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Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives. II. Niobium Oxochloride–Hexamethylphosphoramide and Related Adducts

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The molecular constitution of solutions of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ ($\text{HMPA} = \text{OP}(\text{NMe}_2)_3$), $\text{NbOCl}_3 \cdot \text{OMPA}$ ($\text{OMPA} = [(\text{Me}_2\text{N})_2\text{P}(\text{O})]_2\text{O}$), and $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$ in MeCN , CH_2Cl_2 , and CHCl_3 was investigated, mainly through low-temperature ^1H NMR studies and by stepwise addition of the ligands. It consists of complex mixtures of monomeric species having ligand:metal stoichiometries of 1, 2, and 3 and, for each stoichiometry, of various isomers in equilibrium with each other and with the free ligand. The isomer of $\text{NbOCl}_3 \cdot 2\text{L}$ in which the ligands occupy nonequivalent sites is predominant. All of the equilibria are dynamic on the NMR time scale. The $\text{NbOCl}_3 \cdot \text{HMPA}$ adduct is probably stabilized by coordination of the metal by an additional molecule of MeCN . No such 1:1 adduct was observed to form in CHCl_3 or CH_2Cl_2 . The NMR spectra measured on $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$ and $\text{NbOCl}_3 \cdot \text{OMPA}$ are also consistent with the same general scheme. In acetonitrile both monodentate and bidentate behaviors are suggested for OMPA.

Introduction

Many coordination compounds which have a single well-defined molecular structure in the solid form undergo drastic changes in nature and give complex mixtures once they are put in solution. As part of our investigations into such phenomena, we now report a low-temperature NMR study of the niobium oxochloride complexes $\text{NbOCl}_3 \cdot 2\text{L}$ ($\text{L} = \text{HMPA}$ or $1/2$ OMPA)¹ and of an oxyalkoxychloride complex $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$. It is believed that information obtained through investigations performed on well-chosen examples can afford general understanding of the complex molecular constitution and behavior of solutions of this class of compounds.

Numerous early transition metal oxyhalide adducts have been reported.² Where niobium and tantalum are concerned, their general formulas are $\text{MOX}_3 \cdot 2\text{L}$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{OSR}_2, \text{OPR}_3, \text{OAsR}_3, \text{NR}_3, 1/2$ bpy, $1/2$ diars). They were obtained either directly from the oxyhalides or from the pentahalides by an oxygen vs. halogen exchange reaction with ligands such as triphenylphosphine or triphenylarsine oxide, dimethyl sulfoxide, and hexamethylphosphoramide (HMPA).²

By contrast, surprisingly little structural information is available on this class of compounds. X-Ray studies have been performed only on $\text{NbOCl}_3 \cdot 2\text{CH}_3\text{CN}$ ³ and $\text{NbOCl}_2(\text{OMe}) \cdot \text{bpy}$.⁴ In both cases the oxo-type atom was found to be trans to the ligands. In solution only one study is available for the $\text{NbOCl}_3 \cdot 2\text{OSMe}_2$ adduct.⁵

Results and Discussion

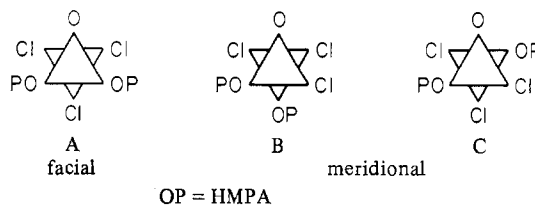
Variable-Temperature NMR Study of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in Acetonitrile. A typical proton NMR spectrum measured at 0°C on a solution of the isolated complex $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in acetonitrile (0.33 *M*) consists of a set of seven doublets ($J_{\text{H-P}} = 9.8 \pm 0.5$ Hz) in the $\text{OP}[\text{N}(\text{CH}_3)_2]_3$ region (δ 2.62–2.77 ppm (Figure 1a)).

The relative peak areas were found to depend considerably on the following factors: nature of the solvent (as shown in Figure 1), concentration, temperature, addition of an excess of ligand. However, it is remarkable that doublets 3–3' and 5–5' always remain of relatively comparable area, while the others vary continuously. This implies the presence of at least six distinct molecular species. Addition of an excess of HMPA to the acetonitrile solution allowed us to identify peak 6' as one branch of the doublet of the free ligand.

All the doublets coalesce to a single one (δ 2.75 ppm, $J_{\text{H-P}} = 9.5$ Hz) when the temperature is raised above 73°C (Figure 2); this demonstrates the existence of fast-exchange processes of the ligands between the various molecular species and their nonequivalent sites. Coalescence temperatures between 3–3', 5–5', 1–1', and 2–2' did not depend on the dilution in the

explored concentration range (0.5–0.05 *M*) but this domain is too small to draw accurate conclusions about the nature of the exchanges.

These observations and the fact that $\text{NbOCl}_3 \cdot 2\text{HMPA}$ is monomeric in acetonitrile (vapor pressure osmometry mol wt 568, calcd 573.5), which implies hexacoordinated niobium, were interpreted to mean that these solutions consist primarily of a mixture of the three possible octahedral isomers, A, B, and C. These are partially dissociated and in equilibrium with



the free ligand. In the meridional isomer B, the two ligands occupy nonequivalent positions, which would account for doublets 3–3' and 5–5' in the NMR spectra remaining constantly of equal area.

Further evidence to support this hypothesis was sought: (1) by stepwise addition experiments of HMPA to NbOCl_3 in acetonitrile in order to investigate the dissociation process of $\text{NbOCl}_3 \cdot 2\text{HMPA}$; (2) by using a bidentate ligand which would prevent the formation of the trans isomer C and simplify the NMR patterns; (3) by substituting one halogen atom by a methoxy group which would increase the number of possible octahedral isomers and the number of NMR signals in a predictable manner. These experiments provided a convergent array of evidence to support and complete the above rationale.

Stepwise Addition of HMPA in Acetonitrile. A progressive addition of HMPA to a solution of NbOCl_3 in deuterioacetonitrile (0.40 *M*) was performed at 0°C . Figure 3 shows the evolution of the spectra as a function of the $R = \text{HMPA}:\text{Nb}$ molar ratio. Figure 4a represents the variation of peak area for doublets 1 to 7 as a function of R ($0 < R < 3.75$).

(1) For $R < 1$ the following reproducible observations were made. Two doublets 1 and 2 of different areas appear. Their relative areas vary with the temperature and they therefore belong to distinct molecular species. Doublet 2 is slightly shifted by further addition of ligand. The areas of these two signals go through maximum intensity for $R = 1$ (95% of all the ligand signal areas), while new signals (3, 5, and 7) appear, thus establishing the existence of intermediate species having a ligand:metal ratio of 1:1.

Our attempts to isolate the intermediate species having an HMPA:Nb ratio of 1 were unsuccessful. The only compound which ever crystallized out was $\text{NbOCl}_3 \cdot 2\text{HMPA}$, independent

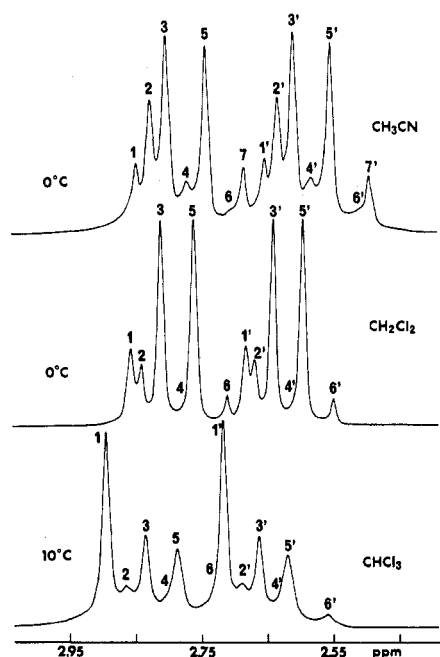


Figure 1. Proton NMR spectra of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ solutions: (a) in acetonitrile (0.33 M at 0°C), (b) in dichloromethane (0.25 M at 0°C), (c) in chloroform (0.19 M at 10°C). The position of peak 4 as given on spectra b and c was determined at other dilutions.

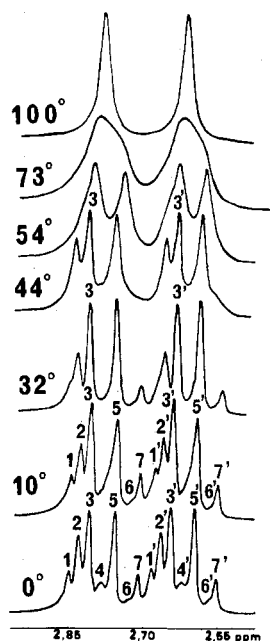


Figure 2. Temperature dependence of proton NMR spectra for a 0.45 M solution of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in acetonitrile.

of the value of R . However, molecular weight measurements performed on an acetonitrile solution for $R = 1$ are consistent with a monomeric intermediate (found 365; calcd for $\text{NbOCl}_3 \cdot \text{HMPA}$ 394). The infrared spectra recorded on the same solution show no absorption which could be assigned to a $\nu(\text{Nb}-\text{O}-\text{Nb})$ vibration (usually $\sim 770 \text{ cm}^{-1}$).⁶ These results establish the monomeric character of the intermediate. However, the fact that pentacoordination is very rare in the chemistry of niobium² and the strong coordination ability of CH_3CN toward NbOCl_3 , which leads to the formation of $\text{NbOCl}_3 \cdot 2\text{CH}_3\text{CN}$ in solution, suggest that one molecule of acetonitrile is very likely to be coordinated to the metal in this intermediate species, which could thus be formulated

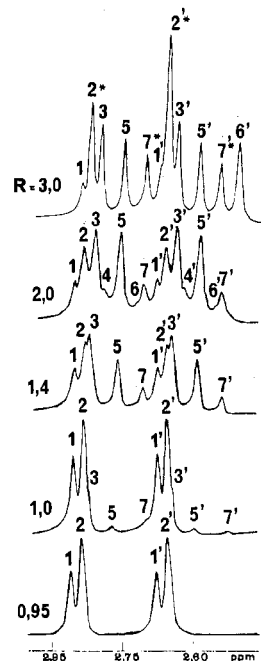


Figure 3. Proton NMR spectra measured at 0°C during a stepwise addition of HMPA to a solution of NbOCl_3 in CD_3CN (0.40 M); $R = \text{HMPA}:\text{Nb}$ molar ratio.

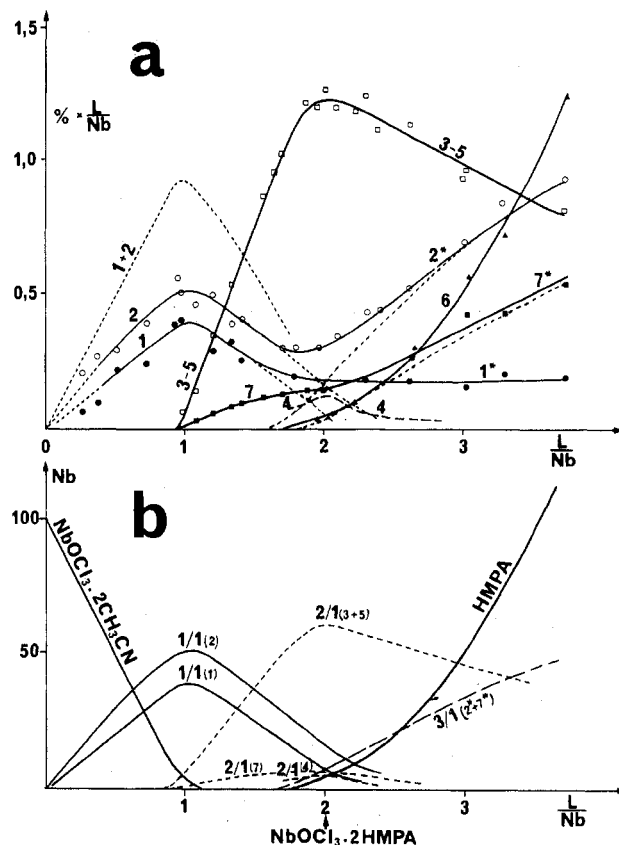
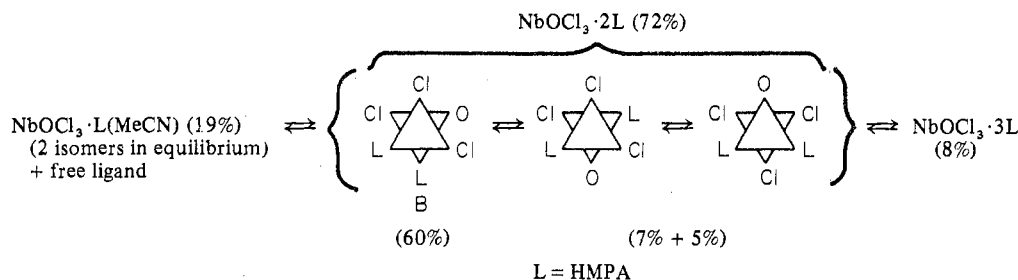


Figure 4. (a) Variation of the relative areas of the NMR signals as a function of $R = \text{HMPA}:\text{NbOCl}_3$; peak numbers correspond to those of Figure 3. (b) Plot of the percentage of the various niobium species as a function of R on the assumption that doublets 1 and 2 belong to 1:1 species; doublets 3 and 5, and 4 and 7 to 1:2 species; and doublets 2* and 7* to a 3:1 species.

$\text{NbOCl}_3 \cdot \text{HMPA} \cdot \text{CH}_3\text{CN}$. It is also noteworthy that no monomeric 1:1 adduct between NbOCl_3 and an oxo ligand has been reported yet.

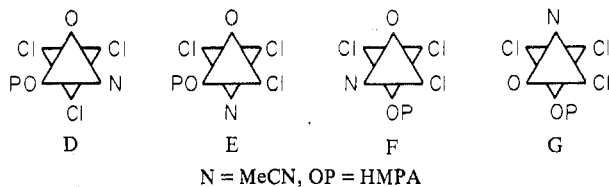
The coordination of NbOCl_3 by acetonitrile, which is

Scheme I



thought to stabilize the intermediate 1:1 species, is further evidenced by the fact that *no* such 1:1 species were observed to form in noncomplexing solvents such as CHCl_3 or CH_2Cl_2 .

The fact that only two doublets **1** and **2** are observed in the low-temperature ^1H NMR spectra for $R = 1$ whereas the four geometric isomers D–G are possible for an octahedral complex



of formula $\text{NbOCl}_3 \cdot \text{HMPA} \cdot \text{CH}_3\text{CN}$ could mean that two of the isomers are favored or that several of them have close chemical shifts or are rapidly interconverting in the solution (down to -40°C). Thus isomers D and E would be expected to have similar chemical shifts, since in both cases the ligand is trans to a chlorine and cis to an oxygen and a nitrogen atom. On the other hand, isomer F, where the oxo ligands are trans to each other, would be expected to be less favored.⁷

(2) For $1 < R \leq 2$, three new doublets (**3**, **5**, and **7**) develop simultaneously. The signal corresponding to the free ligand **6** becomes detectable when $R \approx 1.8$. Another doublet, **4**, became detectable for $R \approx 1.83$; it is not observed for lower R values because of its low intensity and overlap with other peaks. Doublets **3** plus **5** (61% of the total peak area) as well as **4** go through maximum intensities for $R = 2$.

Doublets **3**, **5**, **7**, and **4** were therefore assigned to $\text{NbOCl}_3 \cdot 2\text{HMPA}$ isomers. The spectra recorded for $R = 2$ are identical with those measured on solutions of the pure crystalline $\text{NbOCl}_3 \cdot 2\text{HMPA}$ adduct at the same solvent, concentrations, and temperature conditions.

(3) For $R > 2$ it was found that not only doublet **6** but also doublets **2** and **7** increase again. The fact that **2**, which was previously assigned to a species having a 1:1 ligand:metal ratio, undergoes a new increase in intensity after a minimum for $R \approx 1.8$ can only be explained by the formation of a new species, which has a ligand:metal ratio higher than 2 and which would fortuitously exhibit the same chemical shift. This resonance was therefore labeled **2***–**2'*** for $R > 2$. The same interpretation accounts for the new increasing slope of the intensity variation of doublet **7**.

A quantitative analysis of the spectra shows for example that at $R = 3$ the ratio of coordinated ligand per niobium is equal to 2.5, which also implies the existence of species having a ligand:metal ratio higher than 2.

The spectral information obtained for solutions of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in noncomplexing solvents (see below) indicates that three ligands are coordinated on the metal. These data are in agreement either with the formation of a species of formula $\text{NbOCl}_3 \cdot 3\text{HMPA}$ in which the metal would be heptacoordinated or with the formation of an ionic $\text{NbOCl}_2 \cdot 3\text{HMPA} + \text{Cl}^-$ species in which the metal would remain hexacoordinated. Conductivity measurements performed on a $5 \times 10^{-4} M$ solution of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in acetonitrile

and for $R = 4$ gave $\Lambda = 60 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, which accounts for a nonelectrolyte.⁸ It is worth noting that no $\text{NbOCl}_3 \cdot 3\text{L}$ adduct has been reported hitherto, but heptacoordination has been postulated for a monomeric niobium–oxo species.⁹

Figure 4b is a plot of the molar percentage of the various species as a function of R on the basis of the preceding assumptions that doublets **1** and **2**; **3**, **5**, **4**, and **7**; **2*** and **7*** correspond respectively to species having ligand:metal ratios of 1, 2, and 3. These assumptions were also checked by material balance calculations; i.e., they correspond for each sample examined to the best fit between the niobium content as calculated from the weighing of the ingredients and from the NMR peak area.

The molecular constitution of a 0.03 M solution of $\text{NbOCl}_3 \cdot 2\text{HMPA}$ in acetonitrile can be rationalized as in Scheme I.

Studies in Noncomplexing Solvents. Compound $\text{NbOCl}_3 \cdot 2\text{HMPA}$ was also found to be monomeric in chloroform.¹¹ The proton NMR spectra recorded at low temperature in dichloromethane (Figure 1b) or chloroform (Figure 1c) show only six doublets, two of them (**3** and **5**) again having constantly comparable area.

Addition of an excess of HMPA leads to the assignment of doublet **4** to the free ligand. When a stepwise addition of HMPA to a suspension of NbOCl_3 in CH_2Cl_2 or CHCl_3 was performed, no evidence for the formation of species having a 1:1 ligand:metal ratio could be found. Further ligand addition ($R > 2$) shows a decrease in the intensity of signals **1**–**1'**, **3**–**3'**, and **5**–**5'**, which were therefore attributed to the octahedral isomers of $\text{NbOCl}_3 \cdot 2\text{HMPA}$, while those of signals **2**–**2'** and **6**–**6'** increase. Lesser peak overlap in these solvents than in CH_3CN allowed us to measure more accurate peak areas and to establish that the peak area ratio between **2**–**2'** and **6**–**6'** remains equal to 2, in all conditions of dilution or HMPA:Nb ratio, and furthermore that for this species the ligand:metal ratio is 3. Peaks **2**–**2'** and **6**–**6'** therefore belong very probably to a single molecular species of formula $\text{NbOCl}_3 \cdot 3\text{HMPA}$ in which niobium would be heptacoordinated.

An important solvent effect on the concentration of the various isomers has been noticed: as an example, for the conditions of Figure 1, isomer B (signals **3**–**3'** and **5**–**5'**) amounts to 70% in CH_2Cl_2 and 42% in CHCl_3 , while signal **1**–**1'** goes from 16% in CH_2Cl_2 to 44% in CHCl_3 .

Study of Chelated Compounds. Bidentate ligands, such as octamethylphosphortriamide (OMPA), should reduce the number of ligand signals, since the formation of the trans isomer C is forbidden. Compound $\text{NbOCl}_3 \cdot \text{OMPA}$ was found to be monomeric in acetonitrile (mol wt found 464, calcd 501). Its proton NMR spectrum recorded at -10° in CH_2Cl_2 (Figure 5) exhibits four ligands signals after decoupling (Figure 5b; δ 2.71–2.62 ppm). Signal **4** (3% for a 0.25 M solution) could be assigned to the free ligand. Peak **1** (85% of all the spectrum area) was assigned to an isomer of type A in which both phosphoryl groups are trans to chlorine atoms and equivalent. Peaks **2** and **3**, which keep constantly comparable area in all conditions of dilutions and ligand:metal ratios, would belong to the other isomer (12%); signal **2**, which is closer to peak

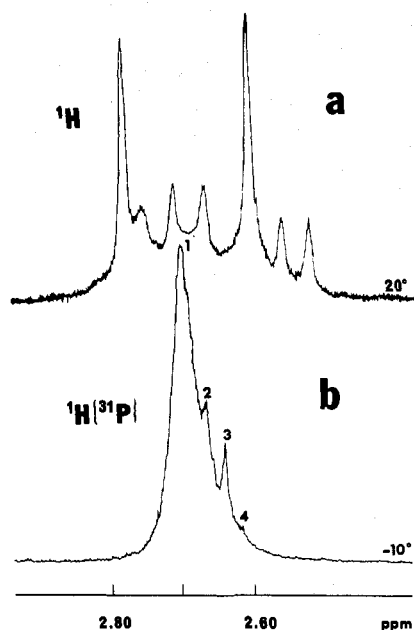
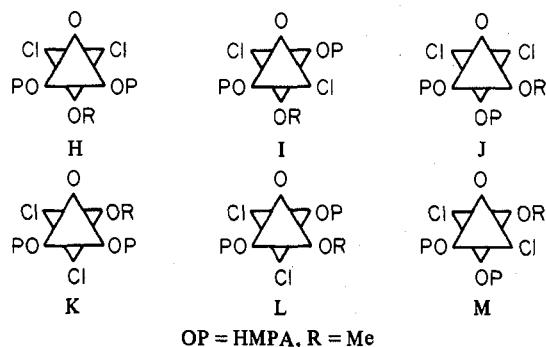


Figure 5. (a) Proton NMR spectrum measured on a 0.25 *M* solution of $\text{NbOCl}_3 \cdot \text{OMPA}$ in dichloromethane. (b) HMPA region after heteronuclear decoupling.

1, was tentatively assigned to the dimethylamino groups trans to chlorine and signal 3 to those trans to oxygen. All the species are in dynamic equilibrium as shown by the coalescence at 62°C. In acetonitrile solutions, the number of peaks in the decoupled spectra increases to 6 (2.66–2.54 ppm). The two new signals (2.64 and 2.53 ppm) always keep comparable area and could come from a species in which the ligand would exhibit monodentate behavior (4% for a 0.20 *M* solution), while the sixth site of the metal would be coordinated by acetonitrile.

Studies of $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$. If our rationale of the molecular constitution of the solutions of these niobium oxychloride complexes is correct, substitution of one halogen atom by a methoxy group will increase the number of possible geometric isomers to 6 (H–M). Three of them (isomer J, K,



and M) exhibit nonequivalent ligand sites and should give doublets of equal area in the NMR spectra. Compound $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$ was therefore prepared. It is monomeric in CH_3CN (mol wt found 520, calcd 569), and its proton NMR spectra in dichloromethane solutions (Figure 6) effectively exhibit ten doublets (2.47–2.67 ppm; doublet 10 could be assigned to the free ligand) in the HMPA region. Doublets 2–5 as well as doublets 3–6 and 4–7 keep comparable area in all dilution experiments. A single signal (δ 4.54 ppm) was observed in the methoxy region.

Again, one of the isomers in which the ligands occupy nonequivalent positions is predominant (doublets 2 and 5; 30–35% in 0.20 *M* solution). The spectra measured in acetonitrile are also compatible with the same general scheme.

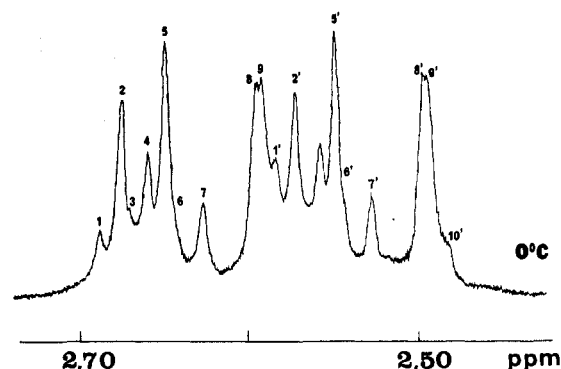


Figure 6. Proton NMR spectrum measured at 0°C in dichloromethane on a 0.20 *M* $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$ solution.

However, their complexity does not permit the recognition of the additional species which would result from a stepwise dissociation. But in this solvent there are two signals in the methoxy region (4.77 and 4.74 ppm), which could arise from the methoxy groups trans to a chlorine and trans to an oxygen atom.

All the species are in dynamic equilibrium in these solutions, as evidenced by the coalescence of the signals in the NMR spectra.

In conclusion, all the data in this paper are consistent and illustrate the fact that solutions of niobium and tantalum oxyhalide adducts consist of complex mixtures of monomeric species having ligand:metal stoichiometries of 1, 2, and 3 and, for each stoichiometry, of various isomers in rapid dynamic equilibrium with each other and with the free ligand on the NMR time scale.

Experimental Section

General Data. All manipulations were carried out under dry nitrogen. Solvents were dried and purified by standard methods.¹⁰ HMPA (gift from Pierrefitte) and OMPA (gift from Murphy Chemical) were purified by vacuum distillations.

Niobium(V) oxychloride was prepared from the pentoxide and aluminum trichloride.¹ The complexes $\text{NbOCl}_3 \cdot 2\text{HMPA}$ and $\text{NbOCl}_3 \cdot \text{OMPA}$ were synthesized according to the literature.¹¹ The metal was analyzed as pentoxide.

NMR spectra were obtained on a JEOL C-60 HL spectrometer equipped with a variable-temperature system and a JNM-SD-HC heteronuclear decoupling attachment and on a Varian XL-100 spectrometer. TMS was used as internal reference. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer. Molecular weight data were obtained using a Knauer vapor pressure osmometer. Conductance measurements were performed with a Tacussel CDN 6 conductometer.

$\text{NbOCl}_2(\text{OCH}_3) \cdot 2\text{HMPA}$. Dry methanol (0.240 g, 7.48 mmol) was added at room temperature to a stirred suspension of niobium oxytrichloride (0.72 g, 3.32 mmol) in toluene (5 ml). After dissolution, HMPA (1.58 g, 8.8 mmol) was added and the solution was stirred for 1 hr. Further addition of petroleum ether (10 ml) gave a cloudy solution which was cooled at –30°. After 1 week the colorless crystals were filtered, washed with petroleum ether, and dried under vacuum (1.93 g; 88%).

The air-sensitive compound (mp 110°) is insoluble in aliphatic hydrocarbons but soluble in most other common organic solvents. *Anal.* Calcd for $\text{C}_{13}\text{H}_{39}\text{NbO}_4\text{N}_6\text{Cl}_2\text{P}_2$: C, 27.50; H, 6.86; N, 14.80; Cl, 12.32; Nb, 16.33. Found: C, 27.15; H, 6.83; N, 14.60; Cl, 12.83; Nb, 16.50. *Ir* (Nujol, cm^{-1}): $\nu(\text{Nb}=\text{O})^2$ 945; $\nu(\text{P}=\text{O})$ 1062; $\nu(\text{Nb}-\text{OR})$ 545, 520; $\nu(\text{Nb}-\text{Cl})$ 304.

Acknowledgment. We wish to thank Dr. M-P. Simonnin, ENSCP Paris, for measuring the 100-MHz NMR spectra.

Registry No. $\text{NbOCl}_3 \cdot 2\text{HMPA}$, 37549-64-7; $\text{NbOCl}_3 \cdot \text{OMPA}$, 37549-65-8; $\text{NbOCl}_2(\text{OMe}) \cdot 2\text{HMPA}$, 56792-72-4.

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Stereochemistry of Carboxylate Complexes.

Crystal Structure of (-)-589-Malatodiaquomanganese(II) Hydrate

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The crystal structure of (-)-589-malatodiaquomanganese(II) hydrate, $[\text{Mn}(\text{C}_4\text{H}_4\text{O}_5)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$, has been determined from three-dimensional single-crystal x-ray diffraction data collected by counter methods on a computer automated diffractometer. The compound crystallizes in the orthorhombic space group $D_2^4-P2_12_12_1$ with four formula units in a cell of dimensions $a = 9.219$ (7) Å, $b = 9.421$ (6) Å, $c = 10.536$ (7) Å. The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.045 for 1167 independent reflections. Each manganese(II) ion is coordinated to one carboxylate oxygen atom and the hydroxyl oxygen from one ligand forming a five-membered chelate ring as well as two carboxylate oxygen atoms from two other different malate ligands. Two water molecules complete the irregular octahedral coordination around the metal. Four of the five oxygen atoms in the malate ligand are involved in coordination to three different Mn(II) ions forming an extensive polymeric network including hydrogen bonding to the single lattice water molecule. The malate conformation is antiperiplanar and the entire structure is compared to the structures of other malate complexes. The range in Mn-O bond lengths is 2.135 (3) to 2.230 (4) Å.

Introduction

Malate ion, $^-\text{OOCCHOHCH}_2\text{COO}^-$, is a multidentate dicarboxylate ligand which may coordinate metal ions in a variety of ways. As part of a continuing general study of the stereochemistry of metal-carboxylate complexes, we have been interested in establishing the relative variability in the mode of metal ion coordination by carboxylate ligands such as malate in the crystalline state.

The stereochemistry of the malate-metal interaction has been determined for the 1:1 compounds of calcium,¹ cobalt(II),^{2,3} and zinc(II).⁴ For each of the above ions x-ray crystallographic studies have revealed the malate ligand coordinates the metal through both carboxylate groups and the hydroxyl oxygen to form five- and six-membered chelate rings. Four-membered chelate rings are present as well in the calcium malate¹ crystal presumably needed to satisfy the eight-coordination stereochemistry requirement of the larger Ca(II) ion. For each of the indicated compounds (in addition to chelation) the malate ligand is bridged to one or more metal ions in a monodentate fashion forming polymeric units.

The manganese(II), zinc(II), and cobalt(II) 1:1 malate compounds all crystallize with the formula unit $\text{MC}_4\text{H}_4\text{O}_5\cdot 3\text{H}_2\text{O}$. The Co(II) and Zn(II) compounds are monoclinic while the Mn(II) crystals are orthorhombic. The obvious difference in crystal structure in the manganese(II) case does not imply the manganese-malate stereochemistry would necessarily be different from that in the zinc(II) and cobalt(II) compounds. But, if a change in the mode of coordination did occur, the crystal packing and structure would necessarily be altered. On this basis we undertook the x-ray crystal structure investigation of manganese(II) (-)-589-malate trihydrate to test the idea that the (-)-589-malate stereochemistry may differ in a series of complexes with similarly charged and sized metal ions.

Experimental Section

Short prismatic crystals of (-)-589-malatodiaquomanganese(II) hydrate were grown by slow evaporation from an aqueous solution prepared by dissolving manganese carbonate in (-)-589-malic acid (Eastman) in a 1:1 molar ratio. Small single crystals of the complex appear nearly colorless although clumps of larger crystals have a decided pink cast.

Examination of indexed Weissenberg photographs showed that the crystals belonged to the orthorhombic system. The observed systematic absence, h odd for $h00$, k odd for $0k0$, and l odd for $00l$, uniquely determined the space group to be $P2_12_12_1$. The lattice constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 12 carefully centered reflections (2θ range 13 to 26°) on a Picker FACS-I automated diffractometer using Mo $K\alpha$ radiation (λ 0.71069 Å).

Crystal Data for $[\text{MnC}_4\text{H}_4\text{O}_5(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$: orthorhombic; space group $P2_12_12_1$; $a = 9.219$ (7) Å; $b = 9.421$ (6) Å; $c = 10.536$ (7) Å; $V = 915.1$ Å³; $Z = 4$; $d_m = 1.75$ (1) g cm⁻³ (by flotation in a mixture of iodobenzene and pentachloroethane); $d_c = 1.748$ g cm⁻³; $\text{FW} = 241.06$; $F(000) = 492$; $\mu(\text{Mo } K\alpha) = 15.3$ cm⁻¹.

Collection and Reduction of the Intensity Data. Three-dimensional x-ray intensity data were collected from a crystal with approximate dimensions $0.28 \times 0.31 \times 0.31$ mm on the diffractometer already mentioned. Zirconium-filtered Mo $K\alpha$ radiation was used. The crystal was mounted along the c^* direction which was made coincident with the instrumental ϕ axis. All reflections out to 55° in 2θ were collected using the θ - 2θ scan technique. A scan range from 1° below the Mo $K\alpha_1$ peak to 1° above the Mo $K\alpha_2$ peak was used. The scan rate was $1^\circ/\text{min}$. The background counting time was 20 sec at the start and end of each scan. During the data collection the intensities of three standard reflections were monitored after each 100 measurements and none showed any significant variation during the data collection. The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$ (assuming an "uncertainty factor", $p = 0.04$) in the manner previously described.⁵ No absorption corrections were applied in view of the low absorption factors and the approximately equidimensional shape of the crystal. As a check