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Synthesis and Molecular Structures of the Magnesium and Aluminum Adducts of a Niobium−Oxo Complex. X-ray Crystal Structures of $[\{NbOCl_4(THF)\}_2Mg(THF)_4]$ and $[\{NbOCl_4(THF)\}_2AlCl(THF)_3]$

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Introduction

The most active Ziegler−Natta catalysts of alkene polymerization are d^0 metallocenes of the XIII, XIV, and XV groups.[1] On the other hand, vanadium catalysts[2] generally show a d^2 or d^3 configuration. However, d^0 vanadium complexes have frequently been used as catalysts but were readily reduced to a lower oxidation state in the presence of a cocatalyst. The synthesis of high polymers based on simple Nb(V) species as catalysts has also been reported.[3] It could be expected that V(V) and Nb(V) complexes would be effective catalysts if they could be stabilized in their high oxidation state.[4] In this contribution, we describe the synthesis and characterization of Mg^{2+} and Al^{3+} niobium−oxo adducts. The chemistry of transition metal−oxo M=O (V, Nb, Ta) adducts with electropositive metal ions such as Mg^{2+} or Al^{3+} as components of the catalyst is unknown yet. In a previous paper we described the synthesis and properties of products formed during reaction between $[MoOCl_3(THF)_2]$ and $[MgCl_2(THF)_2]$.[5] For a Mo/Mg 2:1 molar ratio in THF a crystalline salt $[Mg(THF)_6][MoOCl_4(THF)]_2$ is formed which reacts further with 3 equiv of bis(tetrahydrofuran)magnesium dichloride yielding the ionic $[Mg_2(\mu\text{-}Cl)_3(THF)_6][MoOCl_4(THF)]$ compound. The $[\{MoOCl_4(THF)\}_2Mg(THF)_4]$ and $[MgMo(\mu\text{-}Cl)_3Cl_2O(THF)_3]$ molecular compounds were readily obtained by interaction of $[MoOCl_3(THF)_2]$ with $[MgCl_2(THF)_2]$ in a 2:1 and 1:1 molar ratio in CH_2Cl_2, respectively. However, compounds $[(ReMe_4O)_2Mg(THF)_4]$ and $[\{o\text{-}C_6H_4(CH_2)_2WO\}_2Mg(THF)_4]$ arise from Grignard reagents or MgR_2 with R_2O_7 or WCl_4O in THF.[6,7] Similar adducts with Al^{3+} were unknown.

As an extension of these studies, we chose to investigate the chemistry of niobium−oxo species[8,9] $[NbOCl_4(THF)]^-$ with $MgCl_2$ and $AlCl_3$ in order to compare the basic properties of Nb=O with M=O (M = Mo, W, Re) moieties. In this paper we describe the synthesis of $[\{NbOCl_4(THF)\}_2Mg(THF)_4]\cdot CH_2Cl_2$, $[\{NbOCl_4(THF)\}_2Mg(THF)_4]\cdot 4THF$ and $[\{NbOCl_4(THF)\}_2AlCl(THF)_3]$ species and report the details of their X-ray structures.

Experimental Section

Syntheses were carried out under dry dinitrogen by following standard Schlenk techniques. All solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds $NbCl_5$ and $AlCl_3$ were purchased from Aldrich Chemical Co. The complexes $[NbCl_4(THF)_2]$ and $[MgCl_2(THF)_2]$ were prepared according to literature methods.[10,11] Infrared spectra were recorded on a Perkin-Elmer 180 instrument in Nujol mulls.

Synthesis of $[\{NbOCl_4(THF)\}_2Mg(THF)_4]\cdot CH_2Cl_2$ (1). A suspension of $NbCl_5$ (2.7 g; 10 mmol) and $[MgCl_2(THF)_2]$ (1.2 g; 5 mmol) in a mixture of 60 cm^3 of CH_2Cl_2 and 20 cm^3 of THF was refluxed for 1 h. The solution was filtered off, and the volume was reduced *in vacuo* to *ca.* 45 cm^3 and left to crystallize at room temperature. After 24 h colorless needle-shaped crystals of compound **1** were collected, washed with *n*-hexane (3 × 5 cm^3), and dried *in vacuo*. Yield: 3.68 g (70%). Anal. Calcd for $C_{25}H_{50}Cl_{10}MgNb_2O_8$: Cl, 27.19; Mg, 2.33; Nb, 17.81. Found: Cl, 27.26; Mg, 2.29; Nb, 17.73. IR (Nujol, cm^{-3}): 1292 (w), 1245 (w), 1170 (w), 1020 (vs), 951 (w), 915 (m), 870 (vs), 719 (m), 672 (m), 335 (vs), 310 (s).

Synthesis of $[\{NbOCl_4(THF)\}_2Mg(THF)_4]\cdot 4THF$ (2). A mixture of $[NbCl_4(THF)_2]$ (1.9 g; 5 mmol) and $[MgCl_2(THF)_2]$ (0.6 g; 2.5 mmol) in 60 cm^3 of THF was refluxed for 4 days until the solution had cleared. The solution was filtered off, and the volume was reduced *in vacuo* to *ca.* 40 cm^3 and left to crystallize at room temperature. After 72 h colorless cubic-shaped crystals of compound **2** were collected, washed with *n*-hexane (3 × 5 cm^3), and dried *in vacuo*. Yield: 1.46 g (62%). Anal. Calcd for $C_{40}H_{80}Cl_8MgNb_2O_{12}$: Cl, 29.30; Mg, 2.51; Nb, 19.48. Found: Cl, 29.42; Mg, 2.48; Nb, 19.36. IR (Nujol, cm^{-3}): 1292 (w), 1245 (w), 1170 (w), 1020 (vs), 951 (w), 915 (m), 870 (vs), 719 (m), 672 (m), 335 (vs), 310 (s).

Synthesis of $[\{NbOCl_4(THF)\}_2AlCl(THF)_3]$ (3). $NbCl_5$ (2.7 g; 10 mmol) and $AlCl_3$ (1.3 g; 10 mmol) in a mixture of 50 cm^3 of CH_2Cl_2 and 10 cm^3 of THF solvents was refluxed for 1 h. The solution was filtered off, and the volume was reduced *in vacuo* to *ca.* 25 cm^3 and left to crystallize at room temperature. After 10 days colorless plate-shaped crystals of compound **3** were collected, washed with *n*-hexane (3 × 5 cm^3), and dried *in vacuo*. Yield: 1.24 g (26.8%). Anal. Calcd for $C_{20}H_{40}AlCl_9Nb_2O_7$: Cl, 34.52; Al, 2.92; Nb, 20.10. Found: Cl, 34.58; Al, 2.86; Nb, 19.96. IR (Nujol, cm^{-3}): 1300 (w), 1260 (w), 1168 (w), 1042 (m), 1008 (s), 905 (s), 830 (vs), 740 (w), 495 (m), 446 (s), 391 (s), 360 (s), 335 (vs), 312 (s) 273 (w).

X-ray Data Collection and Refinement of the Structures. Data Collection and Processing. Preliminary data for all crystals were obtained from Weissenberg photographs. Intensities were collected using a Kuma KM4 four-circle diffractometer in the $\omega-2\theta$ mode (with crystals of dimensions 1.0 × 0.6 × 0.6 for **1**, 0.6 × 0.5 × 0.4 for **2**, and 0.5 × 0.5 × 0.5 for **3**) and Mo Kα radiation. Cell parameters were obtained from a least-squares fit of the setting angles of 25 reflections in the range $20° < 2\theta < 27°$ for **1**−**3**. For all crystals the intensities of three standard reflections were monitored every 100 intensity scans. They showed a 16.8% loss of intensity for **3**. Totals of 11 250 ($4° < 2\theta < 57°$), 6454 ($4° < 2\theta < 52°$), and 7253 ($4° < 2\theta < 57°$) reflections were measured for **1**−**3**, respectively, from which 3999, 1453, and 4365 reflections with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL93.[12]

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The number of refined parameters was 415 for **1**, 235 for **2,** and 352 for **3**. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref 13; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were put in calculated positions with d(C$-$H) = 1.08 Å and introduced as fixed contributors in the final stage of refinement. The bond distances O(3)$-$C(1), O(3)$-$C(4), O(7)$-$C(13), O(7)$-$C(16), O(8)$-$C(17), and O(8)$-$C(20) were restrained with d(O$-$C) = 1.466 Å. The bond distances C(1)$-$C(2), C(2)$-$C(3), C(3)$-$C(4), C(13)$-$C(14), C(14)$-$C(15), C(15)$-$C(16), C(17)$-$C(18), C(18)$-$C(19), and C(19)$-$C(20) were restrained with d(C$-$C) = 1.452 Å. The absorption corrections following the DIFABS[14] procedure were applied for **1**$-$**3**: Minimum and maximum absorption corrections were 0.903 and 1.084 for **1**, 0.884 and 1.026 for **2**, and 0.946 and 1.033 for **3**. Weighting schemes of the form $w = 1/\sigma^2(F_o^2) + (0.0558P)^2 + 3.75P$, $w = 1/\sigma^2(F_o^2) + (0.0394P)^2 + 8.04P$, and $w = 1/\sigma^2(F_o^2) + (0.0827P)^2 + 10.08P$ (where P is defined as $(F_o^2 + 2F_c^2)/3$) were applied to **1**$-$**3**, respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was below 0.005 Å for **1** and **3**. The final difference map showed a general background within -0.37 and 0.41 for **1**, -0.31 and 0.24 for **2**, and -0.41 and 1.04 eÅ^{-3} for **3**.

Results and Discussion

As stated above, we were interested in determination whether magnesium and aluminum cations could easily form Nb=OMO=Nb (M = Mg, Al) adducts. We found that the direct reaction of $NbCl_5$ with [$MgCl_2(THF)_2$] in a mixture of THF/CH_2Cl_2 (3:1) solvents yields a species of composition $2NbOCl_3 \cdot MgCl_2 \cdot 6THF \cdot CH_2Cl_2$ (**1**). Similar reaction of [$NbCl_4(THF)_2$] with [$MgCl_2(THF)_2$] in a molar ratio 2:1 in tetrahydrofuran under reflux gave a colorless compound of composition $2NbOCl_3 \cdot MgCl_2 \cdot 10THF$ (**2**). The IR spectra of **1** and **2** are similar and show stretching modes at 1020 (vs) and 870 (vs) cm^{-1} attributed to ν(C$-$O$-$C) of the co-ordinated THF molecules and sharp band at 915 (m) cm^{-1} due to ν(Nb=O) which is shifted to lower frequences compared to ν(Nb=O) 962 cm^{-1} found in the [$NbOCl_4(THF)$]$^-$ anion.[7] The bands at 335 (vs) and 310 (s) cm^{-1} are assigned to ν(Nb-Cl) to ν(Mg$-$O) vibrations.[11]

The addition of $AlCl_3$ to $NbCl_5$ at a 1:2 molar ratio in CH_2Cl_2/THF (5:1) and warming up under reflux results in the formation of the colorless [$\{NbOCl_4(THF)\}_2AlCl(THF)_3$] compound **3**. Its IR spectrum shows the expected bands due to ν(C$-$O$-$C) of coordinated THF molecules at 1042 (m), 1008 (s), and 830 (vs) cm^{-1} and a band at 905 (s) cm^{-1} due to ν(Nb=O) vibrations.

The stoichiometry of **1**$-$**3** and the shifting of the ν(Nb=O) band to lower frequencies in comparison to the [$NbOCl_4(THF)$]$^-$ ion suggested that the [$NbOCl_4(THF)$]$^-$ unit was coordinated by solvated Mg^{2+} and Al^{3+} cations. This was confirmed by an X-ray structural study.

X-ray Diffraction Study of 1$-$**3.** The X-ray analyses of **1** and **2** revealed that the magnesium atom in both compounds is octahedrally coordinated by four tetrahydrofuran molecules and two [$NbOCl_4(THF)$]$^-$ units *via* O atoms in *trans* positions. The structure of compounds **1** and **2** is shown in Figure 1, and bond dimensions are in Table 1. The Mg$-$O(1,2) bond averages 2.107(4) Å (in **1**) and 2.123(6) Å (in **2**) are shorter than the respective Mg$-$O distances of 2.159(6) and 2.175(5) Å in [$\{MoOCl_4(THF)\}_2Mg(THF)_4$][5] but similar to the Mg$-$O distances of 2.11(1) and 2.09(1) Å in [$(ReMe_4O)_2Mg(THF)_4$] and [$\{o\text{-}C_6H_4(CH_2)_2WO\}_2Mg(THF)_4$],[6,7] respectively. When they are viewed along the Nb$-$Mg$-$Nb axis, the Mg(THF)$_4$ units look like a system of propellers. Comparison of the corresponding geometrical parameters of [$\{MoOCl_4(THF)\}_2Mg(THF)_4$][5] with **1** and **2** indicates no noticeable differences.

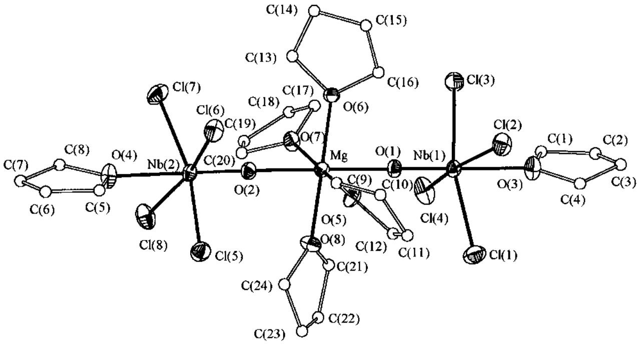

Figure 1. View of the [$\{NbCl_4O(thf)\}_2Mg(thf)_4$] molecule in compounds **1** and **2** (H atoms and CH_2Cl_2 in **1** and THF in **2** omitted for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for **1**$-$**3**

	1	**2**[a]	**3**
Mg$-$O(1)	2.095(4)	2.123(6)	
Mg$-$O(2)	2.118(4)		
Mg$-$O(5)	2.071(4)	2.065(7)	
Mg$-$O(6)	2.073(4)	2.080(7)	
Mg$-$O(7)	2.065(4)		
Mg$-$O(8)	2.090(4)		
Nb(1)$-$O(1)	1.728(4)	1.709(6)	1.751(3)
Nb(1)$-$O(3)	2.324(4)	2.348(8)	2.283(4)
Nb(1)$-$Cl(1)	2.358(2)	2.366(3)	2.336(2)
Nb(1)$-$Cl(2)	2.380(2)	2.364(3)	2.385(2)
Nb(1)$-$Cl(3)	2.374(2)	2.382(3)	2.378(2)
Nb(1)$-$Cl(4)	2.369(2)	2.364(3)	2.347(2)
Nb(2)$-$O(2)	1.718(4)		1.742(3)
Nb(2)$-$O(4)	2.369(4)		2.305(3)
Nb(2)$-$Cl(5)	2.378(2)		2.348(2)
Nb(2)$-$Cl(6)	2.380(2)		2.381(2)
Nb(2)$-$Cl(7)	2.366(2)		2.371(7)
Nb(2)$-$Cl(8)	2.361(2)		2.349(2)
Al$-$Cl(9)			2.196(2)
Al$-$O(1)			1.899(4)
Al$-$O(2)			1.915(4)
Al$-$O(5)			1.944(4)
Al$-$O(6)			1.964(4)
Al$-$O(7)			1.944(4)
O(1)$-$Mg$-$O(2)	179.4(2)		
O(1)$-$Nb(1)$-$O(3)	178.3(2)		178.3(2)
O(2)$-$Nb(2)$-$O(4)	178.6(2)		177.2(2)
Mg$-$O(1)$-$Nb(1)	178.2(2)		
Mg$-$O(2)$-$Nb(2)	178.3(2)		
O(1)$-$Al$-$O(2)			174.5(2)
Al$-$O(1)$-$Nb(1)			169.3(2)
Al$-$O(2)$-$Nb(2)			171.9(2)

[a] Mg occupies $^1/_2$ side, and therefore we give only the independent parameters of the magnesium atom coordination sphere.

The structure of the [$\{NbOCl_4(THF)\}_2AlCl(THF)_3$] (**3**) is shown in Figure 2. Some important molecular geometry parameters are given in Table 1. In the molecule the aluminum atom is octahedrally coordinated by three oxygen atoms of coordinated tetrahydrofuran molecules, one chlorine atom, and two oxo oxygen atoms of two [$NbOCl_4(THF)$]$^-$ units in *trans* positions. Interestingly, the Al$-$O(5,6,7) bond average 1.941(4) Å is similar to the Al$-$O bond average of 1.94(1) Å in the [$AlCl_2(THF)_4$]$^+$ cation.[15] The Al$-$Cl(9) distance, 2.196(2) Å, is slightly shorter than those found in *cis*-[$AlCl_2(donor)_4$]$^+$ complexes: 2.204(2) Å in [$AlCl_2(DME)_4$]$^+$,[15] and 2.201(1) Å in [$AlCl_2(12\text{-}crown\text{-}4)$]$^+$.[16] The structure and bond

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Table 2. Crystal and Structure Refinement Data for Complexes **1**−**3**

	1	**2**	**3**
empirical formula	$C_{40}H_{80}Cl_8MgNb_2O_{12}$	$C_{25}H_{50}Cl_{10}MgNb_2O_8$	$C_{20}H_{40}AlCl_9Nb_2O_7$
M	1246.77	1043.28	924.37
T/K	298(1)	298(1)	300(1)
cryst system	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*2$_1$/*n*	$P\bar{1}$
a/Å	16.943(4)	10.855(3)	12.051(3)
b/Å	13.365(3)	15.672(5)	13.794(4)
c/Å	26.488(6)	26.552(8)	14.948(4)
α/deg	90.0	90.0	67.17(3)
β/deg	102.97(2)	101.73(3)	78.70(2)
γ/deg	90.0	90.0	65.03(3)
V/Å^3	5845(3)	4423(3)	2075(2)
Z	4	4	2
D_c/g•cm^{-3}	1.417(1)	1.567(1)	1.480(1)
D_m/g•cm^{-3}	1.428	1.552	1.470
μ/mm^{-1}	0.82	1.17	1.18
F(000)	2584	2112	928
hkl ranges	0−20; 0−13; −29 to 25	0−13; 0−20; −35 to 31	0−12; −16−16; −18 to 18
unique reflcns	1414	3855	4313
goodness of fit on F^2	1.066	1.043	1.081
final R_1[a]	0.0435	0.0354	0.0377
wR_2[b]	0.1141	0.0840	0.1009
R_{int}	0.0217	0.0273	0.0315

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$. [a] w$R_2 = \{\sum[w(F^2{}_o - F^2{}_c)^2]/\sum[w(F^2{}_o)^2]\}^{1/2}$.

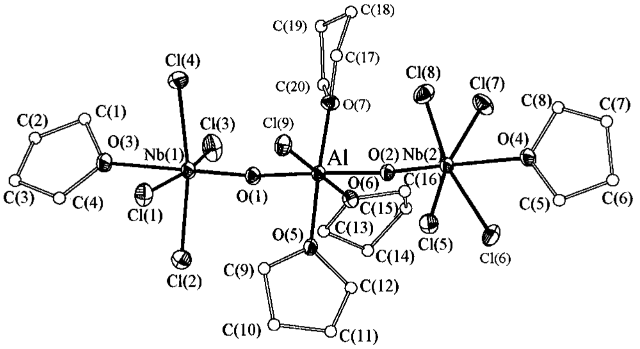

Figure 2. View of the [{$NbCl_4O$(thf)}$_2$AlCl(thf)$_3$] molecule (H atoms omitted for clarity).

lengths and angles of the [$NbOCl_4$(THF)]$^-$ units, in **1**−**3**, are similar to those found in [$Nb_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(THF)_3$][$NbOCl_4$(THF)], [$Nb_3O_2(O_2CCH_3)_6(THF)_3$][$NbOCl_4$(THF)], and [($\eta^5$-$C_5H_5$)Nb(CNCMe$_3$)$_4$][$NbOCl_4$(THF)] compounds.[8]

Conclusions

The adducts of niobium−oxo species [$NbOCl_4$(THF)]$^-$ with Mg^{2+} and Al^{3+} were unknown. Note that the [{$NbOCl_4$(THF)}$_2$Mg(THF)$_4$]·4THF, [{$NbOCl_4$(THF)}$_2$AlCl(THF)$_3$] as well as [{$NbOCl_4$(THF)}$_2$Mg(THF)$_4$]•2CH_2Cl_2 could be obtained in tetrahydrofuran or a mixture of THF/CH_2Cl_2 solvents, respectively, similar to [(ReMe$_4$O)$_2$Mg(THF)$_4$] and [{*o*-$C_6H_4(CH_2)_2$-WO}$_2$ Mg(THF)$_4$],[6,7] whereas the [{MoOCl$_4$(THF)}$_2$Mg(THF)$_4$] and [MgMo(μ-Cl)$_3$Cl$_2$O(THF)$_3$] molecular compounds could be obtained only in halogenated solvents, [Mg(THF)$_6$][MoOCl$_4$(THF)]$_2$ and [$Mg_2(\mu\text{-}Cl)_3$(THF)$_6$][MoOCl$_4$(THF)] salts are formed in THF.[5] It seems most likely that the course of the reaction discussed here depends on the solution equlibrium. The formation of [Mg(THF)$_6$]$^{2+}$, [$Mg_2(\mu\text{-}Cl)_3$(THF)$_6$]$^+$, [MgCl(THF)$_5$]$^+$, [$MgCl_4$]$^{2-}$, [$AlCl_2$(THF)$_4$]$^+$, and [$AlCl_4$]$^-$ ions from $MgCl_2$ and $AlCl_3$ in tetrahydrofuran is well documented.[17,16] On the other hand the abstraction of the oxygen atom from the tetrahydrofuran by $NbCl_4$ and $NbCl_5$ occurs under reflux to produce oxo trihalides and alkyl halides.[18]

The ionization products of $MgCl_2$ or $AlCl_3$ (eqs 1 and 2) react with $NbOCl_3$, and the reaction equilibria would depend upon

$$\begin{array}{rl} [\mathrm{MgCl_2(THF)_2}] + 4\mathrm{THF} \rightarrow & [\mathrm{Mg(THF)_6}]^{2+} + 2\mathrm{Cl}^- \\ & \downarrow + 2\mathrm{NbOCl_3} \qquad (1) \\ & [\{\mathrm{NbOCl_4(THF)}\}_2\mathrm{Mg(THF)_4}] \end{array}$$

$$\begin{array}{rl} \mathrm{AlCl_3} + 5\mathrm{THF} \rightarrow & [\mathrm{AlCl(THF)_5}]^{2+} + 2\mathrm{Cl}^- \\ & \downarrow + 2\mathrm{NbOCl_3} \qquad (2) \\ & [\{\mathrm{NbOCl_4(THF)}\}_2\mathrm{AlCl(THF)_3}] \end{array}$$

the least soluble species. It follows that the [$NbOCl_4$(THF)]$^-$ anion forms with the [Mg(THF)$_6$]$^{2+}$ and [AlCl(THF)$_5$]$^+$ cations the least soluble molecular compounds which then precipitate and cause the shift of the reaction equilibria to the formation of complexes **1**−**3**.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**3** are available. Access information is given on any current masthead page.

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