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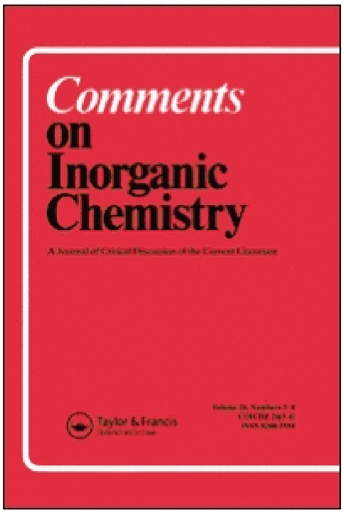

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Chlorothionitrene Complexes of Transition Metals

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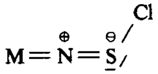
Chlorothionitrene Complexes of Transition Metals

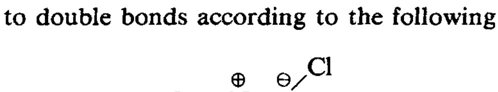
Syntheses, structures, spectral data and chemical properties of chlorothionitrene complexes are reported. These incorporate the novel



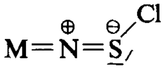
group, M being molybdenum, tungsten, rhenium or osmium.

INTRODUCTION

The chlorothionitrene group can formally be derived from the thiazylchloride molecule by the assimilation of two electrons:



Whereas the ion itself is not known, it does exist as a ligand in transition metal complexes. In these, it is bonded via its nitrogen atom forming a linear metal–N–S group; the M–N and N–S distances correspond to double bonds according to the following formula:



So far, chlorothionitrene complexes of molybdenum, tungsten, rhenium and osmium are known. Their preparation is straightforward,

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their chemistry is quite versatile. Amongst others, they can be used to prepare nitrido complexes containing the M≡N| group.

SYNTHESES

Chlorothionitrene complexes of molybdenum and tungsten can be obtained with high yields by the reactions of trithiazyl chloride with suspensions of molybdenum pentachloride or tungsten hexachloride in dichloromethane at room temperature[1,2]:

$$[MoCl_5]_2 + \frac{2}{3}(NSCl)_3 \rightarrow [MoCl_4(NSCl)]_2 + Cl_2 \qquad (1)$$

$$2\ WCl_6 + \frac{2}{3}(NSCl)_3 \rightarrow [WCl_4(NSCl)]_2 + 2\ Cl_2 \qquad (2)$$

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Part of the formed chlorine reacts with the solvent. Both complexes form very moisture-sensitive crystal powders. The molybdenum compound is black; the tungsten compound is brown-red. According to their IR spectra and a crystal structure determination, they have dimeric structures with chloro bridges. $[WCl_4(NSCl)]_2$ can be sublimed in vacuo at 145 °C without decomposition. In donating solvents such as $POCl_3$, both compounds are soluble with simultaneous complexation:

$$[MCl_4(NSCl)]_2 + 2\ POCl_3 \rightarrow 2\ [MCl_4(NSCl)(OPCl_3)] \qquad (3)$$
$$M = Mo, W$$

The rupture of the chloro bridges of the dimer can also be achieved with chloride ions. In this manner anionic complexes are obtained; with large counterions like tetraphenylphosphonium they are soluble in solvents such as dichloromethane. Addition of carbon tetrachloride to such solutions yields crystalline products which are nearly insensitive to moisture:

$$[MCl_4(NSCl)]_2 + 2\ PPh_4Cl \rightarrow 2\ PPh_4[MCl_5(NSCl)] \qquad (4)$$
$$M = Mo, W$$

The same anionic chlorothionitrene complex of tungsten can also be readily obtained from tungsten hexachloride and thiadithiazyl chloride in a CCl_4 suspension saturated with chlorine:

$$WCl_6 + S_3N_2Cl_2 \rightarrow N(SCl)_2[WCl_5(NSCl)] \qquad (5)$$

This reaction proceeds at room temperature in the course of a few hours with quantitative yield. $N(SCl)_2[WCl_5(NSCl)]$ is a brown-violet crystal powder that is very sensitive to moisture and almost insoluble in CCl_4. It can also be obtained from $[WCl_4(NSCl)]_2$ with excess SCl_2 and chlorine in boiling CCl_4[3]:

$$[WCl_4(NSCl)]_2 + 3\ SCl_2 + 2\ Cl_2 \rightarrow N(SCl)_2[WCl_5(NSCl)] + (SCl_3)_2[WCl_6] \qquad (6)$$

The ionic structure of $N(SCl)_2^+[WCl_5(NSCl)]^-$ follows from the comparison of the IR spectra with those of different compounds with well-known counterions, e.g., $N(SCl)_2[AsF_6]$,[4,5] $N(SCl)_2[Re_2Cl_9]$ [6] and $N(SCl)_2[NbCl_6]$.[7]

Even with an excess of trithiazylchloride it has not been possible to attach a second chlorothionitrene group to molybdenum or tungsten. Instead, cyclo-S_2N_2 is formed and stabilized by complexation:

$$(MoCl_5)_2 + \frac{4}{3}(NSCl)_3 \rightarrow \mu\text{-}(S_2N_2)[MoCl_4(NSCl)]_2 + 2\ Cl_2 \qquad (7)$$

The tungsten compound can also be obtained in a quantitative reaction by thermolysis of the product obtained via the reactions (5) or (6)[8]:

$$2\ N(SCl)_2[WCl_5(NSCl)] \xrightarrow{80°C} \mu\text{-}(S_2N_2)\ [WCl_4(NSCl)]_2 + SCl_2 + Cl_2 \qquad (8)$$

The obtained tungsten compound forms very thin, brilliant red crystal plates that are very fragile. By contrast, the corresponding molybdenum compound is obtained from dichloromethane solution in the form of compact black crystals. In both, the S_2N_2 molecule acts as a bridging group between the metal atoms.

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The succesive introduction of two chlorothionitrene ligands can be achieved with rhenium. Solutions of rhenium pentachloride in $POCl_3$, which contain the well-known solvate $Cl_5Re \cdot POCl_3$,[9] react with the appropriate amounts of trithiazyl chloride according to the following reactions[10,11]:

$$ReCl_5 \cdot POCl_3 + \frac{1}{3}(NSCl)_3 \rightarrow [ReCl_4(NSCl) \cdot OPCl_3] + \frac{1}{2}Cl_2 \quad (9)$$

$$ReCl_5 \cdot OPCl_3 + \frac{2}{3}(NSCl)_3 \rightarrow [ReCl_3(NSCl)_2 \cdot OPCl_3] + Cl_2 \quad (10)$$

Both compounds form black crystal powders that are very sensitive to moisture; they are readily soluble in $POCl_3$, CH_2Cl_2 and CCl_4. They behave differently towards tetraphenylarsonium chloride solutions. Whereas the monochlorothionitrene complex is decomposed to yield tetrachloronitridorhenate (VII), $[ReNCl_4]^-$ (*vide infra*), the dichlorothionitrene complex simply suffers an exchange of the $POCl_3$ ligand and affords the anionic *cis*-dichlorothionitrene-tetrachlororhenate[10,11]:

$$[ReCl_3(NSCl)_2 \cdot OPCl_3] + Cl^- \rightarrow [ReCl_4(NSCl)_2]^- + POCl_3 \quad (11)$$

The corresponding nonionic species $[ReCl_3(NSCl)_2]_2$, which has a dimer structure via chloro bridges, can be obtained in a slow reaction from rhenium pentachloride and thiadithiazyl chloride in a dichloromethane suspension (containing a trace of $POCl_3$ to activate solution)[6]:

$$(ReCl_5)_2 + 2\ S_3N_2Cl_2 \rightarrow [ReCl_3(NSCl)_2]_2 + 2\ SCl_2 \quad (12)$$

A special variant of the chlorothionitrene group was found with osmium. When the thiazylchloride adduct $[OsCl_4(NSCl)_2]$ reacts with tetraphenylarsonium chloride in dichloromethane, the complex $[OsCl_4(NS)_2Cl]^-$ is obtained[12]:

$$[OsCl_4(NSCl)_2] + Cl^- \rightarrow [OsCl_4(NS)_2Cl]^- + Cl_2 \quad (13)$$

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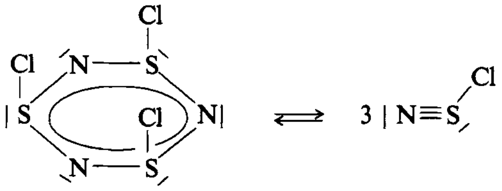
This compound can be regarded as a thionitrosyl–chlorothionitrene complex $[OsCl_4(NS)(NSCl)]^-$ or as a dithionitrosyl complex in which a chloride ion is attached to the thionitrosyl ligands. The latter description is supported by the crystallographic and spectroscopic data and by the ease of abstraction of the chloride ion with a Lewis acid like $GaCl_3$ as well as by the ease of its exchange for a bromide ion.

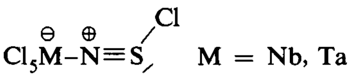
MECHANISM OF FORMATION

Crystalline trithiazyl chloride is known to consist of molecules having a nearly planar S_3N_3 ring with chlorine atoms attached to the sulfur atoms on one side of the ring.[13] In solution dissociation takes place to a small extent.[14] In our experience the equilibrium depends markedly on the nature of the solvent:



(14)

The interaction of a metal halide having Lewis-acid properties can occur with the nitrogen atom of the monomer or with a nitrogen atom of the trimer with subsequent ring cleavage. In either case it results in the formation of a donor-acceptor complex of the metal halide with an NSCl molecule. The $[OsCl_4(NSCl)_2]$ mentioned above is such a complex. With niobium and tantalum pentachloride such complexes can also be isolated as orange-red crystals:



$$\mathrm{Cl_5}\overset{\ominus}{\mathrm{M}}-\overset{\oplus}{\mathrm{N}}\equiv\mathrm{S}{\diagup}^{\mathrm{Cl}} \qquad \mathrm{M} = \mathrm{Nb, Ta} \tag{15}$$

Figure 1 shows the molecular structure of the niobium compound.[15] It is in accord with the formulation (15) given above. The long Nb–N distance of 226 pm reveals a rather weak bond of the NSCl ligand to the niobium atom; the low electron density of the Nb–N group

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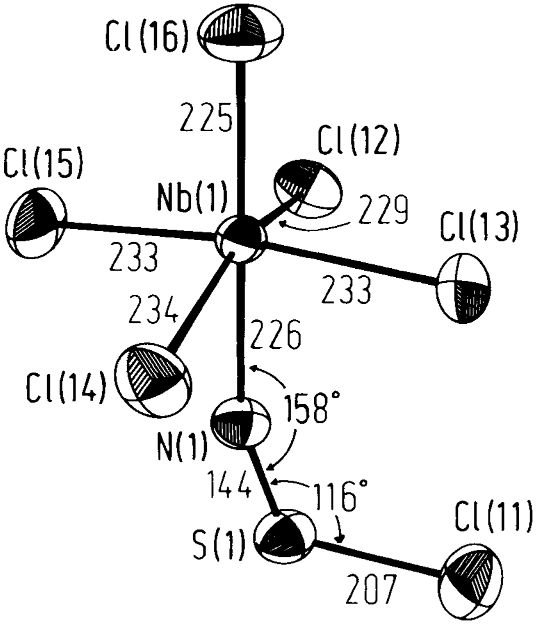
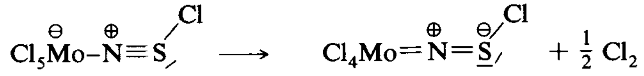


FIGURE 1 Molecular structure of the thiazyl chloride adduct $[Cl_5Nb \cdot N \equiv SCl]$ (Ref. 15). Interatomic distances are given in pm, angles in degrees.

is also manifested by the *trans*-effect (shortened *trans*-Nb-Cl bond) and the tilt of the *cis*-chloro atoms towards the nitrogen atom. The geometry and therefore the bonding within the NSCl group is nearly identical as in the NSCl molecule in the gas phase;[16,17] merely the S–Cl bond in $[Cl_5Nb \cdot NSCl]$ is 9 pm shorter than in the NSCl molecule. The situation is similar to the adducts of thiazyl fluoride $[Co(NSF)_6]AsF_6$,[18] $[Ni(NSF)_6]AsF_6$ [19] and $[Re(CO)_5(NSF)]AsF_6$.[20]

We assume that the primary step in the reactions of $(NSCl)_3$ with the chlorides of molybdenum, tungsten and rhenium similarly involves the formation of an NSCl adduct. Due to the marked avidity of these elements to form metal–nitrogen multiple bonds,[21] chlorine is immediately evolved with formation of the chlorothionitrene ligand, e.g.,



$$\mathrm{Cl_5}\overset{\ominus}{\mathrm{Mo}}-\overset{\oplus}{\mathrm{N}}\equiv\mathrm{S}\overset{\diagup\mathrm{Cl}}{\diagdown} \longrightarrow \mathrm{Cl_4Mo}=\overset{\oplus}{\mathrm{N}}=\overset{\ominus\diagup\mathrm{Cl}}{\underline{\mathrm{S}}\diagup} + \tfrac{1}{2}\,\mathrm{Cl_2} \tag{16}$$

As in the case of nitrido complexes,[21] chlorothionitrene complexes are stable with high oxidation states of the metal. According to the definition given in the Introduction, the chlorothionitrene ligand compensates two positive charges of the metal atom. Therefore the molybdenum and tungsten complexes $[ReCl_3(NSCl)_2 \cdot OPCl_3]$, $[ReCl_3(NSCl)_2]_2$ and $[ReCl_4(NSCl)_2]^-$ have to be considered as d^0 systems and accordingly were found to be diamagnetic.

STRUCTURAL STUDIES

X-Ray Crystallography

Structural details of chlorothionitrene complexes have been elucidated by a number of crystal structure determinations. Figure 2 shows the centrosymmetric molecular structure of $[WCl_4(NSCl)]_2$.[2] The W–Cl bonds involving the bridging chlorine atoms show two markedly different lengths. This is due to the *trans* effect which causes a weakening of the W–Cl bond in *trans*-position to the π-bonded nitrogen atom of the chlorothionitrene ligand. The high electron density of the WN bond is also revealed by the repulsion of the WCl groups

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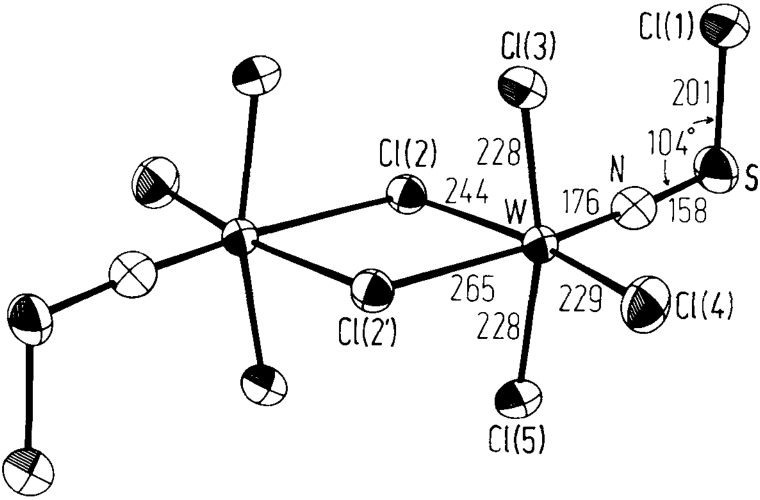

FIGURE 2 Molecular structure of $[WCl_4(NSCl)]_2$.

in *cis*-positions entailing NWCl bond angles greater than 90° (93° to 99°). The situation is opposite to that of the above-mentioned adduct of thiazyl chloride with niobium pentachloride. The WNS group is nearly linear (bond angle 175°) and has bond lengths that correspond to W=N and N=S double bonds. The formulation given in formula (16) also complies with the NSCl bond angles in the sense of the valence shell electron-repulsion theory: the chlorothionitrene ligand, having a sulfur atom with two lone electron pairs, exhibits an NSCl angle of 104°; this is 12° less than in the adduct of thiazyl chloride [$Cl_5Nb \cdot NSCl$] with only one lone pair per sulfur atom.

The same structural features of the chlorothionitrene ligand were found in other examples. Figure 3 shows the structure of the μ-$(N_2S_2)[MoCl_4(NSCl)]_2$ molecule in which each of the two molybdenum atoms is linked to one of the nitrogen atoms of a planar S_2N_2 ring.[8] Again, these links are relatively weak due to the *trans* effect, and the Mo–Cl groups suffer a repulsion by the Mo=N bonds of the chlorothionitrene ligands. However, the manifestation of the repulsion effect is different for the Mo–Cl groups that are coplanar with the S_2N_2 ring and those that are not: the bond angle of the coplanar group Cl(2)–Mo–Cl(4) is 158° while the Cl(3)–Mo–Cl(5) angle is 172°. The reason for this may be some kind of a weak bonding interaction Cl $\cdots$ S (formula (A)) as the Cl $\cdots$ S distance is only 315 pm which is 40 pm shorter than the van der Waals distance. On the other side, the atoms Cl(3) and Cl(5) suffer a repulsion by the 6π-bond system of the S_2N_2 ring (formula (B)). The same structural peculiarities were found for the adducts μ-$(S_2N_2)(SbCl_5)_2$ [22] and μ-$(S_2N_2)(AlCl_3)_2$ [23]; we assume the same kind of interactions in these cases.

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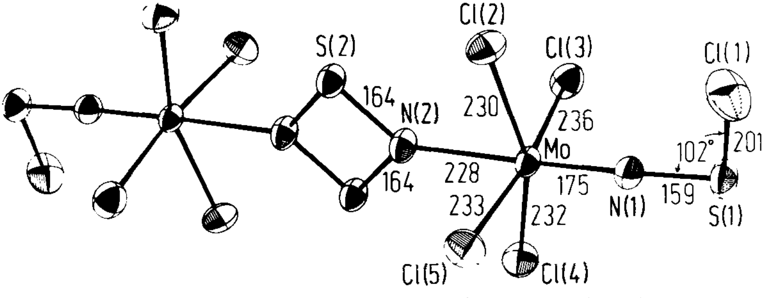
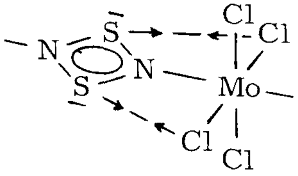
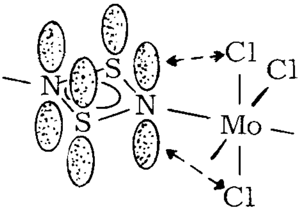


FIGURE 3 Molecular structure of μ-$(N_2S_2)[MoCl_4(NSCl)]_2$.



(A)



(B)

The characteristic geometry of the chlorothionitrene ligand is retained in the anionic complexes. In the case of the $[MoCl_5(NSCl)]^-$ ion[24] (Fig. 4), there is only a slight increase of the S–Cl bond length by 2 pm as compared to the neutral species described above. This increase may be attributed to the negative ionic charge and is smaller than the general increase of bond lengths that is normally observed between a neutral molecule and an anion.

In the case of the $[ReCl_4(NSCl)_2]^-$ ion the lengthening of the S–Cl bonds is more pronounced (mean value 208 pm, Fig. 4).[10,11] In this compound the two chlorothionitrene ligands are arranged in a *cis*-position thus allowing different *d* orbitals of the rhenium atom to be involved in the ReN π-bonds. This is a common observation when two π-bonding ligands are present as, for instance, in $[ReCl_4(NO)_2]^-$.[25] With two chlorothionitrene ligands present, the *trans* effect is less marked, i.e., the two *trans*-Re-Cl bonds are not quite as long as in the complexes with only one ligand; indeed, even the *cis*-Re-Cl bond lengths are about equal, but they may be lengthened due to Cl···H hydrogen bonds present between the atoms Cl(5) and Cl(6) with H atoms of the $AsPh_4^+$ counter ion.[11]

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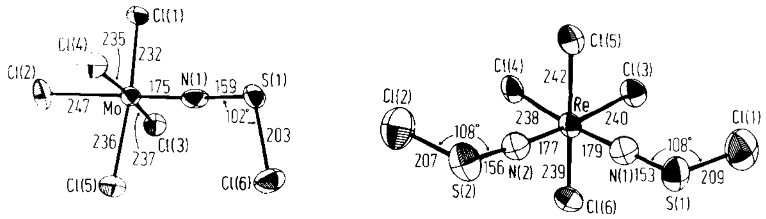

FIGURE 4 Structures of the anions in the compounds $N(SCl)_2^+[MoCl_5(NSCl)]^-$ and $AsPh_4^+[ReCl_4(NSCl)_2]^- \cdot CH_2Cl_2$.

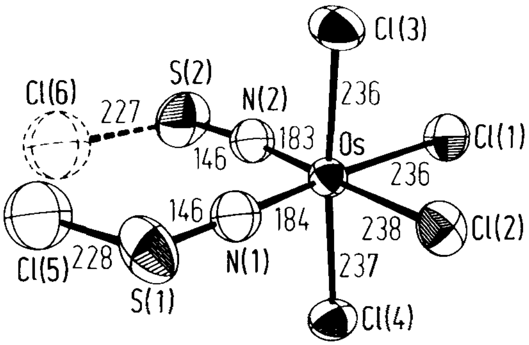

FIGURE 5 Structure of the anion in $\mathrm{AsPh_4^+[OsCl_4(NS)_2Cl]^-}$. The positions Cl(5) and Cl(6) are occupied by one chlorine atom with probabilities of 54% and 46%, respectively. Bond angles Os-N-S: 169.9° and 169.1°.

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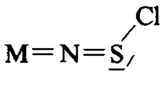
A considerably longer S–Cl bond was found in $\mathrm{[OsCl_4(NS)_2Cl]^-}$, while the NS bonds are somewhat shortened (Fig. 5).[12] In the crystal, the chlorine atom was found to occupy two positions, statistically with site occupation probabilities of about 50%. This may be due to a positional disorder of ions which have one thionitrosyl and one chlorothionitrene ligand; but it is probable that the chlorine fluctuates dynamically between the two positions which are 168 pm apart. This would match the weakness of the S–Cl bonds and the ease with which a $\mathrm{Cl^-}$ ion can be detached. Furthermore, the infrared spectrum can be interpreted better with the dynamical model. Therefore, the compound can also be described as the adduct of a chloride ion with a dithionitrosyl complex.

Infrared Spectra

Of the three stretching vibrations of the



$$\mathrm{M{=}N{=}\underline{S}{}^{\diagup Cl}}$$

group, ν M=N and ν N=S must be strongly coupled with each other due to the linear arrangement of the MNS group, comparable force constants and the low mass of the central atom. On the other hand, the NSCl bond angle of about 105° corresponds approximately to the value of minimum coupling, so that the SCl stretching vibration should be nearly independent of other stretching vibrations (some coupling of ν SCl with δ NSCl may be expected).[26]

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TABLE I

Characteristic infrared absorption frequencies of chlorothionitrene complexes in cm^{-1}

	ν_{as} MNS	ν SCl	ν MCl$_{terminal}$	ν MCl$_2$M	δ NSCl	Ref.
$[MoCl_4(NSCl)]_2$	999	503	385, 358, 330		262	1
$[WCl_4(NSCl)]_2$	1058	508	366	338	271	2
$[MoCl_5(NSCl)]^-$	962	506	348, 341		258	1
$[WCl_5(NSCl)]^-$	958	493	320		268	2
μ-$(N_2S_2)[MoCl_4(NSCl)]_2$	955	492	340, 300			8
μ-$(N_2S_2)[WCl_4(NSCl)]_2$	1068	503	335, 302			8
$[ReCl_3(NSCl)]_2$	1115	475, 452	348, 325	295, 263	245	6
$[ReCl_4(NSCl)_2]^-$	940, 920	431	338, 322, 302			11

All known chlorothionitrene complexes show a strong infrared absorption in the region of 900 to 1100 cm^{-1} which can be assigned to the "antisymmetric" vibration ν_{as} MNS (Table I). It is found at lower frequencies for the molybdenum complexes and at higher frequencies for the tungsten and rhenium compounds. This corresponds to the common experience that 5*d* elements usually perform stronger π-bonds than 4*d* elements.[21] As usual, anionic charge entails lower frequencies. For $[ReCl_4(NSCl)_2]^-$ two ν_{as} ReNS vibrations are observed, as is expected for an ion with C_{2v} symmetry.

The "symmetric" type vibration ν_s MNS usually is of low intensity and cannot be assigned with certainty. There are indications[3] that it is to be found in the region of 500 to 600 cm^{-1}. The SCl stretching vibration is rather invariant, being observed at about 500 cm^{-1}. Only the rhenium compounds show lower values for ν SCl, but this is in accord with the longer SCl bond lengths found in $[ReCl_4(NSCl)_2]^-$. This finding seems to have some implication in the chemistry of chlorothionitrene complexes of rhenium.

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CHLOROTHIONITRENE COMPLEXES AS STARTING MATERIALS IN SYNTHESIS

Some chlorothionitrene complexes have proven to be excellent starting materials for the preparation of nitrido complexes having M≡N triple bonds.[21] Thermolysis of $[MoCl_4(NSCl)]_2$ at 130 °C in vacuo quantitatively yields molybdenum nitride trichloride[1]:

$$[MoCl_4(NSCl)]_2 \xrightarrow{130°C} 2\ MoNCl_3 + 2\ SCl_2 \qquad (17)$$

At 150 °C $[MoNCl_4]_2$ is obtained,[3] a compound having a MoN_2Mo group and which can also be obtained from $MoCl_5$ with iodine azide or nitrogen trichloride[21]:

$$[MoCl_4(NSCl)]_2 \xrightarrow{150°} Cl_4\overset{\ominus}{Mo}{=}\overset{\oplus}{N}{=}\overset{\oplus}{N}{=}\overset{\ominus}{Mo}Cl_4 + S_2Cl_2 \qquad (18)$$

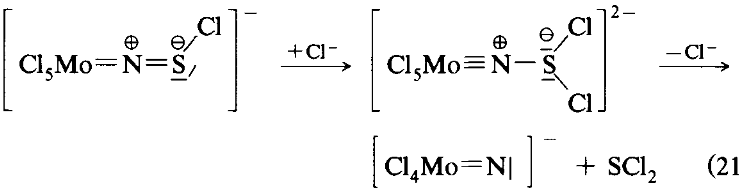
In solution in CH_2Cl_2, $PPh_4[MoCl_5(NSCl)]$ decomposes in the presence of chloride ions with formation of the well-known[21] tetrachloronitridomolybdate:

$$[MoCl_5(NSCl)]^- \xrightarrow{(Cl^-)} [Cl_4Mo{\equiv}N|\ ]^- + SCl_2 \qquad (19)$$

Similarly, $PPh_4[WCl_5(NSCl)]$ is also unstable in solution when chloride ions are present, but a different product is obtained[27]:

$$2\,[WCl_5(NSCl)]^- \xrightarrow{(Cl^-)} [Cl_5W{\equiv}N{-}\overline{\underline{S}}{-}N{\equiv}WCl_5]^{2-} + SCl_2 \quad (20)$$

Bond distances (Fig. 6) in this product correspond approximately to the formulation given in Eq. (20), but there is some delocalization of the π-bonds. The action of the chloride ions in reactions (19) and (20) with the ready formation of SCl_2 indicates an electrophilic character of the sulfur atom in the chlorothionitrene ligand according to the following mechanism:



$$\left[Cl_5Mo{=}\overset{\oplus}{N}{=}\underline{S}\overset{\ominus}{/}Cl\right]^- \xrightarrow{+Cl^-} \left[Cl_5Mo{\equiv}\overset{\oplus}{N}{-}\underset{\textstyle Cl}{\overset{\ominus}{S}}{-}Cl\right]^{2-} \xrightarrow{-Cl^-} \left[Cl_4Mo{=}N|\right]^- + SCl_2 \quad (21)$$

In a similar way the chlorothionitrene complex of rhenium is converted to a nitrido complex[11]:

$$[ReCl_4(NSCl)\cdot OPCl_3] + AsPh_4Cl$$
$$\rightarrow AsPh_4[Cl_4Re\equiv N|] + POCl_3 + SCl_2 \quad (22)$$

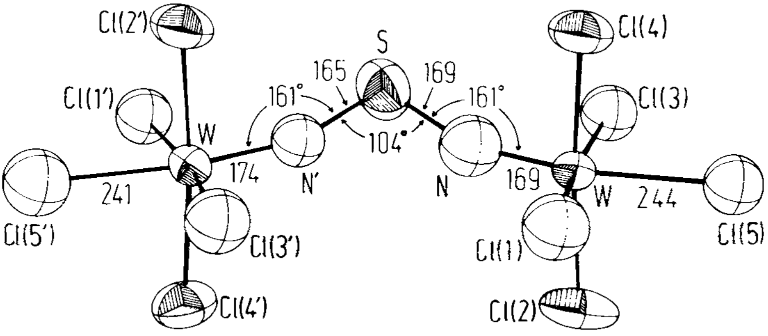


FIGURE 6 Structure of the anion in $PPh_4^+[Cl_5WNSNWCl_5]^-$.

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Nitrido complexes can also be obtained by the action of triphenylphosphane[6]:

$$2[\mathrm{ReCl_4(NSCl)\cdot POCl_3}] + 9\,\mathrm{PPh_3} \rightarrow 2[\mathrm{(Ph_3P)_2Cl_2Re{\equiv}N|}] \\ + 2\,\mathrm{POCl_3} + 2\,\mathrm{PSPh_3} + 3\,\mathrm{PCl_2Ph_3} \qquad (23)$$

This reaction involves reduction of rhenium from +VI to +V. The nitrido complex has been previously synthesized by the reaction of hydrazinium dichloride with sodium perrhenate in the presence of $\mathrm{PPh_3}$ [28]; its structure determination reveals a coordination number of five for the rhenium atom.[29]

When the chlorothionitrene complex of molybdenum is reacted with triphenylphosphane, molybdenum is also reduced from +VI to +V, but the product is a phosphaniminato complex[30]:

$$[\mathrm{MoCl_4(NSCl)}]_2 + 7\,\mathrm{PPh_3} \rightarrow 2[\mathrm{(Ph_3P)Cl_4}\overset{\ominus}{\mathrm{Mo}}{=}\overset{\oplus}{\mathrm{N}}{=}\mathrm{PPh_3}] \\ + 2\,\mathrm{SPPh_3} + \mathrm{Cl_2PPh_3} \qquad (24)$$

The typical atomic grouping $\mathrm{M{=}N{=}PR_3}$ in a phosphaniminato complex is related to that of chlorothionitrene complexes; as in these, usually a linear atom group is found,[21,31] but an example with a bent ReNP group is also known.[32]

Surprising reactions were found to take place between the dichlorothionitrene complexes of rhenium with triphenylphosphane[33] or with $\mathrm{S(NSiMe_3)_2}$ [34]:

$$[\mathrm{ReCl_3(NSCl)_2\cdot OPCl_3}] + \mathrm{PPh_3} \rightarrow [\mathrm{ClPPh_3}]^+ \\ [\mathrm{Cl_4Re(N_2S_2)}]^- + \mathrm{POCl_3} \qquad (25)$$

$$\mathrm{PPh_4}[\mathrm{ReCl_4(NSCl)_2}] + \mathrm{S(NSiMe_3)_2} \rightarrow \mathrm{PPh_4^+}[\mathrm{Cl_4Re(N_2S_2)}]^- \\ + 2\,\mathrm{ClSiMe_3} + \text{unknown products} \qquad (26)$$

The $[\mathrm{Cl_4Re(N_2S_2)}]^-$ ion (Fig. 7) incorporates a new kind of chelate ligand. Its Re–and N–S bond distances again correspond to double bonds, so that the $\mathrm{Re{=}N{=}S}$ groups are of the same kind as in the

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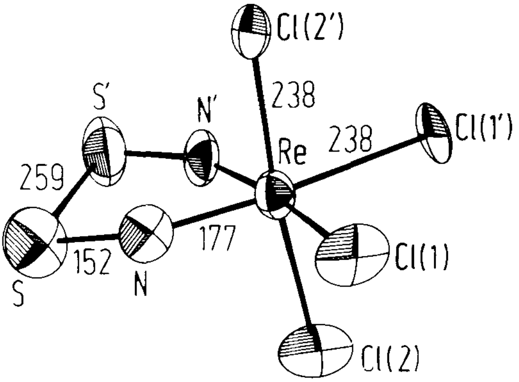

FIGURE 7 Structure of the anion in $AsPh_4[Cl_4Re(N_2S_2)]$. With $PClPh_3^+$ as cation the interatomic distances are S–S 253, S=N 151 and 153, Re=N 180 and 183 pm.

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chlorothionitrene ligand, but the S atoms now are linked with each other. The resulting S–S bond is rather long (255 pm), as this bond has to resist the tension of the bond angles at the Re and N atoms; instead of 90° and 180° for NReN and ReNS, respectively, these angles are forced down to 74° and 145° by the ring closure.

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