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Chlorothionitrene Complexes of Tungsten. Synthesis, Characterization, and Chemical Behavior of Tungsten(VI) Thionitrene Complexes

Jyoti Seth, Minu Gupta, and U. C. Agarwala*
Department of Chemistry, I. I. T., Kanpur, India

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Synopsis. The syntheses of Tungsten(VI) chlorothionitrene complexes have been described and their chemical behavior was studied. The compounds were characterized by microanalyses, vibrational, electronic, ESR, NMR spectral and other Chemical studies.

Although the chemistry of metal nitrosyls has been extensively studied,[1,2] it is only recently that there has been considerable interest in the study of the reactivity of NSCl with various transition metal complexes for the syntheses of thionitrosyls.[3–9] Characterization of its interaction products indicates that S-N species formed from NSCl and bonded to the metal center are quite diverse. Due to this intriguing behavior of thionitrosyl chloride, many investigations have been devoted to study such complexes. In addition, our efforts in recent years have been in a direction to search the possibility of using trimeric thionitrosyl chloride as a thionitrosylating agent for the synthesis of metal thionitrosyls,[3–5,10,11] a field which is still in an embryonic state. While making these efforts, the reactions of $(NSCl)_3$ with substituted tungsten(II) carbonyl complexes having 2,2′-bipyridine or 1,10-phenanthroline as coligand afforded complexes in which NSCl is bonded to W(VI) in the form of chlorothionitrene group $\mathrm{M{=}N{=}S}\diagdown_{\mathrm{Cl}}$, a bonding mode which has been fairly studied. This paper focuses on the detailed syntheses and characterization of these componds.

Experimental

Materials and Methods. All the chemicals used were of reagent or AnalaR grade. Tungsten hexacarbonyl, tungsten hexachloride, 2,2′-bipyridine and 1,10-phenanthroline, and Sephadex LH-20 resin were purchased from the Aldrich Chemical Company and were used as such. The starting materials $[W(CO)_3(L\text{-}L)X_2]$ (L-L=bpy or *o*-phen; X=Br or I), $[W(NSCl)Cl_4]_2$ and trimeric thionitrosyl chloride were prepared by the literature methods.[12–14] Solvents were purified and dried by standard methods.[15] and degassed prior to use. All experiments were performed under nitrogen atmosphere. Details of the physicochemical methods are given elsewhere.[16]

Preparations. (A) Reaction Medium-Dichloromethane. (a) Reaction of $(NSCl)_3$ with $[W(CO)_3(L\text{-}L)X_2]$ (L-L=bpy or *o*-phen; X=Br or I). A solution of $(NSCl)_3$ (ca. 0.03 mmol) in 10 ml of dichloromethane was added to a stirred solution of $[W(CO)_3(L\text{-}L)X_2]$ (ca. 0.1 mmol) in 15 ml of dichloromethane. After the mixture was stirred for approximately 1 h and gas evolution had ceased, the resulting solution was concentrated under reduced pressure to about 5 ml. The product (I) was precipitated from the concentrate with light petroleum ether, which was filtered and washed with a little of benzene and then with copious amounts of petroleum ether. The product was recrystallized from dichloromethane-petroleum ether. The recrystallized product was further purified by column chromatography using Sephadex LH-20 column (25 cm×2.5 cm) and 1 : 1 mixture of dichloromethane and chloroform as the eluent (elution rate, approximately 1—2 ml min^{-1}). A broad brown band formed on the column top was eluted by CH_2Cl_2 and the eluent was concentrated under reduced pressure to about 5 ml and kept at 0 °C for a few days for crystallization. Thereby microcrystals (II) were deposited on the sides of the flask. These were collected washed with a little benzene, petroleum ether, dried under vacuum. The same compound was also obtained by precipitating it from the concentrated eluent with light petroleum ether and drying it under vacuum (yield 50%). The compounds I and II were found to be identical as has been found from chemical analysis, mp, mixed mp, IR and UV-visible spectral data. The compound has the formulation $[W(NSCl)Cl_3X'\ (L\text{-}L)]$ (X′=Cl or Br).

(b) (Reactions of 2,2′-Bipyridine and 1,10-Phenanthroline with $[W(NSCl)Cl_4]_2$. A stoichiometric amount of bpy or *o*-phen was added to a stirred suspension of $[W(NSCl)Cl_4]_2$ (ca. 0.1 mmol) in 25 ml of dichloromethane and stirring was continued for 1 h when the solution attained brown color. It was filtered and the filtrate was concentrated under reduced pressure. The concentrate was processed as described in A(a) (yield 60%).

(B) Reaction Medium-Tetrahydrofuran. The reactions were carried out by the same procedure as described in A(a) and A(b) except that tetrahydrofuran was used as the reaction medium in the place of dichloromethane. The working up of the reaction product, recrystallization of the compounds and their purification by column chromatography were done as described in (A).†

(C) Thermolysis of $[W(NSCl)Cl_3X'\ (L\text{-}L)]$ (L-L=bpy or *o*-phen; X′=Cl or Br). Thermolysis of $[W(NSCl)Cl_3X'(L\text{-}L)]$ (exactly weighed) was carried out at about 250 °C for 4 h in a two necked flask having an inlet and outlet tube. Through the inlet tube a slow stream of nitrogen gas was allowed to pass slowly, while the gaseous products coming out of the outlet tube were bubbled into water. The hydrolyzed products were then analyzed for sulfur and chloride ion. The compound after thermolysis changed to pinkish grey color and was analyzed for $[WNCl_2X'\ (L\text{-}L)]_n$ (III).

In another experiment, the known weight of $[W(NSCl)Cl_3X'\ (L\text{-}L)]$ was heated at 250 °C for 4 h over a watch glass. After cooling the change in weight was recorded. The loss in weight of the complex corresponded approximately to one mole of SCl_2 per mole of the complex.

Results and Discussion

The reactions of trimeric thionitrosyl chloride with $[W(CO)_3(L\text{-}L)X_2]$ yielded the novel compounds of empirical formula $[W(NSCl)Cl_3X'(L\text{-}L)]$ (**1**) (cf. Table 1). Apart from being a ligand linked to the metal ion as $(NSCl)^{-2}$, the trimeric thionitrosyl chloride oxidizes tungsten from II to VI oxidation state. In

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† In THF, compounds became oily during recrystallization process.

Table 1. Color, Mp,[a] Microanalysis, Thermolysis, and UV-Visible Data of Complexes

Sample No.	Compound	Color[b]	Elemental analysis in % Exptl (Calcd)					Thermolysis % loss Exptl (Calcd)			UV-visible data λ_{max}/nm
			C	H	N	S	X	% loss in wt.	% S	% Cl	
1	[W(NSCl)Cl_4 bipy]	GR	21.6	1.8	7.2	5.9	30.9	19.4	5.2	13.2	250, 310, 380, 475, 510
			(21.2)	(1.4)	(7.4)	(5.7)	(31.4)	(18.2)	(5.7)	(12.6)	
2	[W(NSCl)Cl_3Br bipy]	O	19.2	1.9	6.4	5.6	36.1	18.2	5.0	13.0	255, 320, 375, 480, 515
			(19.7)	(1.3)	(6.9)	(5.2)	(36.4)	(16.9)	(5.2)	(11.6)	
3	[W(NSCl)Cl_4 *o*-phen]	YB	24.7	1.4	6.8	5.1	29.8	18.9	5.0	12.5	250, 315, 380, 475, 510
			(24.5)	(1.3)	(7.1)	(5.4)	(30.1)	(17.5)	(5.4)	(12.0)	
4	[W(NSCl)Cl_3Br *o*-phen]	B	22.4	1.7	6.3	4.9	34.8	17.8	4.2	12.0	248, 320, 375, 475, 520
			(22.7)	(1.2)	(6.6)	(5.0)	(35.0)	(16.3)	(5.0)	(11.2)	
5	[W(NSCl)Cl_4 bipy]·THF	RB	26.9	2.8	6.2	4.8	27.2	28.2	4.0	11.8	250, 310, 380, 485, 515
			(26.4)	(2.5)	(6.6)	(5.0)	(27.8)	(27.5)	(5.0)	(11.1)	
6	[W(NSCl)Cl_3Br bipy]·THF	OY	24.2	3.1	6.0	5.0	32.2	26.3	4.1	11.4	250, 315, 375, 480, 520
			(24.6)	(2.3)	(6.2)	(4.7)	(32.6)	(25.7)	(4.7)	(10.4)	
7	[W(NSCl)Cl_4 *o*-phen]·THF	Y	28.9	2.1	6.5	5.1	26.4	28.0	4.2	11.2	255, 310, 380, 475, 510
			(29.1)	(2.4)	(6.3)	(4.8)	(26.8)	(26.5)	(4.8)	(10.7)	
8	[W(NSCl)Cl_3Br *o*-phen]·THF	B	26.9	2.8	6.2	4.2	31.1	26.1	3.5	11.0	250, 320, 375, 480, 520
			(27.2)	(2.3)	(5.9)	(4.5)	(31.5)	(24.8)	(4.5)	(10.1)	

a) All the compounds decomposed around 230 °C. b) GR=greenish red, O=orange, YB=yellow brown, B=brown, RB=reddish brown, OY=orangish yellow, Y=yellow.

Table 2. IR Spectra of Representative Complexes[a]

[W(NSCl)Cl_3X′(L-L)]		[WNCl_2X′(L-L)]	
910 (m)		999 (VS)	
940 (m)	ν_{as} (WNS)	900 (m)	ν_{as} (W≡N)
970 (m)			
500 (w)	ν (SCl)	450 (s)	
430 (w)	ν_S (WNS)		
340 (s)		370 (m)	ν (WCl)
320 (m)	ν (WCl)	340 (m)	
270 (w)	δ (NSCl)		

a) IR bands due to coordinated 2,2′-bipyridine and 1,10-phenanthroline were observed in the expected region.

iodo complexes, both the iodide ions and in bromo ones only one bromide ion were substituted by the chloride ions in their respective products. The approximate amount of liberated iodine during the reaction was iodometrically estimated which conformed to two moles of iodide ions per mole of the complex.

The compounds are soluble in halo-substituted solvents and decompose in methanol to yield polymeric nitrido compound of empirical formula [W_2N(L-L)-S_2Cl_5] as suggested by analytical and IR data. These when solubilized in $POCl_3$ yielded the moisture sensitive adduct [W(NSCl)Cl_3X′ (L-L)]·$POCl_3$ similar to the behavior of [W(NSCl)Cl_4]$_2$.

The compounds in general were preserved at low temperature (0 °C) as they undergo slow decomposition at room temperature yielding a pinkish grey compound. This was further corroborated by the results of the thermolysis experiments (vide infra). The gaseous products obtained by pyrolyzing the compound were hydrolyzed by bubbling in water and the halogen and sulfur contents were estimated. The results corresponded to the loss of a molecule of SCl_2 per molecule of the compound, as also suggested by the loss of weight of the compound after thermolysis. It appears that the complexes lose a molecule of SCl yielding pink nitrido complexes from which another chloride ion could be lost to preserve the charge balance similar to the earlier reported $\mathrm{M{=}N{=}S}\diagdown_{\mathrm{Cl}}$ complexes.[6)] These may further be reduced partially to other polymeric tungsten nitrides in +V oxidation state.

The infrared spectra of all the compounds showed three medium to intense bands in the region 1000—900 cm^{-1} assignable to the stretching modes of M=N=S moiety.[6,14,17,18)] The bonding mode of NSCl moiety is further corroborated by the following chemical evidence.

The coordinatively unsaturated compound [W(NSCl)-Cl_4]$_2$ had been shown to have $[\mathrm{W{=}N{=}S}\diagdown_{\mathrm{Cl}}]$ unit by X-ray crystal structure studies. The reaction of this compound with bpy or *o*-phen yielded compounds of the type [W(NSCl)Cl_4(L-L)] which were found to be identical to the compounds synthesized by the procedure A(a). The identical nature of these complexes, as also shown by X-ray powder patterns, gives one sufficient reason to believe that the (NSCl) moiety in our compounds have a $[\mathrm{M{=}N{=}S}\diagdown_{\mathrm{Cl}}]$ type of bonding, assuming reactions of bpy or *o*-phen do not affect the bonding mode of (NSCl).[19)] Further the bands due to ν(WNS) of [W(NSCl)Cl_3X′ (L-L)] disappeared in the vibrational spectra of the pinkish grey thermolysis product and an intense band appeared at 990 cm^{-1}, assigned to ν(W≡N).[20,21)] The shift of ν(W≡N) band position to lower wave numbers compared to that of W(VI) nitrido compounds (viz. 1040 cm^{-1}) could be attributed to the partial reduction of W(VI) to W(V)[20,21)] (vide infra). The assignments of bands due to lack of crystal structure are somewhat tentative and additional studies are required to confirm their identity.

The electronic spectral features of the compounds are given in Table 1. The spectra showed a band at around 250 nm, assigned to $\pi(X)\rightarrow d\pi(W(VI))$ charge transfer transition.[23] The band at around 500 nm was found to be split in general and one of its components along with 380 nm band could be attributed to the π(bpy or *o*-phen)$\rightarrow d\pi(W(VI))$ charge transfer transition. Preliminary solvent dependent studeis indicated the solvatochromism[23,24] associated with one of the components of the band at around 500 nm and this was utilized as a criterion for differentiating the charge transfer band. Its other component may possibly arise due to intraligand transition involving $=\mathrm{N}=\mathrm{S}\diagdown_{\mathrm{Cl}}$ moiety or due to charge transfer transition of the $[\mathrm{M}=\mathrm{N}=\mathrm{S}\diagdown_{\mathrm{Cl}}]$ unit. All the compounds were found to be diamagnetic and their ESR spectra were recorded, wherein no signal was obtained. This indicates the presence of tungsten in VI oxidation state, substantiating further the linkage of NSCl as $\mathrm{M}=\mathrm{N}=\mathrm{S}\diagdown_{\mathrm{Cl}}$.

In the compounds preparted in tetrahydrofuran the solvated formulation viz. $[\mathrm{W(NSCl)Cl_3X'(L\text{-}L)}]\cdot$THF could be preferred over the coordinated one based on the following observations.

(i) The NMR spectra showed practically no shift in the resonances of the THF protons as compared to that of the free THF molecule.

(ii) The color and the mp's of the compounds were almost similar to those of the compounds prepared in dichloromethane.

(iii) The compounds were analyzed to $[\mathrm{W(NSCl)Cl_4(L\text{-}L)}]\cdot$THF. The efforts to remove the solvated THF completely by different means were unsuccessful.

On the basis of the foregoing discussions the compounds were assigned the heptacoordinate structure $[\mathrm{W(NSCl)Cl_3X'(L\text{-}L)}]$ with the metal ion in VI oxidation state. Although seven coordination is commonly not encountered in compounds of tungsten in higher oxidation states, it is however not unlikely.[25]

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