPh_3)(AsPh_3)$. These pentacoordinated complexes are also obtained by the reaction of $(NSCl)_3$ with $RhCl_3 \cdot 3H_2O$ in the presence of L. The IR spectra of the complexes $Rh(NS)Cl_2L_2$ and $Rh(NS)ClBr(PPh_3)_2$ show absorption bands in the range 1118–1120 cm^{-1}, due to ν_{NS} (*46, 53, 54, 56*).

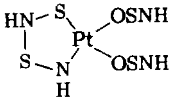
I. IRIDIUM

Reaction of $(NSCl)_3$ in THF separately with $Ir(CO)Cl(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$ yields the brown complex $Ir(CO)(NS)Cl_2(PPh_3)_2$. The reaction of $Ir(CO)Cl(PPh_3)_2$ with $(NSCl)_3$ in THF in an oxygen atmosphere affords a bright green complex of composition $Ir(CO)(NSO)Cl_2(PPh_3)_2$ with 40% yield (*46*). The same compound is also obtained when $Ir(CO)Cl(O_2)(PPh_3)_2$ is treated with $NSCl(THF)_x$. This indicates that the Vaska complex in solution takes up oxygen from the atmosphere to form the oxygen-containing complex, which, on reaction with $(NSCl)_3$, forms the NSO iridium complex. Covalent and ionic (*2–4, 6, 57, 60, 61*) derivatives containing the NSO group are well known. The gas-phase reaction of NH_3 with thionyl chloride has long been known (*6, 60*) to produce thionylimide and ammonium chloride. The IR (*67*), microwave (*37*), ultraviolet (*1*), and photoelectronic spectra (*68*) of HNSO have been reported. The IR spectrum of $Ir(CO)(NSO)Cl_2(PPh_3)_2$ exhibits absorption bands at 2060 cm^{-1}, due to ν_{CO}, and three bands at 1160, 1060, and 565 cm^{-1}, which are attributed to the $\nu_{as}(NSO)$, $\nu_{sym}(NSO)$ stretching modes and $\delta(NSO)$ of the NSO ligand, respectively. These frequencies are comparable to the asymmetric and symmetric stretching and bending modes of coordinated SO_2, which is isoelectronic with the NSO^- group.

J. PLATINUM

The major product of the reaction of $Pt(PPh_3)_4$ and $S_4N_4H_4$ in acetone has been determined to be $(Ph_3P)_2Pt(OSNH)_2$ from single-crystal X-ray diffraction data. $(Ph_3P)_2Pt(OSNH)_2$ exists as a square-planar complex with a cis arrangement of ligands. Each triphenylphosphine ligand is trans to an OSNH, which is coordinated to platinum via oxygen (*8–10, 30*). The structure shows some divergence between the two HNSO ligands, particularly O—S bond lengths 126(1) and 134(2) pm and Pt—O—S angles 138.1(10) and 129.5(9)°. Better agreement is shown by S—N bond lengths 148(2) and 145(2) pm, and O—S—N angles 121.9(12) and 122.0(9)°. The S—O and S—N distances are shorter than those determined by microwave spectroscopy (*37*) for *cis*-thionylimide [S—O 145.1(5), S—N 151.2(5) pm]. The possibility that the ligands are also arranged in the thiazyl *S*-hydroxide form cannot be eliminated. The thiazyl *S*-hydroxide HOSN has been reported (*68*).

$Pt(OSNH)_2S_2N_2H_2$ has been prepared by the reaction of an aqueous solution of K_2PtCl_4 with $S_4N_4H_4$ in acetone (*9*). The absorption spectrum in DMF of $Pt(OSNH)_2S_2N_2H_2$ shows three absorption bands at 450, 310, and 300 nm, possibly due to electronic transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{2g}$, and $^1A_{1g} \rightarrow {}^1E_g$, respectively. These three transitions are typical of square-planar d^8 configurations. The proposed structure is



K. METAL COMPLEXES WITH THIAZYL FLUORIDE AND THIAZYL TRIFLUORIDE LIGANDS

The chemistry of these complexes has been reviewed by Glemser and Mews (*23*). Therefore, these complexes are mentioned here only briefly. They are prepared in liquid SO_2 by treating the metal complexes of $[M(SO_2)_x](AsF_6)_2$ (M = Co or Ni) and $[Re(CO)_5SO_2]AsF_6$ with NSF or $[M(SO_2)_x](AsF_6)_2$ (M = Mn, Fe, Co, Ni, or Cu), $AgAsF_6$, $[M(CO)_5SO_2]AsF_6$ (M = Mn or Re), and $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]AsF_6$ with NSF_3. The M^{2+} cations are able to coordinate to six NSF but only to four NSF_3 ligands. An interesting observation was made that in NSF as well as in NSF_3 complexes the N—S bond length is shorter than in the free ligands.

III. Reactions of Thionitrosyl Complexes

The reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ with NOCl and $NOPF_6$ gives the nitrosyl complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ and the nitrosylthionitrosyl complex $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6$, respectively (*25*).

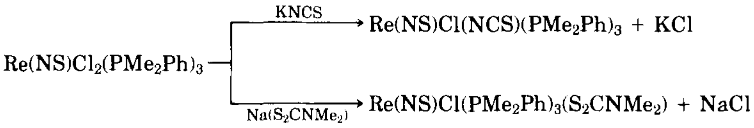
$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) + NOPF_6 \xrightarrow{CH_3CN/CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6 + CO$$

This cationic nitrosylthionitrosyl complex exhibits a ν_{CO} at 2122 cm^{-1}, a ν_{NO} at 1790 cm^{-1}, and a ν_{NS} at 1243 cm^{-1}. $[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6$ undergoes nucleophilic attack by I^- to give $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$. The thionitrosyl complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ does not react with triphenylphosphine, although its nitrosyl analog reacts with triphenylphosphine to yield $(\eta^5\text{-}C_5H_5)Cr(CO)(PPh_3)(NO)$. $[Cr(NS)(CNCMe_3)_5]PF_6$ has also been reported to react with $NOPF_6$ or $AgPF_6$ to give $[Cr(NS)(CNCMe_3)_5](PF_6)_2$ (*29*).

$$[Cr(NS)(CNCMe_3)_5]PF_6 + NOPF_6 \rightarrow [Cr(NS)(CNCMe_3)_5](PF_6)_2 + NO$$

The IR spectra of $[Cr(NS)(CNCMe_3)_5](PF_6)_2$ includes absorptions at 2225 cm^{-1} (attributable to ν_{CN}) and 1220 cm^{-1} (attributable to ν_{NS}). The thionitrosyl stretching frequency occurs at higher energy than that exhibited by the $[Cr(NS)(CNCMe_3)_5]PF_6$ complex. This is consistent with a decrease in electron density at the metal center which manifests itself in less back donation from the metal d orbital to the $NS\pi^*$ orbitals (*64*).

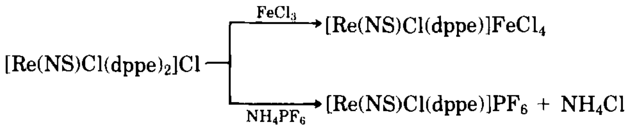
The desulfurization of thionitrosyl complexes of molybdenum, rhenium, and osmium to the parent nitrido complexes have been observed by refluxing the complexes with $n\text{-}Bu_3P$ in toluene or acetonitrile (*12*). The reaction of $Re(NS)Cl_2(PMe_2Ph)_3$ with KNCS or $Na(S_2CNMe_2)$ leads to $Re(NS)ClL(PMe_2Ph)_3$ [L = NCS or (S_2CNMe_2)].



$$Re(NS)Cl_2(PMe_2Ph)_3 \xrightarrow{KNCS} Re(NS)Cl(NCS)(PMe_2Ph)_3 + KCl$$

$$Re(NS)Cl_2(PMe_2Ph)_3 \xrightarrow[Na(S_2CNMe_2)]{} Re(NS)Cl(PMe_2Ph)_3(S_2CNMe_2) + NaCl$$

The cationic thionitrosyl complex $[Re(NS)Cl(dppe)_2]Cl$ also reacts with $FeCl_3$ or NH_4PF_6 with formation of the $FeCl_4^-$ or PF_6^- salt.



$$[Re(NS)Cl(dppe)_2]Cl \xrightarrow{FeCl_3} [Re(NS)Cl(dppe)]FeCl_4$$

$$[Re(NS)Cl(dppe)_2]Cl \xrightarrow[NH_4PF_6]{} [Re(NS)Cl(dppe)]PF_6 + NH_4Cl$$

The ruthenium dithionitrosyl complex $Ru(NS)_2Cl_2(PPh_3)_2 \cdot CH_2Cl_2$ was found to react with NOX (X = Cl or Br) to yield the nitrosyl thionitrosyl complexes $Ru(NO)(NS)ClX(PPh_3)_2$ (X = Cl or Br) at room temperature (25 ° C) whereas refluxing the reaction mixture with excess NOX or N_2O_3 led to formation of the nitrosyl complexes $Ru(NO)ClX_2(PPh_3)_2$ (X = Cl or Br) (*33*). The IR spectra of Ru(NO)(NS)-

$Cl(PPh_3)_2$ exhibits ν_{NO} at 1880 cm^{-1} and ν_{NS} at 1320 cm^{-1}. Reaction of $Ru(NS)_2Cl_2(PPh_3)_2CH_2Cl_2$ with H_2O affords $Ru(NS)(NSOH)Cl(PPh_3)_2$ and HCl.

$$Ru(NS)_2Cl_2(PPh_3)_2CH_2Cl_2 + H_2O \rightarrow Ru(NS)(NSOH)Cl(PPh_3)_2 + HCl$$

In the IR spectrum of the complex $Ru(NS)(NSOH)Cl(PPh_3)_2$ it was found that the band at 1330 cm^{-1} disappeared and a new band due to the coordinated NSOH group appeared, although the position of the band at 1120 cm^{-1} remained the same. Whether the thionylimide is bonded via oxygen or nitrogen to ruthenium is not known. Reactions of $Ru(NS)_2Cl_2(PPh_3)_2 \cdot CH_2Cl_2$ with X_2 ($X_2 = Cl_2, Br_2$, or I_2) result in the formation of charge-transfer complexes with the composition $Ru(NS)_2Cl_2(PPh_3)_2CH_2Cl_2 \cdot X_2$.

When nitrosyl halides NOX (X = Cl or Br) react with $Rh(CO)(NS)Cl_2L_2$ (L = PPh_3 or $AsPh_3$), the displacement of the thionitrosyl group and the formation of carbonylnitrosyl complexes of rhodium(III), $Rh(CO)(NO)ClXL_2$ (X = Cl or Br; L = PPh_3 or $AsPh_3$), (*54*) are observed. The mechanism of the reaction is not yet known. The complex $Rh(NS)(PPh_3)_3$ reacts with chlorine to give the pentacoordinated complex $Rh(NS)Cl_2(PPh_3)_2$ (*46*).

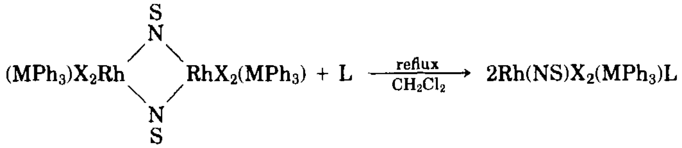
$$Rh(NS)(PPh_3)_3 + Cl_2 \rightarrow Rh(NS)Cl_2(PPh_3)_2 + PPh_3$$

BRIDGED THIONITROSYL COMPLEXES

It was mentioned earlier that the thionitrosyl group (NS) can form metal–N(S)–metal bridge complexes. Reaction of trithiazyltrichloride in THF or CCl_4–$CHCl_3$ (1 : 1) with $Rh(NO)Cl_2(PPh_3)_2$ leads to the formation of a novel complex of composition $[Rh(\mu\text{-}NS)Cl_2(PPh_3)]_2$, which has been isolated as brown, shining crystals (*49, 50*). A plausible mechanism involves the prior formation of the six-coordinate intermediate sulfur monoxide complex $[Rh(NS)(SO)Cl_2(PPh_3)]_2$, ($\nu_{SO}$ = 1035 cm^{-1}), which reacts readily with triphenylphosphine to give $[Rh(\mu\text{-}NS)Cl_2PPh_3]_2$, $SPPh_3$, and $OPPh_3$. The formation of triphenylphosphine sulfide and triphenylphosphine oxide from $[Ir(S_2O_2)(dppe)_2]Cl$ with triphenylphosphine has been reported by Schmid and Ritter (*62, 63*).

Similar reactions of $NSCl(THF)_x$ with $Rh(NO)L_3$ (L = PPh_3 or $AsPh_3$), $Rh(NO)ClBr(PPh_3)_2$, $Rh(NO)Br_2(PPh_3)_2$, or $Rh(NO)Cl_2(AsPh_3)_2$ result in the formation of brown complexes with the composition $Rh(\mu\text{-}NS)X_2(MPh_3)_2$ (X = Cl or Br; M = P or As) (*46, 56*). All these thionitrosyl bridged complexes are air stable, nonelectrolytic, diamagnetic solids. The IR spectra exhibit a slightly broad band at 840 cm^{-1}, which is attributed to the bridging thionitrosyl group. The absence of a band around 1630 cm^{-1} [due to ν_{NO} (*48*) and the appearance of a new band at 840 cm^{-1} indicate the replacement of the nitrosyl group by the thionitrosyl group.

In order to prove further the bridging nature of the NS group, the reactions of $[Rh(\mu\text{-}NS)X_2(MPh_3)]_2$ with PPh_3 and $AsPh_3$ have been carried out. These reactions result in the cleavage of the bridge and yield complexes of composition $Rh(NS)X_2(MPh_3)_2$.



M = P L = PPh_3
M = P L = $AsPh_3$
M = As L = PPh_3
M = As L = $AsPh_3$

The IR spectra of the complexes $Rh(NS)X_2L_2$ show absorption bands around 1118–1120 cm^{-1} [due to terminal (NS)] and disappearance of the band at 840 cm^{-1}. This supports the view that the band at 840 cm^{-1} in the complexes $[Rh(\mu\text{-}NS)X_2L]_2$ is the characteristic band of a bridging thionitrosyl group.

Displacement of an NO group by NS is observed in iridium nitrosyl complexes, but, contrary to rhodium and iridium complexes, Ru(II) and Os(II) complexes of composition $M(NO)X_3(PPh_3)_2$ (M = Ru or Os; X = Cl or Br) do not react with $(NSCl)_3$ (*46*).

It is obvious from these reactions that the NO group is replaced by the NS group in those metal nitrosyl complexes in which ν_{NO} appears at relatively low frequencies.

IV. Properties of Thionitrosyl Complexes

The ligand NS might be expected to have bonding properties similar to those of NO. As in nitrosyl complexes the most readily accessible and sensitive technique for identifying metal thionitrosyl complexes is IR spectroscopy. A variety of other physical techniques has been applied to thionitrosyl complexes, but these have concentrated on comparing analogous nitrosyl and thionitrosyl systems.

A. THEORETICAL STUDIES

It has been shown previously that NS is a better σ donor and π acceptor than NO. Physical measurements have supported the conclusion that NS binds more strongly to an electron-rich metal than does NO. An investigation of the electronic structure of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ by photoelectron spectroscopy (*31*) and theoretical calculations has been reported by Lichtenberger and Fenske (*40*). Their study confirms the early predictions, based on molecular orbital theory, that the NS group is a slightly better σ donor than NO. The improved donor ability results from the additional charge on the nitrogen atom, both from the less electronegative sulfur atom and the improved π-acceptor ability of NS. As in the case of CO and CS (*28*), this also has an important influence on their chemical and physical properties.

B. IR STUDIES

Nitrosyl stretching-frequency modes in metal nitrosyl complexes have a characteristic intense absorption in the region between 1500 and 2000 cm^{-1}, depending on the type of bonding involved in the nitrosyl complexes. At present the frequency range for different modes in thionitrosyl complexes has been found to be between 840 and 1370 cm^{-1}. The NS stretching frequency in the linear M—NS structure generally appears at higher values (*26*), in the range between 1150 and 1370 cm^{-1}. The complexes that absorb in the region 1110–1130 cm^{-1} have been considered to involve bonding of the terminal bent type (Table I).

The IR spectrum of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ exhibits absorption bands at 2033 and 1962 cm^{-1} (due to ν_{CO}) and at 1180 cm^{-1} (due to ν_{NS}). The ν_{CO} bands of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$ appear at higher frequencies than those of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. The IR spectrum of the green complex $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ shows absorption bands at 2110, 1118, 340, and 260 cm^{-1} in addition to the characteristic bands of PPh_3. The bands at 2110 and 1118 cm^{-1} are characteristic stretching frequencies of terminal carbonyl and thionitrosyl groups. The band at 340 cm^{-1} is typical of ν_{RhCl}, whereas the band at 260 cm^{-1} could be due to either ν_{RhCl} or to bridging chlorine modes. The IR spectra of $Rh(CO)(NS)Cl_2L_2$ ($L = PPh_3$ or $AsPh_3$) exhibits absorption bands at $\nu_{CO} = 2105$, $\nu_{NS} = 1120$, and $\nu_{RhCl} = 330$ cm^{-1}. According to the magnetic data these complexes are diamagnetic, suggesting rhodium to be present either in a +1 $[Rh(I)NS^+]$ or a +3 $[Rh(III)NS^-]$ oxidation state. The high frequency of ν_{CO} is also reasonable for a Rh(III) system.

TABLE I

IR Data of Thionitrosyl Complexes

Complex	ν_{NS} (cm^{-1})	References	Complex	ν_{NS} (cm^{-1})	References
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$	1180	*(38)*	$Ru(NO)(NS)ClBr(PPh_3)_2$	1320	*(33)*
	1150	*(29)*	$Ru(NS)(NSOH)Cl(PPh_3)_2$	1120	*(33)*
$[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(NS)]PF_6$	1243	*(25)*	$Os(NS)Cl_3(PPh_3)_2$	1294	*(51)*
$[Cr(NS)(CNCMe_3)_5]PF_6$	1135	*(29)*	$Os(NS)Cl_3(AsPh_3)_2$	1290	*(51)*
$[Cr(NS)(CNCMe_3)_5](PF_6)_2$	1220	*(29)*	$Os(NS)Cl_3(PMe_2Ph)_2$	1285	*(12)*
$[Cr(NS)(NCMe)_5](PF_6)_2$	1245	*(29)*	$Os(NS)Cl_3(bipy)$	1282	*(12)*
$Mo(NS)(S_2CNMe_2)_3$	—	*(12)*	$Os(NS)Cl_3(py)_2$	1284	*(12)*
$Mo(NS)(S_2CNEt_2)_3$	—	*(12)*	$Os(NS)ClBr_2(AsPh_3)_2$	1270	*(12)*
$Mo(NS)[S_2CN(CH_2)_4]_3$	—	*(12)*	$Os(NS)ClBr_2(bipy)$	1280	*(12)*
$Re(NS)Cl_2(PMe_2Ph)_3$	1180	*(12)*	$Co(NS)Cl_2[P(OPh)_3]_2$	1130	*(66)*
$Re(NS)Cl_2(PEt_2Ph)_3$	1167	*(12)*	$[Rh(CO)(NS)Cl_2(PPh_3)]_2$	1118	*(34, 53)*
$Re(NS)Cl_2(PMePh_2)_3$	1172	*(12)*	$[Rh(CO)(NS)Cl_2(AsPh_3)]_2$	1120	*(54)*
$Re(NS)ClBr(PEt_2Ph)_3$	1168	*(12)*	$Rh(CO)(NS)Cl_2(PPh_3)_2$	1120	*(53, 54)*
$Re(NS)Cl(SCN)(PMe_2Ph)_3$	1177	*(12)*	$Rh(CO)(NS)Cl_2(AsPh_3)_2$	1120	*(54)*
$Re(NS)Cl(S_2CNMe_2)(PMe_2Ph)_2$	1150	*(12)*	$Rh(CO)(NS)(PPh_3)_2$	1122	*(54)*
$[Re(NS)Cl(dppe)_2]PF_6$	1177	*(12)*	$Rh(NS)(PPh_3)_3$	1100	*(46)*
$[Re(NS)Cl(dppe)_2]Cl$	1185	*(12)*	$[Rh(NS)Cl_2(PPh_3)]_2$	1120	*(46)*
$[Re(NS)Cl(dppe)_2]FeCl_4$	1173	*(12)*	$Rh(NS)Cl_2(PPh_3)_2$	1120	*(50, 53)*
$[Re(NS)Cl(dppe)_2]S_2CNEt_2$	1183	*(12)*	$Rh(NS)Cl_2(AsPh_3)_2$	1120	*(50, 53)*
$Re(NS)Cl_3(PMe_2Ph)_2$	1228	*(12)*	$Rh(NS)Cl_2(PPh_3)(AsPh_3)$	1120	*(49)*
$Re(NS)Cl_3(PEt_2Ph)_2$	1230	*(12)*	$Rh(NS)ClBr(PPh_3)_2$	1120	*(49)*
$Re(NS)Cl_3(PMePh_2)_2$	1220	*(12)*	$Rh(NS)Br_2(PPh_3)_2$	1118	*(49)*
$Re(NS)Cl_3(PPh_3)_2$	1214	*(12)*	$Rh(NS)ClBr(PPh_3)(AsPh_3)$	1120	*(49)*
$Re(NS)Cl_3(Pn\text{-}PrPh_2)_2$	1226	*(12)*	$[Rh(\mu\text{-}NS)Cl_2(PPh_3)]_2$	840	*(50)*
$[Re(CO)_5(NS)](AsF_6)_2$	1371	*(43)*	$[Rh(\mu\text{-}NS)Cl_2(AsPh_3)]_2$	840	*(50)*
$Ru(NS)Cl_3(PPh_3)_2$	1297	*(51)*	$[Rh(\mu\text{-}NS)ClBr(PPh_3)]_2$	840	*(49)*
$Ru(NS)Cl_3(AsPh_3)_2$	1295	*(51)*	$[Rh(\mu\text{-}NS)Br_2(PPh_3)]_2$	840	*(49)*
$Ru(NS)_2Cl_2(PPh_3)_2 \cdot X$	1300	*(33)*	$Ir(CO)(NS)Cl_2(PPh_3)_2$	1115	*(46)*
($X = CH_2Cl_2$, $CHCl_3$, or $CHBr_3$)	1120		$Ir(NS)Cl_2(PPh_3)_2$	1115	*(46)*
$Ru(NO)(NS)Cl_2(PPh_3)_2$	1320	*(33)*	$Ni(NS)Cl(PPh_3)_2$	1186	*(47)*

TABLE II

COMPARISON OF CARBONYL STRETCHING FREQUENCIES IN NITROSYL AND THIONITROSYL COMPLEXES

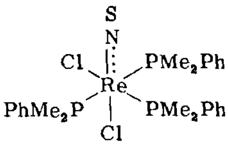
Complex	X = O ν_{CO} (cm^{-1})	X = S ν_{CO} (cm^{-1})	References
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NX)$	2038, 1955	2033, 1962	*(38)*
$Rh(CO)(NX)Cl_2(PPh_3)_2$	2090	2105	*(54)*
$Ir(CO)(NX)Cl_2(PPh_3)_2$	2055	2050	*(39, 52)*

A comparison of the spectroscopic properties of the carbonyl complexes $(\eta^5\text{-}C_5H_5)Cr(CO)_2NX$, $Rh(CO)(NX)Cl_2(PPh_3)_2$, and $Ir(CO)(NX)Cl_2(PPh_3)_2$ (X = O or S; Table II) indicates that the NS ligand is more effective in removing electron density from the central metal atom than is the NO ligand.

C. NMR STUDIES

The ^{1}H-NMR spectrum of $(\eta^5\text{-}C_5H_5)Cr(CO)_2NS$ consists of a single sharp peak that occurs at a slightly lower field than the corresponding absorption due to the cyclopentadienyl protons of the nitrosyl analogs. Similarly, the ^{13}C-NMR chemical shifts of the cyclopentadienyl and carbonyl carbons are further downfield from Me_4Si for the complex $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. The ^{1}H-NMR spectrum of $Mo(NS)(S_2CNMe_2)_3$ in nitrobenzene at room temperature shows a 1 : 2 : 3 triplet consisting of two overlapping doublets (due to the dithiocarbamate methyl groups).

The ^{1}H-NMR spectrum of $Re(NS)Cl_2(PMe_2Ph)_3$ consists of two triplets and a doublet in the tertiary phosphine alkyl group region, indicating a meridional configuration:



The ^{31}P-NMR spectra of $[ReCl(N)(dppe)_2]Cl$ and $[ReCl(NS)(dppe)_2]Cl$ both have a singlet at approximately 120 ppm, confirming that four phosphorus atoms lie in the plane, with the NS and Cl in a trans position.

D. MASS SPECTRAL DATA

In their attempt to gain further insight into the bonding of Cr—NX (X = O, S), Legzdins *et al.* (*24, 38*) investigated the low-resolution mass spectral data of (η^5-C_5H_5)Cr$(CO)_2$(NX) complexes, and both types of complexes were observed to undergo similar fragmentations: $C_5H_5Cr(CO)_2(NX)^+$, $C_5H_5Cr(CO)(NX)^+$, $C_5H_5Cr(NX)^+$, $C_5H_5Cr^+$, and Cr^+. The $C_5H_5Cr(NS)^+$ ion is markedly more abundant in the mass spectrum of the thionitrosyl complex than is the corresponding ion in the spectrum of the nitrosyl complex. It was noted that carbonyls were lost in preference to the thionitrosyl group.

The mass spectrum of the complexes $Mo(NS)(S_2CNR_2)_3$ [R_2 = Me_2, Et_2, or $(CH_2)_4$] all show peaks attributable to the parent ions, together with those assigned to $[Mo(S_2CNR_2)_3]^+$ and $[MoS(S_2CNR_2)_2]^+$.

E. X-RAY STRUCTURAL DETERMINATIONS

The structures of (η^5-C_5H_5)Cr$(CO)_2$(NS) (*24, 25*) and $Mo(NS)(S_2CNMe_2)_3$ (*12, 32*) have been determined by X-ray crystallography. In both complexes the thionitrosyl ligand coordinates essentially linearly to the metal via the nitrogen atom, with M—NS angles of 176.8(1) and 172.0(7)°, respectively, suggesting that the NS ligand is functioning as a three-electron donor. The molecular geometry of the chromium thionitrosyl complex is similar to that exhibited by the molecules (η^5-C_5H_5)Mn$(CO)_3$ (*7*) and (η^5-C_5H_5)Cr$(CO)_2$(NO) (*5*), and the Cr—C(C_5H_5), Cr—C(O) and C—O bond lengths are comparable to those found in other cyclopentadienylchromium carbonyls (*64*). The structure of $Mo(NS)(S_2CNMe_2)_3$ is pentagonal bipyramidal, with a linear apical NS group. A comparison of the thionitrosyl complex $Mo(NS)(S_2CNMe_2)_3$ with the nitrosyl complex Mo(NO)(S_2CN-*t*-Bu_2)$_3$ (*13*) indicates that in both complexes the M—N distance and M—N—X (X = S, O) angle are equal, within the limits of experimental error (Table III).

TABLE III

CRYSTALLOGRAPHIC DATA FOR THIONITROSYL COMPLEXES

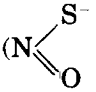
Complex	M—NS (pm)	N—S (pm)	M—N (pm)	References
(η^5-C_5H_5)Cr$(CO)_2$(NS)	176.8(1)	155.1	169.4(3)	(*24, 25*)
$Mo(NS)(S_2CNMe_2)_3$	172.0(7)	159	173	(*32*)

F. Electronic Spectral Data

The electronic spectrum of $[Rh(CO)(NS)Cl_2(PPh_3)]_2$ shows bands at 15,300, 21,745, and 27,760 cm^{-1}. The spectra of the complexes $Rh(CO)(NX)Cl_2(PPh_3)_2$ (X = O or S) show bands at 25,000, 29,410, and 22,220, 27,200 cm^{-1}, respectively. The very high intensity of these bands suggests that they should be charge transfer and not d–d transition bands. All d–d transitions are masked by intense charge-transfer bands, and hence no d–d bands appeared in any of the spectra of these complexes.

V. Prospects

It is evident that the chemistry of thionitrosyl will continue to be a fertile area of research. One major difference between metal nitrosyl and thionitrosyl is the present scarcity of complexes containing multiple NS groups. It is probable that future research will show that these types of complexes will be difficult to obtain because of the destabilizing effect resulting from the strong acceptor capacity of the NS ligand. Finally, it is anticipated that the catalytic potential of these complexes will become an important research area. The availability of these complexes now makes possible a systematic study of the different modes of bonding of NS groups to transition metals. The following are some of the problems that will be investigated in the future.

1. The syntheses and reactions of thionitrosyl complexes of the other transition and nontransition metal ions
2. The reactions of electrophilic and nucleophilic reagents with the thionitrosyl group
3. Syntheses of complexes having two or more thionitrosyl groups in the molecule
4. Syntheses of complexes in which sulfur is end-on coordinated with the NS group
5. Conversion of the thionitrosyl group to nitride complexes by pulling sulfur out of the coordinated NS by metal ions such as Hg^{2+}, Hg^{+}, Pd^{2+}, Ag^{+}, Pb^{2+}, etc.
6. Reactions of the coordinated NS group with molecular oxygen or other oxidizing agents to convert NS to an oxygen- or nitrogen-bonded NSO^- ligand or to a thionitro ( $N(S^-)(=O)$) group

7. Reactions of molecular oxygen complexes with thionitrosyl chloride
8. Preparation of metal complexes with the ligands $R_2NN{=}S$, $RN{=}S{=}S$, $S{=}NN{=}S$, $RN{=}S$, NSe, and NTe

ACKNOWLEDGMENTS

We wish to thank the Deutsche Forschungsgemeinschaft for financial support. K. K. Pandey is also grateful to the Alexander von Humboldt Foundation for a fellowship.

REFERENCES

1. Allegretti, J. M., and Merer, A. J., *Can. J. Phys.* **50,** 404 (1972).
2. Armitage, D. A., and Brand, J. C., *J. Chem. Soc., Chem. Commun.* p. 1079 (1979).
3. Armitage, D. A., and Clark, M. J., *J. Organomet. Chem.* **24,** 629 (1970).
4. Armitage, D. A., and Sinden, A. W., *J. Organomet. Chem.* 44, C43 (1972).
5. Atwood, J. L., Shakir, R., Malito, J. T., Herberhold, M., Kremnitz, W., Bernhagen, W. P. E., and Alt, H. G., *J. Organomet. Chem.* **165,** 65 (1979).
6. Becke-Goehring, M., Schwarz, R., and Spiess, W., *Z. Anorg. Allg. Chem.* **293,** 294 (1957). HOSN is only briefly stable at room temperature and forms red violet derivatives LiOSN and NaOSN.
7. Berndt, A. F., and Marsh, R. E., *Acta Crystallogr.* **16,** 118 (1963).
8. Bhattacharyya, A. A., McLean, J. A., and Turner, A. G., *Inorg. Chim. Acta* **34,** L199 (1979).
9. Bhattacharyya, A. A., and Turner, A. G., *Inorg. Chim. Acta* **53,** L89 (1981).
10. Bhattacharyya, A. A., Turner, A. G., Holt, E. M., and Alcock, N. W., *Inorg. Chim. Acta* **44,** L185 (1980).
11. Bishop, M. W., Chatt, J., and Dilworth, J. R., *J. Chem. Soc., Chem. Commun.* p. 780 (1975).
12. Bishop, M. W., Chatt, J., and Dilworth, J. R., *J. Chem. Soc., Dalton Trans.* p. 1 (1979).
13. Brennan, T. F., and Bernal, I., *Inorg. Chim. Acta* **7,** 283 (1973).
14. Byflett, R., Carrington, A., and Russell, D. K., *Mol. Phys.* **20,** 271 (1971).
15. Carrington, A., Howard, B. J., Levy, D. H., and Robertson, J. C., *Mol. Phys.* **15,** 187 (1968).
16. Chapman, D., Warn, R. J., Fitzgerald, A. D., and Yoffe, A. D., *Trans. Faraday Soc.* **60,** 294 (1964).
17. Chatt, J., and Dilworth, J. R., *J. Chem. Soc., Chem. Commun.* p. 508 (1974).
18. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry—A Comprehensive Text," 4th ed., p. 93.
19. Dressler, K., *Helv. Phys. Acta* **28,** 563 (1955).
20. Dyke, J. M., Morris, A., and Trickle, I. R., *J. Chem. Soc., Faraday Trans. 2* **73,** 147 (1977).
21. Enemark, J. H., and Feltham, R. D., *Coord. Chem. Rev.* **13,** 339 (1974).
22. Fowler, A., and Bakker, C. J., *Proc. R. Soc. London, Ser. A* **136,** 28 (1932).

23. Glemser, O., and Mews, R., *Angew. Chem.* **92,** 904 (1980): *Angew. Chem., Int. Ed. Engl.* **19,** 883 (1980).
24. Greenhough, T. S., Kolthammer, B. W. S., Legzdins, P., and Trotter, J., *J. Chem. Soc., Chem. Commun.* p. 1036 (1978).
25. Greenhough, T. S., Kolthammer, B. W. S., Legzdins, P., and Trotter, J., *Inorg. Chem.* **18,** 3548 (1979).
26. Haymore, B. L., and Ibers, J. A., *Inorg. Chem.* **14,** 3060 (1975).
27. Heal, H. G., *Adv. Inorg. Chem. Radiochem.* **15,** 375 (1972).
28. Herberhold, M., *Nachr. Chem., Tech. Lab.* **29,** 365 (1981).
29. Herberhold, M., and Haumaier, L., *Z. Naturforsch. B* **35B,** 1277 (1980).
30. Holt, E. M., Alcock, N. W., Bhattacharyya, A. A., and Turner, A. G., *Inorg. Chim. Acta* **47,** 255 (1981).
31. Hubbard, J. L., and Lichtenberger, D. L., *Inorg. Chem.* **19,** 1388 (1980).
32. Hursthouse, M. B., and Motevalli, M., *J. Chem. Soc., Dalton Trans.* p. 1362 (1979).
33. Jain, K. C., Pandey, K. K., and Agarwala, U. C., *Inorg. Chem.* (to be published).
34. Jain, K. C., Pandey, K. K., Katiyar, S. S., and Agarwala, U. C., *Proc. Int. Conf. Coord. Chem., 21st, 1980* p. 440 (1980).
35. Jenouvrier, A., and Daumont, D., *J. Mol. Spectrosc.* **61,** 313 (1976).
36. Johnson, B. F. G., and McCleverty, J. A., *Prog. Inorg. Chem.* **7,** 277 (1966).
37. Kirchoff, W. H., *J. Am. Chem. Soc.* **91,** 2437 (1969).
38. Kolthammer, B. W. S., and Legzdins, P., *J. Am. Chem. Soc.* **100,** 2247 (1978).
39. Kubota, M., and Phillips, D. A., *J. Am. Chem. Soc.* **97,** 5637 (1975).
40. Lichtenberger, D. L., and Fenske, R. F., *Inorg. Chem.* **15,** 2015 (1976).
41. McCleverty, J. A., *Chem. Rev.* **79,** 53 (1979).
42. Mews, R., *Adv. Inorg. Chem. Radiochem.* **19,** 223 (1976).
43. Mews, R., and Liu, C., *Angew. Chem.* **95,** 156 (1983).
44. O'Hare, P. A. G., *J. Chem. Phys.* **52,** 2992 (1970).
45. O'Hare, P. A. G., *J. Chem. Phys.* **54,** 4124 (1971).
46. Pandey, K. K., unpublished work.
47. Pandey, K. K., unpublished observations. Reaction of $NSCl(THF)_x$ with $NiCl_2(PPh_3)_2$ in the presence of sodiumborohydride affords $Ni(NS)Cl(PPh_3)_2$, whereas in the absence of sodiumborohydride the products are $NiCl_2$ and $SPPh_3$.
48. Pandey, K. K., and Agarwala, U. C., *J. Inorg. Nucl. Chem.* **42,** 293 (1980).
49. Pandey, K. K., and Agarwala, U. C., *Indian J. Chem.* **20**(1), 74 (1981).
50. Pandey, K. K., and Agarwala, U. C., *Inorg. Chem.* **20**(4), 1308 (1981).
51. Pandey, K. K., and Agarwala, U. C., *Z. Anorg. Allg. Chem.* **461,** 231 (1980).
52. Pandey, K. K., and Agarwala, U. C., *Indian J. Chem.* **20,** 240 (1981).
53. Pandey, K. K., Datta, S., and Agarwala, U. C., *Z. Anorg. Allg. Chem.* **468,** 228 (1980).
54. Pandey, K. K., Jain, K. C., and Agarwala, U. C., *Inorg. Chim. Acta* **48**(1), 23 (1981).
55. Raghuveer, K., and Narasimham, N. A., *J. Mol. Spectrosc.* **70,** 323 (1978).
56. Raju, D. K. M., M.Phil. Thesis, Indian Institute of Technology, Kanpur (1980).
57. Roesky, H. W., *Sulfur Org. Inorg. Chem.* **4,** 15 (1982).
58. Roesky, H. W., Emmert, R., Clegg, W., Isenberg, W., and Sheldrick, G. M., *Angew. Chem.* **93,** 623 (1981); *Angew. Chem., Int. Ed. Engl.* **20,** 591 (1981).
59. Salahub, D. R., and Messmer, R. P., *J. Chem. Phys.* **64,** 2039 (1976).
60. Schenk, P. W., *Chem. Ber.* **75,** 94 (1942).
61. Scherer, O. J., and Hornig, P., *Angew. Chem.* **78,** 776 (1966); *Angew. Chem., Int. Ed. Engl.* **5,** 729 (1966).
62. Schmid, G., and Ritter, G., *Chem. Ber.* **108,** 3008 (1975).

63. Schmid, G., and Ritter, G., *Angew. Chem.* **87,** 673 (1975); *Angew. Chem., Int. Ed. Engl.* **14,** 645 (1975).
64. Sneeden, R. P. A., "Organochronium Compounds." Academic Press, New York, 1975.
65. Teichman, R. A., and Nixon, R. E., *Inorg. Chem.* **15,** 1993 (1976).
66. Tiwari, R. D., Pandey, K. K., and Agarwala, U. C., *Inorg. Chem.* **21,** 845 (1982).
67. Toher, P. O., and Spratley, R. D., *Can. J. Chem.* **53,** 2311 (1975).
68. Toher, P. O., and Spratley, R. D., *Can. J. Chem.* **53,** 2318 (1975).
69. Uehara, H., and Morino, Y., *Mol. Phys.* **17,** 239 (1969).