

## Synthesis and Characterization of some Monomeric Niobium(III) Complexes

M. E. CLAY and T. M. BROWN\*

Department of Chemistry, Bateman Science Center, Arizona State University, Tempe, Ariz. 85287, U.S.A.

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The reaction of  $Nb_2Cl_6 \cdot 3$ -tetrahydrothiophene with pyridine and substituted pyridines of increased basicity has been investigated. New niobium(III) monomers of the type  $NbCl_3L_3$  where  $L$  = pyridine, 4-methylpyridine and 3,5-dimethylpyridine have been isolated in good yields. All these compounds were characterized by elemental analysis, infrared spectroscopy, magnetic susceptibility and electron paramagnetic resonance. The monomers have been substituted with thiocyanate and dialkyldithiocarbamate ligands.

### Introduction

Monomeric halide complexes of niobium are numerous in the plus four and plus five oxidation state. However, except for the organometallic derivatives of niobocene [1], there are no reported non-polymeric niobium(III) halides. The reduction of higher oxidation state niobium halides with various reducing agents such as sodium amalgam [2], magnesium [3, 4] and diborane [5] in the presence of neutral donor ligands produced dimeric complexes having the formulation  $Nb_2Cl_6L_3$  or  $Nb_2Cl_6L_4$  where  $L$  represents an oxygen, nitrogen, phosphorus or sulfur ligand. The substitution of the above mentioned dimers with other monodentate ( $L$ ) or bidentate ( $B$ ) ligands usually gives rise to complexes of the type  $Nb_2Cl_6L_4$  or  $Nb_2Cl_6B_2$  in which two octahedra share a common edge [5, 6].

We now wish to report the reaction between  $Nb_2Cl_6 \cdot 3$ -tetrahydrothiophene and pyridine and substituted pyridines more basic than pyridine such as 4-methylpyridine and 3,5-dimethylpyridine. These pyridines split the niobium dimer and result in the formation of the only known niobium(III) halide adducts  $NbCl_3L_3$ . The characterization of these new compounds is described as well as their potential use for the preparation of additional niobium(III) monomeric compounds.

\*Author to whom correspondence should be addressed.

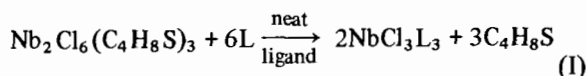
TABLE I. Magnetic Properties of the Pyridine Complexes.

	Temp. K	$10^6 \chi_m$ emu/mol	$10^6 \chi_m'^a$ emu/mol	$\mu_{\text{eff}}$ B.M.
$NbCl_3(PY)_3$	175	3330	3570	2.24
	142	4250	4500	2.27
	96.2	6680	6920	2.32
	80.2	7850	8100	2.29
$NbCl_3(PIC)_3$	296	1440	1730	2.03
	291	1540	1830	2.07
	246	1720	2010	2.00
	166	2580	2870	1.96
	98.1	4340	4630	1.91
	76.1	5390	5680	1.87
$Ta_2Cl_6(PY)_4$	290	-184	215	0.71

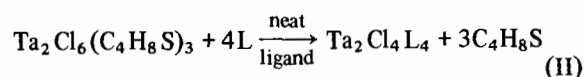
$$^a \chi_m' = \chi_m - \chi_D$$

### Results and Discussion

Monomeric niobium(III) compounds were prepared according to reaction scheme I.



$L$  = pyridine, 4-methylpyridine, 3,5-dimethylpyridine whereas the analogous tantalum dimeric unit of the parent complex remained intact and products as shown in reaction scheme II were obtained.



All of the resulting compounds are extremely sensitive to oxygen and water which accounts for the difficulty in obtaining good analyses on all of the compounds. They do, however, appear to be stable indefinitely when stored in a vacuum.

The infrared spectra of the compounds are normal for coordination compounds of pyridine and methyl substituted pyridines. In every case, the spectra were

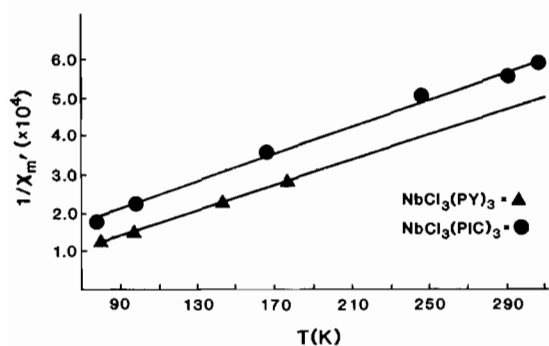


Fig. 1.  $1/\chi_{\text{corr}}$  vs. Temperature for two of the Niobium(III) monomers.

free from evidence of oxygen or tetrahydrothiophene impurities.

Both the magnetic susceptibility data and the EPR results indicate the presence of niobium monomers. Magnetic moments for the niobium(III) complexes and the tantalum-pyridine dimer are given in Table I. The niobium(III) complexes are temperature dependent and follow Curie-Weiss behavior with values of  $\theta$  at 7.81 °K and -23.8 °K for the pyridine and the 4-methylpyridine complex, respectively. The value of  $\mu_{\text{eff}}$  (obtained from the slopes of the plots of  $1/\chi_{\text{m}}$  vs. temperature in Fig. 1) for the niobium compounds are indicative of magnetically dilute  $d^2$  ions with a small degree of spin-orbit coupling. By contrast, the tantalum complex was found to be only slightly paramagnetic and temperature independent. This result is indicative of a strongly metal-metal bonded dimeric complex, so that the original dimeric unit in the parent complex is maintained throughout ligand substitution.

EPR spectra were taken at ambient temperatures for solutions of the pyridine and 4-picoline complexes. These spectra are illustrated in Fig. 2. The values of  $A$  are 179.4 G and 179.1 G for the pyridine and 4-picoline complexes respectively, while  $g$  is 2.05 for the former and 2.04 for the latter. Both monomers gave well resolved spectra which are lacking any indications of strong metal-metal interactions. The number of peaks observed is that expected for a niobium monomer ( $2nI + 1 = 10$ ) where  $n = 1$  and  $I$  is the nuclear spin of  $9/2$  for niobium. The spectra of the pyridine and 4-picoline complexes are very similar and a plot of  $\delta H_{\text{mI}}$  vs.  $(2m_I - 1)$  is linear indicating that second order shifts in the observed  $H$  values of the hyperfine lines are present. Furthermore, the peak intensity ratio of the niobium(III) halide complexes clearly show a distortion from octahedral symmetry. This result is, of course, expected for a six-coordinate complex with two different ligands and a  $d^2$  configuration. The tantalum(III) dimer being essentially dia-

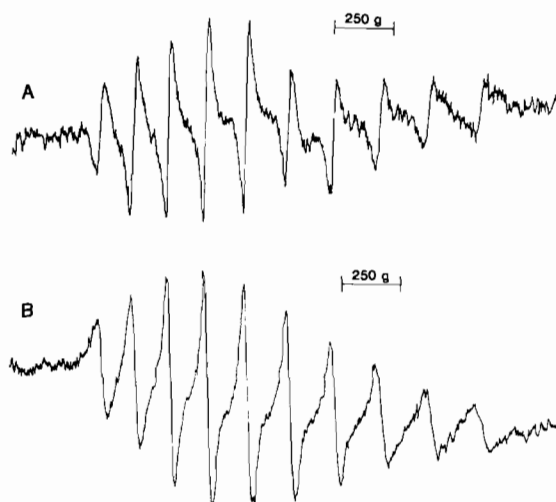
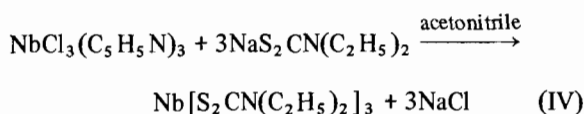
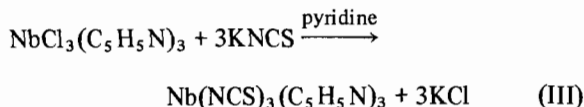


Fig. 2. EPR spectrum of A)  $\text{NbCl}_3(\text{pyridine})_3$  and B)  $\text{NbCl}_3(4\text{-picoline})_3$ .

magnetic, gave no EPR signals even at the highest instrument sensitivities.

The utility of using the niobium monomers as starting materials for the preparation of other niobium(III) compounds is shown in reaction schemes III and IV.



The thiocyanate ion proved to be capable of replacing the chloride ions in the pyridine complex with the retention of the pyridine ligands. The dark green complex which resulted from this reaction was observed to be somewhat more stable than the chloride complex. In the case of the dithiocarbamate, complete substitution of chloride and pyridine occurred. Substitution with other ligands is currently being investigated.

### Experimental

General vacuum line techniques were employed in conjunction with inert atmosphere glove boxes. The Nb(III) compounds were prepared and handled under vacuum when possible since they were extremely sensitive to decomposition upon exposure to even minute amounts of air or water.  $\text{Nb}_2\text{Cl}_6(\text{C}_4\text{H}_8\text{S})_3$  was prepared by methods described elsewhere [1]. The pyridines were all purified by standard

Compound		C	H	N	Cl	Color
NbCl <sub>3</sub> PY <sub>3</sub>	Calc.	41.26	3.47	9.63	24.36	red
	Found	40.90	3.59	9.40	24.01	
NbCl <sub>3</sub> PIC <sub>3</sub>	Calc.	45.16	4.43	8.78	22.22	red
	Found	45.04	4.65	8.68	22.00	
NbCl <sub>3</sub> LUT <sub>3</sub>	Calc.	48.43	5.24	8.07	—	red-orange
	Found	46.66	5.09	7.68	—	

distillation methods before being distilled under a vacuum onto CaH<sub>2</sub> for storage.

IR spectra were obtained with a Beckman IR 12 spectrophotometer as nujol or fluorolube mulls between NaCl and Teflon plates.

Magnetic susceptibility measurements were obtained using the Faraday method. Hg[Co(NCS)<sub>4</sub>] was used as a calibrant along with a standard Pt weight.

EPR spectra were collected on an X-band reflection spectrometer with a Varian V-4531 microwave cavity and first-derivative signal detection. The magnetic field was calibrated using Fremy's salt and g-factors were standardized with a pure lithium standard. A modulation frequency of 100 KHz and a microwave frequency of 9.063 GHz were used during the experiments.

Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee.

#### Preparation of Niobium(III) Compounds

In a typical reaction, one-half gram of the dimer Nb<sub>2</sub>Cl<sub>6</sub>(C<sub>4</sub>H<sub>8</sub>S)<sub>3</sub> was added to a reaction flask which was then evacuated. Approximately 30 ml of the appropriate pyridine ligand was then distilled onto the niobium complex and the reaction mixture was allowed to stir at 60 °C for 24 hours. The excess ligand was removed under a vacuum and the product was kept under a dynamic vacuum for 48 hours at 60 °C to insure complete removal of excess solvent. Using the same procedure, the compounds in the above table were prepared using pyridine (PY), 4-methylpyridine (PIC) and 3,5-dimethylpyridine (LUT).

#### Attempted Preparation of TaCl<sub>3</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>3</sub>

Using the procedures for the preparation of the Nb(III) monomers, the corresponding Ta(III)-tetrahydrothiophene dimer was refluxed in the various pyridines. In all cases, *no* tantalum monomers were obtained and the only compounds formed were those having the composition Ta<sub>2</sub>Cl<sub>6</sub>L<sub>4</sub> with the dimeric unit intact.

#### Reaction of NbCl<sub>3</sub>L<sub>3</sub> with NCS<sup>-</sup> and S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

The various niobium monomers were reacted with KNCS and NaS<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in stoichiometric amounts in CH<sub>3</sub>CN. Compounds approximating the formulation Nb(NCS)<sub>3</sub>L<sub>3</sub> and Nb[S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub> were obtained. Difficulties were encountered due to interaction with the solvent. In nonpolar solvents the monomeric complexes redimerize in the presence of dithiocarbamates to give Nb<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>6</sub>.

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