Inorganica Chimica Acta, 41 (1980) 283–286

Synthesis and Characterisation of Niobium(III) Trichloride Ether and Sulfide Derivatives

L. G. HUBERT-PFALZGRAF, M. TSUNODA and J. G. RIESS

Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au C.N.R.S., Parc Valrose, 06034 Nice, France

Received February 11, 1980

The reduction of niobium(V) chloride by magnesium in CH_2Cl_2 and in the presence of various ethers and sulfides has been investigated. New niobium(III) species – molecular: Nb_2Cl_6(p-dioxane)$_2$, $[NbCl_2(OC_6H_4CHO)(THF)_2]_2$ and '$Nb_2Cl_6(THF)_4$'; and cluster: $Nb_3Cl_8(SMe_2)_2(Et_2O)$ – have been isolated in good yields. The access to a previously reported niobium(III) molecular compound, $Nb_2Cl_6(SMe_2)_3$, has been improved. All these compounds were characterized by elemental analysis, infrared and proton NMR spectroscopy. Dimeric species, with formally a double bond between the metallic centers, account for the diamagnetism of all the molecular compounds.

Introduction

We recently reported a convenient one-step synthesis of $Nb_2Cl_6(PhPMe_2)_4$, a niobium(III) starting material, by reduction of Nb_2Cl_{10} by magnesium in the presence of the phosphorus ligand [1]. In view of the scarcity of non-polymeric, soluble – *i.e.* molecular – niobium(III) halide complexes, these results have stimulated further studies on the reduction of niobium pentachloride by magnesium in various complexing media. These media: ethers (tetrahydrofurane, diethylether, 1,4-dioxane), sulfides (dimethylsulfide) or amines (triethylamine) were chosen with the aim of obtaining niobium derivatives which could constitute convenient starting materials for developing the molecular chemistry of niobium in oxidation state III. We now wish to report the synthesis and characterisation of several new niobium(III) derivatives: $[NbCl_3(p\text{-dioxane})]_2$, $[NbCl_2(OC_6H_4CHO)(THF)_2]_2$, $Nb_3Cl_8(SMe_2)_2(Et_2O)$ and '$Nb_2Cl_6(THF)_4$'. Furthermore we have been able to step up to a yield of 65% the preparation of $Nb_2Cl_6(SMe_2)_3$, previously obtained from $[Nb_2Cl_{10}]_2$ by a two-step reduction procedure in only 28% [2].

Results and Discussion

The reactions were first attempted in conditions similar to those applied to the synthesis of $Nb_2Cl_6(PhPMe_2)_4$: excess of Mg turnings, ligand to niobium molecular ratio of 4:1 and dichloromethane as the solvent; however, it soon appeared that the reaction conditions had to be adjusted precisely for each ligand. So with 1,4-dioxane we were able to isolate $Nb_2Cl_6(p\text{-dioxane})_2$ in 45% yield. The decrease in yield as compared with that obtained in the preparation of $Nb_2Cl_6(PhPMe_2)_4$ is mainly due to the formation, during the progress of the reaction, of some oxoniobium derivatives which were not reduced but were eliminated along with the insoluble magnesium derivatives.

When tetrahydrofurane was used as a ligand, the reduction occurred very quickly (1 h) and was highly exothermic. The separation of the magnesium byproducts was less easy, but a black, slightly paramagnetic product, whose analysis corresponds to the expected $NbCl_3(C_4H_8O)_2$ formula was nevertheless isolated when the reaction mixture was worked up rapidly. Longer reaction times generally resulted in an ill-defined, but soluble, black compound containing both niobium and magnesium, which has the empirical formula $[(C_4H_8O)_4Nb_2Cl_6Mg]$. The IR data of $NbCl_3(C_4H_8O)_2$ show that the coordination sphere contains not only THF, but also small amounts (5–15%) of unsaturated alcohols (C_4H_7OH), as evidenced by the presence of ν(OH) and ν(C=C) stretching absorptions at 3400, 1640 and 1620 cm^{-1} respectively. These alcohols result from the opening of the tetrahydrofurane. Similar degradations of THF were also observed for the $MoCl_5$–Mg–THF system [3]. Our various attempts to avoid these side reactions (reduction of the temperature (–40 °C) or of the THF/Nb ratio, dilution *etc.*) succeeded only in limiting their extent. The use of zinc turnings instead of magnesium turnings only increased the difficulties in the separation of the by-products. The reduction of $NbCl_4(THF)_2$ by magnesium turnings in CH_2Cl_2 produced a similar mixed THF/alcohol Nb(III) compound. Finally, the use of de-activated Mg turnings (by partial air oxidation) gave the product having the lowest alcohol content ($\simeq 5\%$).

The alcoholic ligands could be displaced by adding an excess of salicylaldehyde to the reaction medium containing '$NbCl_3(C_4H_8O)_2$', which then allowed the isolation of the substitution product $[NbCl_2(OC_6H_4CHO)\cdot(THF)_2]_2$ in good yield (75%).

The evaluation of numerous complexing media showed that, in the presence of some ligands, magnesium was unable to reduce $NbCl_5$, even over long reaction periods (≃ 1 month). This was the case, for instance, with dimethylsulfide, and the addition of a catalytic amount of iodine [4] remained without effect on the reaction. On the other hand, the addition of THF, in a THF:niobium molar ratio of 4:1, induced the reduction, as evidenced by changes in the coloration and formation of the $MgCl_2$ by-products. However, the competition between the initial ligand and the unsaturated alcohols due to the degradation of THF resulted in difficulties in obtaining a pure product. Better results could be obtained by the use of the less basic diethylether to induce the reductions. Even then degradation to alcohols also occurred sometimes, but pure products could be obtained by a subtle control of the Et_2O:Nb molar ratio. The addition of diethylether, in a Et_2O:Nb ratio of 5:1, resulted in a slow reduction, which led to a blue compound, $Nb_3Cl_8(Me_2S)_2(Et_2O)$, isolated in 50% yield; on the other hand, when the Et_2O:Nb molar ratio was increased to 8:1, the reduction became faster and the violet compound $Nb_2Cl_6(SMe_2)_3$ could be isolated in 65% yield.

Our attempts to obtain molecular adducts of niobium(III) halides with nitrogen donors (acetonitrile, NMe_3, *etc.*) in a similar way generally failed, as a result of the degradation of the donors. No defined niobium derivatives could be isolated, as the organic products formed (diamino-olefines, and diimines in the case of acetonitrile [5]; primary and secondary amines [6] in the case of NMe_3) led to the formation of complex mixtures of polymeric niobium derivatives.

The new products are all highly air-sensitive, especially in solution. They were characterised by elemental analysis, IR spectroscopy and magnetic susceptibility measurements in the solid state, and by ^1H NMR and molecular weight determinations in solution (Table I). The solubility of all the freshly prepared compounds (except for $Nb_3Cl_8(SMe_2)_2(Et_2O)$) indicates their molecular nature.

The observation of well-resolved NMR spectra suggests their diamagnetic nature, which was confirmed by magnetic measurements in the solid state. This implies strong metal–metal interactions in species that are at least dimeric. The dimeric nature of the compounds was further established by osmometric measurements in the case of $[NbCl_3(p\text{-dioxane})]_2$ (*M*, calcd. 575, found 640 in $CHCl_3$) and $[NbCl_2(OC_6H_4CHO)(THF)_2]_2$ (*M* calcd. 858, found 843 in THF).

The absence in the IR of $Nb_2Cl_6(p\text{-dioxane})_2$ of a $\nu(COC)$ stretching at 1120 cm^{-1} would be in agreement with a bidentate or bridging character of the ether, as found for instance for $[TiX_4\cdot C_4H_8O_2]_m$ [7]. It seems likely therefore that this product, which is also less soluble than the other Nb(III) derivatives, would be better formulated as $Nb_2Cl_6(\mu\text{-dioxane})_2$ in the solid state. However, the NMR data in CD_3CN solutions show only one type of proton, even at −40 °C, but they are only slightly downfield-shifted with respect to the free ligand ($\Delta\delta$ = 0.12 ppm). As dissociation reactions cannot be completely excluded, the characterisation of $Nb_2Cl_6(\mu\text{-dioxane})_2$ in solution was achieved by an exchange between dioxane and phenyldimethylphosphane, which led to the NMR pattern characteristic of $Nb_2Cl_6(PhPMe_2)_4$ [1].

The coordination of salicylaldehyde through its carbonyl group in $[NbCl_2(OC_6H_4CHO)(THF)_2]_2$ is evidenced by the lowering of the $\nu(CO)$ stretching frequency by 40 cm^{-1} [8]. The coordination of additional tetrahydrofurane molecules was confirmed by the presence of THF resonances in the NMR spectra. The two THF ligands appear equivalent down to −40 °C.

The spectroscopic data of $Nb_2Cl_6(SMe_2)_3$ are in agreement with those previously reported by Naito [2]. In the NMR, the dimethylsulfide ligands are inequivalent and in a 2:1 ratio, the bridging ligand being downfield-shifted. In fresh acetonitrile solutions the signals are strongly shifted to higher fields; moreover the compound is rapidly oxidized, within *ca.* 2 hrs, to give the green $Nb_2Cl_6(C_6H_4N_2)(MeCN)_2$ adduct [5, 9], which was isolated and identified by IR.

Access to molecular tantalum(III) derivatives by similar routes is currently being investigated.

Experimental

All handling was done under dry argon using Schlenk tubes or vacuum line techniques. Solvents were purified by standard methods and carefully deoxygenated by purging with argon for several hours. Niobium pentachloride was prepared by chlorination of the metal (gift from Produits Chimiques Ugine Kuhlmann). Magnesium turnings were a commercial product (Prolabo). Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 577 spectrometer. NMR spectra were recorded on a Bruker WH-90 spectrometer operating in the Fourier transform mode. Molecular weight data were obtained on a Knauer vapor pressure osmometer. Magnetic suceptibility measurements were obtained on the solid state by the Faraday method using a Drush magnet and a Cahn electrobalance. The elemental analyses were performed by the Centre de Microanalyse of the C.N.R.S..

TABLE I. Analytical and Spectroscopic Data.[a]

Compound	Analysis % Found (Calcd.)				IR (Nujol mulls) (cm^{-1})		^{1}H NMR (25 °C) δ in ppm (solvent)
	C	H	Cl	S	ν(Nb–Cl)^c ν(Nb–L)^c	Main Ligand Vibrations (L = ligand)	
$Nb_2Cl_6(C_4H_8O_2)_2$	16.00 (16.69)	2.80 (2.80)	36.58 (37.04)		360sh, 330s, 310sh, 285sh, 240s	1095, 1060, 1048, 1015 (ν(C–O–C))	3.68 (CD_3CN; –40 °C)
'$NbCl_3(C_4H_8O)_2$'	27.86 (27.93)	4.60 (4.69)	27.91 (30.98)		380sh, 305sh, 284s, 270s, 262s	3400 ν(OH); 1640, 1620 ν(C=C); 1092, 1020 ν(C–O–C); 913, 800	1.84, 3.68 (CD_2Cl_2)
$Nb_3Cl_8(SMe_2)_2(Et_2O)$	11.82 (12.61)	2.61 (2.91)	37.80 (37.32)	8.52 (8.40)	340s, 300sh	1040, 975, 950 ν(C–O–C) 815	Decomposition or insoluble
$Nb_2Cl_6(SMe_2)_3$	12.15 (13.30)	3.07 (3.10)	36.71 (36.42)	15.60 (16.41)	355sh, 340s, 322s 318sh, 285m, 238m, 220m	1035, 1020; 980, 975, 685 675 ν(C–S)	2.62, 3.34 (2:1) ($CDCl_3$) 2.08, 2.78 (2:1) (CD_3CN^b)
$\{NbCl_2(OC_6H_4CHO)(THF)_2\}_2$	42.04 (41.93)	5.01 (4.93)	17.64 (16.55)		380sh, 360sh, 320s	1620 ν(C=O), 1025 ν(C–O–C)	1.82, 3.72; 7.02, 7.55 (CD_2Cl_2)

[a] s = strong, sh = shoulder, m = medium. [b] Fresh solution. [c] The metal–chlorine (bridging or terminal) like the metal ligand modes generally fall in the 400–200 cm^{-1} area I.R. Beattie, T. R. Gilson and G. A. Ozin, *J. Chem. Soc. (A)*, 2765 (1968).

Synthesis of $Nb_2Cl_6(SMe_2)_3$

A solution of Me_2S (0.83 ml, 11.33 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a suspension of $NbCl_5$ (0.92 g, 3.40 mmol) and Mg turnings (0.27 g, 11.11 mmol) in CH_2Cl_2 (20 ml) at room temperature. A cherry red solution was obtained. A solution of Et_2O (3.2 ml, 30.8 mmol) in CH_2Cl_2 (5 ml) was then added to the reaction mixture. After 30 min, the solution became cloudy as $MgCl_2$ started forming. After stirring for 24 h, a dark violet suspension was obtained. The reaction mixture was filtered, and the precipitate carefully washed with CH_2Cl_2. The filtrate was evaporated to dryness and extracted at room temperature for 30 min with CH_2Cl_2 (40 ml). After filtration (which left a dark brown powder), the dark violet filtrate was evaporated to dryness, giving 0.65 g (65%) of violet crystals of $Nb_2Cl_6(SMe_2)_3$, which are slightly soluble in $CHCl_3$, CH_2Cl_2 and toluene, and more soluble in THF or MeCN.

Synthesis of $Nb_3Cl_8(SMe_2)_2(Et_2O)$

A solution of Me_2S (1.10 ml, 15 mmol) in CH_2Cl_2 (10 ml) was added to a suspension of $NbCl_5$ (1.21 g, 4.50 mmol) and Mg turnings (0.34 g, 13.98 mmol) in 25 ml of the same solvent at room temperature. A cherry red solution was obtained. A solution of Et_2O (2.5 ml, 24 mmol) in CH_2Cl_2 (10 ml) was added to this mixture. After stirring for 5 days, the dark red solution changed to a black-green suspension. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The residue was extracted at room temperature with CH_2Cl_2 for 30 min, leaving 0.50 g (50%) of blue $Nb_3Cl_8(SMe_2)_2(Et_2O)$, insoluble in CH_2Cl_2, $CHCl_3$ and toluene, and soluble in MeCN, but with immediate decomposition.

Synthesis of $[NbCl_2(OC_6H_4CHO)\cdot(THF)_2]_2$

An excess of THF (3 ml), freshly distilled from sodium benzophenone, was allowed to react at 0 °C with a suspension of $NbCl_5$ (750 mg, 2.7 mmol) and Mg turnings (300 mg) in 20 ml of CH_2Cl_2. The reaction mixture changed rapidly from yellow to dark brown while the Mg(II) by-products precipitated. The mixture was stirred at room temperature for two more hours. Salicylaldehyde (1.3 ml, 48 mmol) was then added and the mixture was stirred for 24 h. Magnesium and its derivatives were then filtered out and washed with CH_2Cl_2. The filtrate was concentrated to 2 ml and left to crystallize for two days at –30 °C. After recrystallisation from CH_2Cl_2, 900 mg (75%) of black $[NbCl_2(OC_6H_4CHO)(THF)_2]_2$ crystals, slightly soluble in toluene and acetonitrile, more soluble in dichloromethane or THF, were obtained.

Synthesis of Nb_2Cl_6(p-dioxane)$_2$

A solution of 1,4-dioxane (1.5 ml, 17.60 mmol) in 7 ml of CH_2Cl_2 was added dropwise to a suspension of $NbCl_5$ (730 mg, 2.70 mm) and Mg turnings (230 mg) in 25 ml of CH_2Cl_2. After 30 min, a dark red-brown mixture was obtained. This was stirred for 3 days. The precipitate of Mg derivatives was collected and washed with CH_2Cl_2. Crystallisation started during the concentration of the filtrate (to *ca.* 5 ml), and was improved by addition of toluene (5 ml) and by cooling to –30 °C for 2 days. The brown-grey crystals of $Nb_2Cl_6(p\text{-}C_4H_8O_2)$ were removed by filtration, washed with toluene and dried (350 mg, 45%). They are insoluble in toluene and CH_2Cl_2, soluble in CH_3CN or THF.

Synthesis of 'NbCl$_3$(C$_4$H$_8$O)$_2$'

A solution in 10 ml of CH_2Cl_2 of tetrahydrofurane (2 ml), freshly distilled from sodium benzophenone, was added slowly to a stirred suspension of $NbCl_5$ (557 mg, 2.06 mmol) and partly oxidized Mg turnings (400 mg) (dampened Mg heated to 120 °C) in 10 ml of CH_2Cl_2 at 0 °C. The first drops of THF caused the dissolution of the niobium pentachloride, and a green-brown coloration. With the addition of more THF (THF/Nb $\simeq 4$) the reaction became slightly exothermic, a fine white precipitate of $MgCl_2$ formed, and the color became dark brown, and then black. The addition of the THF solution took 30 min, stirring was maintained for another half hour at 0 °C. The magnesium derivatives were then removed by filtration and carefully washed with CH_2Cl_2. The black solution was concentrated to 3 ml and stored at –30 °C. Black crystals (120 mg) were filtered and washed with pentane. A second crop was obtained from the filtrate by adding hexane, yielding altogether, after immediate recrystallisation in CH_2Cl_2:toluene, 500 mg (70%) of black crystals, insoluble in aliphatic hydrocarbons and toluene, soluble in CH_2Cl_2, CH_3CN and THF. Longer reaction time led to the isolation of a black product containing magnesium: *Anal.* Calcd for $C_{16}H_{32}Cl_6$-$MgNb_2O_4$: C, 26.96; H, 4.53; Cl, 29.91; Mg, 3.51. Found: C, 27.20; H, 4.60; Cl, 25.91; Mg, 3.06%.

Acknowledgements

Financial support from the C.N.R.S. (ATP No. AI-2650) and the Fundaçao de Amparo à Pesquisa do Estado de Sao Paulo (Brazil) (fellowship to MT) is gratefully acknowledged.

References

1 L. G. Hubert-Pfalzgraf and J. G. Riess, *Inorg. Chim. Acta, 29,* L251 (1978); D. L. Kepert, 'The Early Transition Metals', Academic Press, London (1972).

2 A. D. Allen and S. Naito, *Can. J. Chem., 54,* 2948 (1976).

3 P. Sobota and B. Jezowska-Trzebiatowska, *Coord. Chem. Rev., 26,* 71 (1978).

4 C. Miniscloux, G. Martino and L. Sajus, *Bull. Soc. Chim.,* 2183 (1975).

5 P. A. Finn, M. Schaefer King, P. A. Kilty and R. E. McCarley, *J. Am. Chem. Soc., 96,* 220 (1974).

6 L. S. Jenkins and G. R. Willey, *Inorg. Chim. Acta, 29,* L205 (1978).

7 R. A. Walton, *Progr. in Inorg. Chem., XVI,* 130 (1972); G. W. A. Fowles, D. A. Rice and R. A. Walton, *Spectrochim. Acta, 26A,* 143 (1970); G. W. A. Fowles, D. A. Rice and R. A. Walton, *J. Chem. Soc.,* 1842 (1968).

8 C. Gopinathan and J. Gupta, *Ind. J. Chem.,* 103 (1974).

9 F. A. Cotton and W. T. Hall, *J. Am. Chem. Soc., 101,* 5094 (1979).