# Preparation and crystal structures of donor-functionalized 2,2′-oxydiethanol complexes of titanium, yttrium, magnesium and sodium

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The complexes [*cis*-$TiCl_2(\eta^3$-digol)(THF)], [$YCl_3(\eta^3$-$H_2$digol)(THF)], [$Mg_2(\mu$-$Cl)_2(\eta^3$-$H_2digol)_2(THF)_2]Cl_2$ and [$Na_2(\mu,\eta^2$-$H_2digol)_2(\eta^3$-$Hdigol)_2$] have been synthesized and structurally characterized by X-ray diffraction. Complex **1** consists of a dichlorotitanium(IV) core with a doubly deprotonated *mer*-coordinated tridentate 2,2′-oxydiethanlato(2−) and THF ligands. Compound **2** has a distorted pentagonal bipyramidal structure with chlorine ligands in the axial positions. In the [$Mg_2(\mu$-$Cl)_2(\eta^3$-$H_2digol)_2(THF)_2]^{2+}$ cation of **3**, each magnesium atom is octahedrally coordinated by two μ − Cl atoms, the chelate tridentate $\eta^3$-$H_2$digol ligand and the oxygen atom of the coordinated THF molecule. The structure of **4** includes two six-coordinated sodium atoms linked by two OH bridges. Three oxygen atoms of $\eta^3$-Hdigol and one ether oxygen atom of the $\eta^2$-$H_2$digol ligands complete the coordination sphere of the sodium atoms. One of the oxygen atoms of the $\eta^2$-$H_2$digol hydroxyl group remains uncoordinated.

We have begun carrying out systematic investigations of the structural chemistry of 2,2′-oxydiethanol metal compounds. A survey of excellent reviews on metal alkoxides as important precursors in the sol-gel route for the preparation of thin oxide layers and oxide materials with special physical properties[1] revealed that the chemistry of polyethylene glycols is relatively unexplored. Polyethylene glycols have been hinted at as possible phase-transfer catalysts and separation agents.[2,3] Donor-functionalized 2,2′-oxydiethanol ligands can perfectly surround metals as at least three coordination sites are at their disposal: an alcoholate double function for charge neutralization and a donor function to compensate the electronic demands of the metal ion. Hirashima *et al.* have published several accounts of the tri- and tetraethylene glycols of hydrated lanthanide nitrates.[4,5] Some work with alkali and alkaline-earth metals has also appeared.[6–8] The 2,2′-oxydiethanol complex of molybdenum [*cis*-Mo(μ-O)O($\eta^3$-digol)] with *mer*-coordination of the tridentate ligand has been described as well.[9] We will follow the abbreviations used for the 2,2′-oxydiethanol in that paper: 2,2′-oxydiethanol = $H_2$digol, 2,2′-oxydiethanolato(1−) = Hdigol and 2,2′-oxydiethanolato(2−) = digol.

This study was intended to further the understanding, from a solid-state point of view, of the factors such as coordination number, coordination geometry, metal size and oxidation state, that control the transformation of $H_2$digol to Hdigol and digol ligands. Here, we report the synthesis and structural study of the monomeric [*cis*-$TiCl_2(\eta^3$-digol)(THF)] (**1**), [$YCl_3(\eta^3$-$H_2$digol)(THF)] (**2**) and dimeric [$Mg_2(\mu$-$Cl)_2(\eta^3$-$H_2digol)_2(THF)_2]Cl_2$ (**3**) [$Na_2(\mu$, $\eta^2$-$H_2digol)_2(\eta^3$-$Hdigol)_2$] (**4**) compounds.

## Results

### Preparation of compounds 1–4

Titanium alkoxides have been extensively studied for several decades by Bradley and others.[1] In a continuation of these studies we found that the direct reaction of $TiCl_4$ with $H_2$digol in a 1 : 1 molar ratio in toluene gives a bright-yellow precipitate. After recrystallization from THF the yellow air-sensitive compound **1** of composition $TiCl_2 \cdot$ digol · THF was formed, eqn (1), which is stable under dinitrogen.

$$TiCl_4 + H_2\text{digol} \xrightarrow{\text{toluene—THF}} [\textit{cis}\text{-}TiCl_2(\eta^3\text{-digol})(THF)] + 2\ HCl \quad (1)$$

Liberation of HCl during reaction 1, the absence of ν(OH) vibrations in the IR spectrum and the stoichiometry suggested that compound **1** is a [*cis*-$TiCl_2(\eta^3$-digol)(THF)] species with a $\eta^3$-digol coordinated ligand. This formulation was confirmed by an X-ray structural study.

Yttrium trichloride, which is a common starting material for syntheses of many types of complexes, typically crystallizes in the presence of donor ligands such as THF to form the [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] salt or polymeric [$YCl_3 \cdot 2$ THF] species;[10] compounds such as [$YCl_3(DME)_2$] (DME = dimethoxyethane)[11] and [$YCl_3$(EO3)(18-crown-6)]$_n^5$ (EO3 = triethylene glycols) are seen as well. Although yttrium alkoxides and aryloxides generally are polymeric,[1] we expected that the yttrium $\eta^3$-digol alkoxide, similar to **1**, should be monomeric. Compound **2** was obtained by two routes, the first being accidental. Treatment of [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] with **4** (the product of a reaction of $H_2$digol with metallic sodium) gave colorless compound **2**. It was structurally characterized as [$YCl_3(\eta^3$-$H_2$digol)(THF)] by X-ray crystallography, as described below. Having established the structure of compound **2**, we sought a rational synthesis of it and found that it can be obtained in high yield directly by treatment of $YCl_3$ with $H_2$digol in THF.

$$YCl_3 + H_2\text{digol} \xrightarrow{\text{THF}} [Y(\eta^3\text{-}H_2\text{digol})(THF)Cl_3] \quad (2)$$

To explain how the metal size and oxidation state compensate the electronic demands of the tridentate $H_2$digol ligand, the magnesium species [$Mg_2(\mu$-$Cl)_2(\eta^3$-$H_2digol)_2(THF)_2]Cl_2$, **3**, was investigated. Compound **3** was synthesized from [$MgCl_2(THF)_2$] and **4** in THF. The IR spectrum shows bands at 3400vs, 3150vs and 1625w cm$^{-1}$, assigned to ν(OH) which suggested the coordinated protonated form of $H_2$digol. This was confirmed by an X-ray structural study.

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To understand the transformation of $YCl_3$ and $MgCl_2$ into the yttrium and magnesium $\eta^3$-$H_2$digol compounds **2** and **3**, it was important to determine the crystal structure of $[Na_2(\mu, \eta^2\text{-}H_2digol)_2(\eta^3\text{-}Hdigol)_2]$. Reaction of metallic sodium with $H_2$digol in a 1 : 2 ratio in THF gave colorless needle-shaped crystals.

$$2\ Na + 4\ H_2digol \xrightarrow{THF} [Na_2(\mu, \eta^2\text{-}H_2digol)_2(\eta^3\text{-}Hdigol)_2] + H_2 \qquad (3)$$

Diffraction study of the crystal established that **4** is a dimeric compound.

## Crystal structures

The crystalline compound **1** is composed of discrete monomeric molecules. Its structure is depicted in Fig. 1 and selected geometrical parameters are listed in Table 1. The structural analysis has shown the complex to be of formula [*cis*-$TiCl_2(\eta^3$-digol)(THF)] with *mer*-coordination of the tridentate deprotonated digol ligand, which forms two buckled five-membered rings. Two chlorine atoms and the oxygen atom of THF complete the octahedral sphere of the titanium atom. The smallest angles about the titanium atoms [74.9(1)°] are between alkoxo and ether oxygen atoms of the digol molecule. The Ti—Cl(1) and Ti—Cl(2) distances of 2.298(1) and 2.321(1) Å are comparable to corresponding values in [*cis*-$TiCl_4(THF)_2$][12] and $[TiCl_3(\eta^2$-thffoH)(THF)][13](thfo = 2-tetrahydrofurfuroxide) compounds, where the average values of the Ti—Cl distances are 2.298(3) and 2.321(3) Å, respectively. The Ti—$O_{(alkoxo)}$ bond lengths of 1.811(2) and 1.816(2) Å are similar to those found in $[TiCl_3(\eta^2$-thffo)(THF)][13] [1.806(2) Å] but are slightly longer than in $[Ti_2Mg_2(\mu\text{-}Cl)_4(\mu\text{-}OEt)_4(\mu_3\text{-}OEt)_4(OEt)_8]$[14] [1.753(4)–1.770(5) Å]. The Ti—$O_{(ether)}$ bond lengths of 2.158(2) and 2.185(2) Å correspond to those found in other titanium compounds.[15,16]

The structure of **2** is shown in Fig. 2. Selected bond lengths, bond angles and torsion angles are listed in Table 2. The presented compound in the solid state is monomeric. It has a distorted pentagonal bipyramidal geometry with chlorine ligands in the axial positions. The yttrium atom is surrounded by four oxygen atoms and three chlorine atoms. The chelate tridentate protonated $\eta^3$-$H_2$digol ligand develops two similar five-membered rings. The O—Y—O angles vary from 64.8(2)° to 95.7(1)° with the smallest angle being between hydroxyl and ether oxygen atoms of the $H_2$digol ligand. The Cl(1), Cl(2) and Cl(3) atoms are located 2.580(2), 2.643(2) and 2.595(2) Å away from the yttrium atom, respectively. These distances are similar to those found in the $[YCl_3(DME)_2]$[11] and $[YCl_3(C_4H_7O)\{CH_2CO_2Et\}_2]$[17] compounds. The Y—$O_{(hydroxyl)}$($H_2$digol) bond lengths [2.372(4) and 2.368(5) Å] are comparable to the Y—$O_{(ether)}$(THF) distance [2.355(4) Å] and, as expected, are somewhat shorter than the Y—$O_{(ether)}$($H_2$digol) distance [2.436(4) Å]. These Y—$O_{(hydroxyl)}$ and Y—$O_{(ether)}$ distances are similar to the corresponding bond lengths that have been observed in compounds containing seven-coordinate Y atoms.[10,11] Two hydroxyl groups of the $H_2$digol ligand are involved in hydrogen bonds, the first with oxygen atoms of an uncoordinated THF molecule and the second one with a chlorine atom from a neighboring yttrium complex: O(11)—H(11)···O(30) and O(12)—H(12)···Cl(2)$^{(i)}$; (*i*) = $-x, -y, 1 - z$.

The crystal structure of **3** consists of $[Mg_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2digol)_2(THF)_2]^{2+}$ cations and $Cl^-$ anions in a 1 : 2 ratio, as well as $CH_2Cl_2$ solvent molecules. The geometry of the

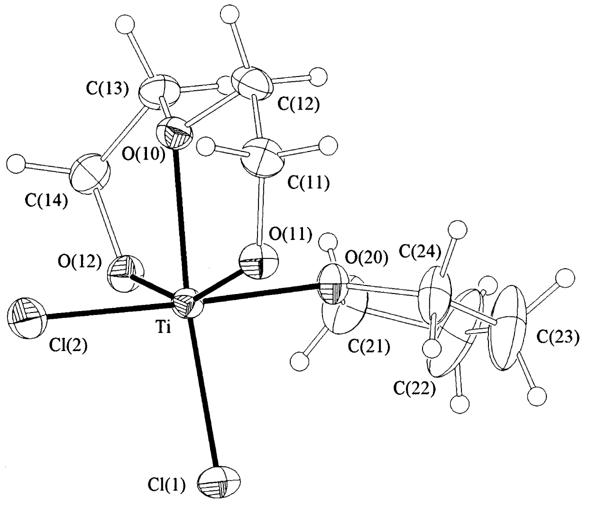

**Fig. 1** The molecular structure of **1** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level

**Table 1** Selected bond lengths/Å and bond angles/° for **1**

| | | | |
|---|---|---|---|
| Ti—O(11) | 1.811(2) | Ti—O(10) | 2.185(2) |
| Ti—O(12) | 1.816(2) | Ti—Cl(1) | 2.298(2) |
| Ti—O(20) | 2.158(2) | Ti—Cl(2) | 2.321(2) |
| Cl(1)—Ti—Cl(2) | 95.6(1) | O(12)—Ti—O(10) | 74.9(1) |
| O(11)—Ti—Cl(1) | 104.4(1) | O(12)—Ti—O(20) | 85.2(1) |
| O(11)—Ti—Cl(2) | 94.0(1) | O(10)—Ti—Cl(1) | 173.4(1) |
| O(11)—Ti—O(12) | 149.0(1) | O(10)—Ti—Cl(2) | 91.0(1) |
| O(11)—Ti—O(10) | 75.1(1) | O(20)—Ti—Cl(1) | 87.0(1) |
| O(11)—Ti—O(20) | 85.3(1) | O(20)—Ti—Cl(2) | 177.4(1) |
| O(12)—Ti—Cl(1) | 104.6(1) | O(20)—Ti—O(10) | 86.3(1) |
| O(12)—Ti—Cl(2) | 94.2(1) | | |

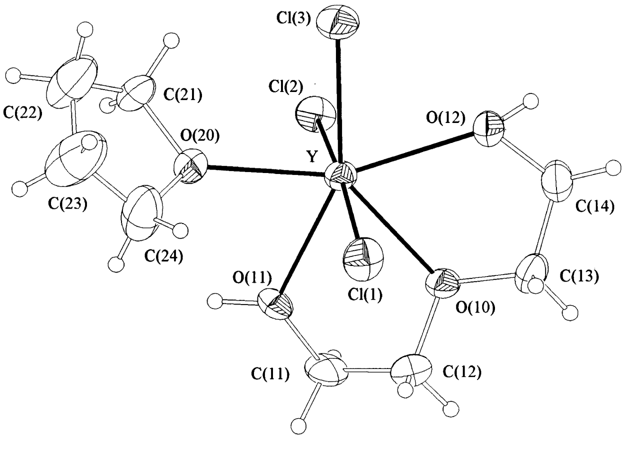

**Fig. 2** The molecular structure of **2** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level

**Table 2** Selected bond lengths/Å and bond angles/° for **2**

| | | | |
|---|---|---|---|
| Y—Cl(1) | 2.580(2) | Y—O(12) | 2.368(5) |
| Y—Cl(2) | 2.643(2) | Y—O(10) | 2.436(4) |
| Y—Cl(3) | 2.595(2) | Y—O(20) | 2.355(4) |
| Y—O(11) | 2.372(4) | | |
| Cl(1)—Y—Cl(2) | 171.0(2) | O(12)—Y—O(10) | 64.8(2) |
| Cl(1)—Y—Cl(3) | 95.7(1) | O(10)—Y—Cl(1) | 82.2(2) |
| Cl(2)—Y—Cl(3) | 93.3(1) | O(10)—Y—Cl(2) | 91.4(2) |
| O(11)—Y—Cl(1) | 86.9(2) | O(10)—Y—Cl(3) | 140.8(2) |
| O(11)—Y—Cl(2) | 84.7(2) | O(20)—Y—Cl(1) | 91.5(2) |
| O(11)—Y—Cl(3) | 153.7(2) | O(20)—Y—Cl(2) | 89.0(2) |
| O(11)—Y—O(10) | 65.5(2) | O(20)—Y—Cl(3) | 81.9(2) |
| O(12)—Y—Cl(1) | 92.7(2) | O(20)—Y—O(10) | 137.1(2) |
| O(12)—Y—Cl(2) | 90.2(2) | O(20)—Y—O(11) | 71.9(2) |
| O(12)—Y—Cl(3) | 76.3(2) | O(20)—Y—O(12) | 158.1(2) |
| O(12)—Y—O(11) | 129.8(2) | | |

$[Mg_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2digol)_2(THF)_2]^{2+}$ cation in **3** is presented in Fig. 3 and selected bond distances and angles are given in Table 3. The centrosymmetric cation of the salt **3** in the crystalline state is a dimer composed of two octahedra, which share a common edge. Each magnesium atom is octahedrally coordinated by two μ-Cl atoms, the chelate tridentate protonated $\eta^3$-$H_2$digol ligand and the oxygen atom of the THF molecule. Angles around the magnesium atom (Table 3) differ from ideal octahedral values. This deformation of the coordination sphere is mainly due to constraints arising from formation of two five-membered rings as well as the $Mg(\mu\text{-}Cl)_2Mg'$ bridge. It is worth noting that the planar $Mg(\mu\text{-}Cl)_2Mg'$ bridges form a parallelogram, with Mgμ—Cl(1) and Mg′μ-Cl(1) bond distances of 2.597(3) and 2.379(3) Å, respectively. In the plane of this parallelogram also lie the Cl(1), O(10), O(20), Cl(1)′, O(10)′ and O(20)′ atoms. The non-bonded Mg···Mg′ distance of 3.628(4) Å is longer than the corresponding value of 3.169 Å that was found in the tri-μ-chlorohexakis(tetrahydrofuran) dimagnesium(II) cation[18] where two magnesium atoms are bridged by three chlorine atoms. The $Mg—O_{(ether)}(H_2digol)$ is *ca.* 0.056(5) Å longer than the $Mg—O_{(hydroxyl)}(H_2digol)$ distances. These Mg—O distances are comparable to those found in other compounds: for example in the $[Mg(THF)_6]^{2+}$ cation[19] $Mg—O_{(ether)}$ bond lengths vary from 2.088(6) to 2.156(6) Å and in the $[Mg(EtOH)_6]^{2+}$ cation[20] the $Mg—O_{(hydroxyl)}$ distance is 2.069(3) Å. Each of the hydroxyl groups of the $\eta^3$-$H_2$digol ligand forms strong hydrogen bonds with uncoordinated $Cl^-$ anions: O(11)—H(11)···Cl(6) and O(12)H(12)···Cl(6)$^{(i)}$; $(i) = 2 - x, -y, 1 - z$.

The crystal structure of $[Na_2(\mu, \eta^2\text{-}H_2digol)_2(\eta^3\text{-}Hdigol)_2]$, **4**, is shown in Fig. 4 and some important molecular geometry parameters are given in Table 4. Each sodium atom is six-coordinated by two μ-hydroxyl O(12) and (12′) atoms, the ether oxygen atom O(10) of the $\eta^2$-$H_2$digol and three oxygen atoms of the $\eta^3$-Hdigol ligands. One of the oxygen atoms of the $\eta^2$-$H_2$digol hydroxyl group remains uncoordinated. The Na—O bond lengths and the O—Na—O bond angles range from 2.302(3)–2.547(3) Å and 65.1(1)°–114.8(2)°, respectively. These geometrical parameters are in accordance with those found in other six-coordinated sodium compounds.[21,22] The O(11)—H(11) and O(22)—H(22) groups are linked through intramolecular hydrogen bonds to O(11) atoms [O(11)—H(11)···O(12′), O(22)—H(22)···O(11′)]; the O(11)—H(11) group is also involved in intermolecular hydrogen bridges with the O(12) atom from the symmetry-related Hdigol molecule [O(21)—H(21)···O(11)$^{(i)}$; $(i) = 1 - x, 2 - y, 2 - z$].

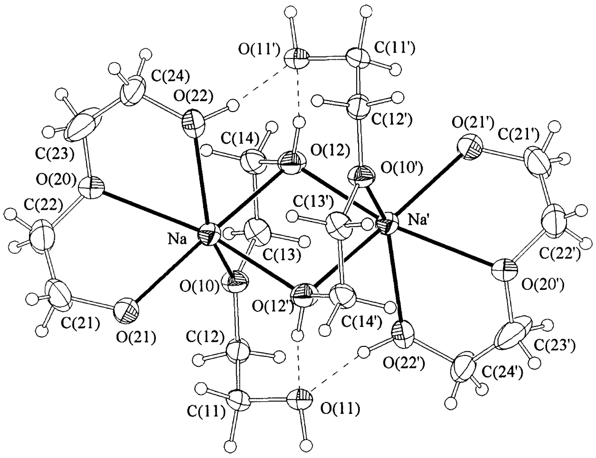

**Fig. 4** The molecular structure of **4** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level

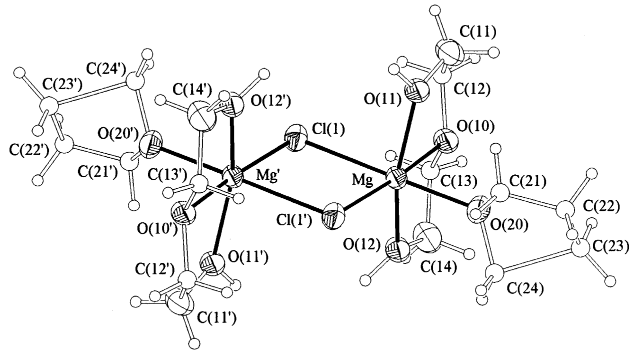

**Fig. 3** The molecular structure of **3** with atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level

## Discussion

The results presented here show that the 2,2′-oxydiethanol species can be easily coordinated by a metal center and transformed to Hdigol and digol. During reaction 1 monomeric *mer*-coordinated $\eta^3$-digol titanium(IV) {$[cis\text{-}TiCl_2(\eta^3\text{-}digol)(THF)]$, **1**} is formed. Up to now the monomeric titanium dialkoxides have been unknown. The corresponding reaction with $YCl_3$ led to the formation of $[YCl_3(\eta^3\text{-}digol)(THF)]$, **2**. It has a distorted pentagonal bipyramidal structure and the yttrium atom is surrounded by three $\eta^3$-$H_2$digol oxygen atoms, one THF oxygen atom and three chlorine atoms. The reaction of $MgCl_2$ with $H_2$digol in tetrahydrofuran gave the $[Mg_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2digol)_2(THF)_2]Cl_2$, **3**, salt. In the crystalline state the centrosymmetric cation $[Mg_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2digol)_2(THF)_2]^{2+}$ is a dimer composed of

**Table 3** Selected bond lengths/Å and bond angles/° for **3**

| | | | |
|---|---|---|---|
| Mg—Cl(1) | 2.597(3) | Mg—O(10) | 2.102(5) |
| Mg—Cl(1′) | 2.379(3) | Mg—O(20) | 2.090(4) |
| Mg—O(11) | 2.041(4) | Mg—Mg′ | 3.628(4) |
| Mg—O(12) | 2.056(4) | | |
| Cl(1′)—Mg—Cl(1) | 86.5(1) | O(12)—Mg—O(10) | 77.2(2) |
| O(11)—Mg—Cl(1) | 90.2(2) | O(12)—Mg—O(20) | 89.8(2) |
| O(11)—Mg—Cl(1′) | 102.7(2) | O(10)—Mg—Cl(1′) | 175.4(2) |
| O(11)—Mg—O(12) | 154.4(2) | O(10)—Mg—Cl(1) | 88.9(2) |
| O(11)—Mg—O(10) | 77.2(2) | O(20)—Mg—Cl(1) | 178.9(2) |
| O(11)—Mg—O(20) | 90.0(2) | O(20)—Mg—Cl(1′) | 94.5(2) |
| O(12)—Mg—Cl(1) | 89.6(2) | O(20)—Mg—O(10) | 90.1(2) |
| O(12)—Mg—Cl(1′) | 102.9(2) | Mg′—Cl(1)—Mg | 93.5(1) |

Primed atoms are related to the unprimed ones by: $-x + 2, -y, -z + 1$

**Table 4** Selected bond lengths/Å and bond angles/° for **4**

| | | | |
|---|---|---|---|
| Na—O(12) | 2.547(3) | Na—O(22) | 2.457(3) |
| Na—O(12′) | 2.302(3) | Na—O(20) | 2.483(3) |
| Na—O(10) | 2.487(3) | Na—Na′ | 3.561(3) |
| Na—O(21) | 2.332(3) | | |
| O(12′)—Na—O(21) | 97.4(2) | O(22)—Na—O(20) | 68.9(1) |
| O(12′)—Na—O(22) | 114.8(2) | O(22)—Na—O(10) | 140.8(2) |
| O(12′)—Na—O(10) | 84.4(2) | O(22)—Na—O(12) | 81.9(1) |
| O(12′)—Na—O(20) | 167.2(2) | O(20)—Na—O(10) | 100.1(2) |
| O(12′)—Na—O(12) | 85.6(2) | O(20)—Na—O(12) | 107.1(2) |
| O(10)—Na—O(12) | 65.1(1) | C(12)—O(10)—Na | 131.3(2) |
| O(21)—Na—O(22) | 107.4(2) | C(13)—O(10)—Na | 114.4(2) |
| O(21)—Na—O(20) | 69.9(2) | C(14)—O(12)—Na′ | 132.5(3) |
| O(21)—Na—O(10) | 103.1(2) | C(14)—O(12)—Na | 97.1(2) |
| O(21)—Na—O(12) | 167.5(2) | Na′—O(12)—Na | 94.4(1) |

Primed atoms are related to the unprimed ones by: $-x, -y + 2, -z + 2$

**Table 5** Crystal data and structure refinement details for complexes **1**, **2**, **3** and **4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_8H_{16}Cl_2O_4Ti$ | $C_{12}H_{26}O_5Cl_3Y$ | $C_{20}H_{44}Cl_{12}Mg_2O_8$ | $C_{16}H_{38}Na_2O_{12}$ |
| $M$ | 295.01 | 445.60 | 886.57 | 468.45 |
| $T$/K | 298(2) | 298(2) | 299(2) | 299(2) |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $Pn$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ |
| $a$/Å | 7.262(3) | 14.020(5) | 9.994(2) | 8.057(2) |
| $b$/Å | 8.702(3) | 9.404(2) | 9.973(2) | 17.771(4) |
| $c$/Å | 9.788(3) | 15.696(6) | 11.450(2) | 8.986(2) |
| $\alpha$/deg | | | 65.23(3) | |
| $\beta$/deg | 90.16(3) | 110.82(3) | 83.70(3) | 114.68(3) |
| $\gamma$/deg | | | 79.46(3) | |
| $U$/Å$^3$ | 618.5(4) | 1934.3(11) | 1018.0(3) | 1169.1(5) |
| $Z$ | 2 | 4 | 1 | 2 |
| $D_c$/g cm$^{-3}$ | 1.584 | 1.530 | 1.433 | 1.331 |
| $\mu$/mm$^{-1}$ | 1.115 | 3.443 | 0.882 | 0.142 |
| $F$(000) | 304 | 912 | 456 | 504 |
| No. of data collected | 1941 | 2159 | 2308 | 1584 |
| No. of data with $I > 2\sigma(I)$ | 1789 | 1390 | 2102 | 1448 |
| No. of parameters varied | 136 | 198 | 210 | 148 |
| $R_1$[a] | 0.0262 | 0.0354 | 0.0598 | 0.0649 |
| $wR_2$[b] | 0.0692 | 0.0931 | 0.1680 | 0.1705 |

[a] $R_1 = \Sigma(F_0 - F_c)/\Sigma F_0$

[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

two octahedra related by a crystallographic inversion center and sharing an edge. In the case of monodentate O-donor ligands such as THF the formation of dimeric cationic species such as $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$is well-documented.[19,23]

In species **4**, instead of the expected digol ligand, Hdigol and $H_2$digol molecules act as ligands. This fact explains why, during the reactions of **4** with [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] and $MgCl_2$, compounds **2** and **3** are formed respectively, in which $H_2$digol molecules are coordinated to the metal centers. It follows that in the described reactions compound **4** acts as a donor of $H_2$digol while Hdigol remains in the sodium coordination sphere.

## Experimental

### Materials and techniques

All manipulations were carried out under dry dinitrogen following standard Schlenk techniques. All solvents were distilled under dinitrogen from the appropriate drying agents prior to use. $TiCl_4$, $YCl_3$, $MgCl_2$ and 2,2′-oxydiethanol were purchased from Aldrich Chemical Co. The [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] compound was prepared by the reported procedure.[10] Infrared spectra were recorded on a Perkin–Elmer 180 instrument in Nujol mulls.

### Syntheses

[*cis*-$TiCl_2$($^3$-digol)(THF)] (**1**). To a solution of $TiCl_4$ (5.7 g, 30 mmol) in toluene (120 cm$^3$) was added dropwise $H_2$digol (2.8 cm$^3$, 30 mmol). The mixture was stirred at room temperature. After 72 h, the light-yellow precipitate was filtered off and washed with toluene (3 × 5 cm$^3$). The solid was redissolved in 80 cm$^3$ THF and stirred for 1 h. Next, the yellow species **1** was filtered and the filtrate was concentrated *in vacuo* to 50 cm$^3$ and held at 273 K. Good-quality crystals, suitable for X-ray examination, were taken directly from the filtrate. Yield: 4.3 g (49%). Anal. calcd. for $C_8H_{16}O_4Cl_2Ti$: Cl, 24.04; Ti, 16.23. Found: Cl, 24.21; Ti, 16.28%. IR (Nujol, cm$^{-1}$): 270w, 332s, 359vs, 380sh, 392s, 453m 554vs, 720m, 801w, 812w, 920w, 918s, 937s, 992w, 1020vs, 1033sh, 1220m, 1245w.

[$YCl_3(\eta^3\text{-}H_2$digol)(TF)] (**2**). *Method 1.* The compound [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (4.5 g, 10 mmol) was dissolved in 50 cm$^3$ THF and compound **4** (1.2 g, 5 mmol) was added. The reaction mixture was stirred for 24 h then the solution was filtered and its volume was reduced *in vacuo* to 20 cm$^3$ and left at 273 K to form colorless crystals, which were filtered and used for X-ray structural determination.

*Method 2.* To a solution of [*trans*-$YCl_2(THF)_5$][*trans*-$YCl_4(THF)_2$] (4.5g, 10 mmol) in 50 cm$^3$ THF was added $H_2$digol (1.6 g, 10 mmol) and the mixture was stirred. A white precipitate formed immediately, which was filtered off and washed with THF (3 × 5 cm$^3$). Yield 3.4 g (92%). Anal. calcd for $C_8H_{18}O_4Cl_3Y$: C, 25.73; H, 4.86; Cl, 28.48 Found: C, 26.02; H, 5.14; Cl, 28.23%. IR (Nujol, cm$^{-1}$): 240s, 268s, 560m, 924vs, 992w, 1038vs, 1070vs, 1100vs, 1232s, 1276m, 1640w, 3200vs,br.

[$Mg_2(\mu\text{-}Cl)_2(\eta^3\text{-}H_2$digol$)_2(THF)_2]Cl_2$ (**3**). To a solution of [$MgCl_2(THF)_2$] (1 g, 4 mmol) in 50 cm$^3$ of $CH_2Cl_2$ and 5 cm$^3$ THF was added species **4** (0.5 g, 1 mmol) and the mixture was heated under reflux for 4 h. The solution was cooled to room temperature, filtered and left to crystallize. After 2 weeks colorless crystals were filtered off, washed with *n*-hexane (3 × 5 cm$^3$) and dried *in vacuo*. Yield 0.7 g (57%). Anal. calcd for $C_{16}H_{36}O_8Cl_4Mg_2$: C, 35.29; H, 6.67; Cl, 25.71. Found: C, 35.33; H, 6.52; Cl, 25.79%. IR (Nujol, cm$^{-1}$): 228vs, 315s, 347s, 398s, 520m,br, 640w,br, 792vs, 861w, 908vs, 927m, 1010sh, 1033vs, 1070vs, 1100vs, 1235m, 1266s, 1625w, 3150vs, 3400vs.

[$Na_2(\mu, \eta^2\text{-}H_2$digol$)_2(\eta^3$-Hdigol$)_2$] (**4**). To a suspension of metallic sodium (2.3 g, 100 mmol) in THF (100 cm$^3$) $H_2$digol (28.4 cm$^3$, 300 mmol) was added and stirred under reflux. Next, the solution was filtered and left to crystallize at room temperature. After 24 h the colorless crystals were collected, washed with THF (3 × 5 cm$^3$) and dried *in vacuo*. Yield: 22 g (90%). Anal. calcd for $C_{16}H_{38}O_{12}Na_2$: C, 41.02; H, 8.18; Na, 9.8. Found: C, 41.13; H, 8.21; Na, 9.90%. IR (Nujol, cm$^{-1}$): 274w,br, 305w, 325w, 370s, 394s, 520w 532s, 556m, 712m, 804m, 825m, 868vs, 902vs, 920vs, 1058s, 1073vs, 1084sh, 1110vs.

### X-ray crystallography

The crystals were sealed in glass capillaries under a dinitrogen stream. Intensities were collected using a Kuma KM4 four-circle diffractometer[24] in the $\omega - 2\theta$ scan mode (with crystals of dimensions 0.7 × 0.4 × 0.3 mm for **1**, 0.6 × 0.5 × 0.3 mm for **2**, 0.5 × 0.4 × 0.2 mm for **3** and 0.4 × 0.3 × 0.3 mm for **4**) and Mo Kα radiation (0.71073 Å). After each group of 100 reflections three standard intensities were monitored and no evidence of crystal decay was observed for **1** and **4**. In the cases of **2** and **3** the intensities of the standard reflections decreased by 9.5% and 12.3%, respectively, and the recorded data were rescaled according to the intensities of the control reflections. All data were corrected for Lorentz and polarization factors. For **1** and **2** the absorption corrections following the ABSORB[25] procedure were applied: minimum and maximum absorption corrections were 0.926, 1.047 for **1** and 0.870, 1.120 for **2**. The structures were solved by direct methods (SHELXS86)[26] and refined on $F^2$ by a full-matrix least-squares calculation (SHELXL93).[27] The carbon-bonded H atoms (except these of the disordered $CH_2Cl_2$ molecules, which were not refined) were included in the calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 $U_{eq}$ of the attached C atom. In structures **2**, **3** and **4** the H atoms of the hydroxyl groups were located from the difference Fourier map and refined with distance restraints. In structure **3** some atoms of the $CH_2Cl_2$, THF and $H_2$digol molecules were partially disordered and they were refined in two or more positions with isotropic thermal factors (see supporting information). The crystal data and some features of the structure refinement are summarized in Table 5. CCDC reference number 440/049.

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