Preparation and Crystal Structure of Tri-μ-chloro-hexakis(tetrahydrofuran)dimagnesium(II) Pentachloro(tetrahydrofuran)titanate(IV) †

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The direct reaction between $[MgCl_2(thf)_2]$ and $[TiCl_4(thf)_2]$ in tetrahydrofuran (thf) yields a yellow crystalline salt, $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3][TiCl_5(thf)]$. The homobimetallic cation $[(thf)_3Mg(\mu\text{-}Cl)_3\text{-}Mg(thf)_3]^+$ contains a magnesium-magnesium interatomic distance of 3.169 Å and the Mg^{2+} atoms are bridged by three Cl atoms.

In many chemical reactions Group 1—3 elements in non-aqueous solutions, having donor properties, are used as reducing agents for transition-metal halogenides. Such reactions yield complexes, which, in our opinion, can react either with the substrate transition-metal halogenide or with the reaction products during the course of the reaction; *e.g.* $[MgCl_2(thf)_2]$ is known to react with $FeCl_3$ in tetrahydrofuran (thf) to produce $[MgCl(thf)_5][FeCl_4]$, which in thf undergoes reduction to $[Cl_2Fe(\mu\text{-}Cl)_2Mg(thf)_4]$.[1] The reduction is most likely caused by the thf, which reacts with Fe^{3+}, with ring opening and polymerization.[1] Stoicheiometric reaction of $[MgCl_2(thf)_2]$ with $TiCl_4$ in ethyl acetate is known to yield ~~$[Cl_4Ti(\mu\text{-}Cl)_2Mg(CH_3COOC_2H_5)_4]$.~~[2]

In this paper we report the results of our studies of the compound formed on reacting $[MgCl_2(thf)_2]$ and $[TiCl_4\text{-}(thf)_2]$ in thf, and the results of the solid-state *X*-ray diffraction study.

Results and Discussion

Saturated solutions of $[MgCl_2(thf)_2]$ and $[TiCl_4(thf)_2]$ (2:1 molar ratio) in tetrahydrofuran were mixed under dinitrogen. After 24 h yellow, air-sensitive crystals of $[(thf)_3Mg(\mu\text{-}Cl)_3\text{-}Mg(thf)_3][TiCl_5(thf)]$ (1) precipitated out. The structure of complex (1) is presented in the Figure. Atomic parameters are shown in Table 1 and selected bond lengths and angles are summarised in Table 2. The structure of the $[(thf)_3Mg(\mu\text{-}Cl)_3\text{-}Mg(thf)_3]^+$ cation shows one of the interesting features of magnesium chemistry, namely, the ability of the metal to adjust its co-ordination number according to the demands of a particular constitution. In this homobimetallic di-octahedral magnesium cation the two Mg^{2+} atoms are bridged by three Cl atoms. The average Mg–Cl bridge distance is 2.502(4) Å, which is close to the value of 2.517 Å in $MgCl_2$.[3] The magnesium–magnesium distance of 3.169(4) Å is similar to that in the complex $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3][MoOCl_4(thf)]$ and indicates no metal-metal interaction. The six-co-ordinate Mg^{2+} cations are also co-ordinated by three thf molecules. The molecular parameters of the co-ordinated thf groups are close to those observed in $[Mg(thf)_4]^{2+}$ cations of other compounds.[1,4] The angles Cl–Mg–Cl and O–Mg–Cl (Table 2) differ slightly from the ideal octahedral values.

The titanium atom in the $[TiCl_5(thf)]^-$ anion is pseudo-octahedrally co-ordinated with shorter axial than equatorial Ti–Cl bonds. Electrostatic repulsion between the co-ordinated Cl atoms could explain the increase of the angles Cl(4)–Ti–Cl(5,6,7,8) to an average of 94.2(7)°. A similar phenomenon was observed in the dimeric complex $[Cl_3(Cl_3PO)\text{-}Ti(\mu\text{-}Cl)_2Ti(OPCl_3)Cl_3]$.[5] In the case of $[TiCl_6]^{2-}$, which deviates only slightly from octahedral symmetry,[6] the bond lengths of 2.35 Å are greater than in our complex. The structural type $[TiCl_5(thf)]^-$ has been hitherto unknown in titanium chemistry, because titanium halogenides obtained by different procedures generally form dimers; *e.g.* in the reaction of $TiCl_4$ with PCl_5, $[PCl_4][Cl_4Ti(\mu\text{-}Cl)_2TiCl_4]$ as well ~~as $[PCl_4][Cl_3Ti(\mu\text{-}Cl)_3TiCl_3]$ are formed, depending on the~~ reaction conditions.[7]

In order to find out whether the $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3]^+$ cation is also formed in other reactions $[MoCl_4(thf)_2]$ was reacted with an excess of $[MgCl_2(thf)_2]$. The reaction produced green $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3][MoOCl_4(thf)]$, the structure and properties of which will be discussed in a forthcoming paper.

Experimental

All reactions were carried out under dinitrogen using dried thf and Schlenk-tube techniques. The complexes $[TiCl_4(thf)_2]$ and $[MgCl_2(thf)_2]$ were obtained by literature methods.[8,9] Microanalyses were performed at the University of Wrocław.

Tri-μ-chloro-hexakis(tetrahydrofuran)dimagnesium(II) *Pentachloro(tetrahydrofuran)titanate*(IV).—$[TiCl_4(thf)_2]$ (2.1 g) and $[MgCl_2(thf)_2]$ (2.9 g) were dissolved separately in 25 cm^3 and 31 cm^3 of tetrahydrofuran respectively under N_2. The solutions were filtered, mixed, and left for crystallization. After 24 h yellow crystals had precipitated which were filtered off and washed with thf (3 × 5 cm^3). Yield: 2.7 g, 48%.

X-*Ray Crystal Structure Determination.—Crystal data.* $[C_{24}H_{48}Cl_3Mg_2O_6][C_4H_8Cl_5OTi]$, $M = 884.9$, $a = 17.16(1)$, $b = 12.845(8)$, $c = 20.82(1)$ Å, $\beta = 112.80(7)°$, $U = 4\,231$ Å^3, D_m (by flotation) $= 1.38$ g cm^{-3}, $Z = 4$, $D_c = 1.39$ g cm^{-3}, $F(000) = 1\,848$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å.

A specimen (0.8 × 0.7 × 0.8 mm) was cut from a large crystal and sealed in a capillary. Intensity data were recorded on a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo-K_α radiation. Reflections were collected in the ranges $4 < 2\theta < 10°$, $10 < 2\theta < 30°$, and $30 < 2\theta < 40°$ because the crystal suffered slow decomposition,

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† *Supplementary data available* (No. SUP 23897, 15 pp.): structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

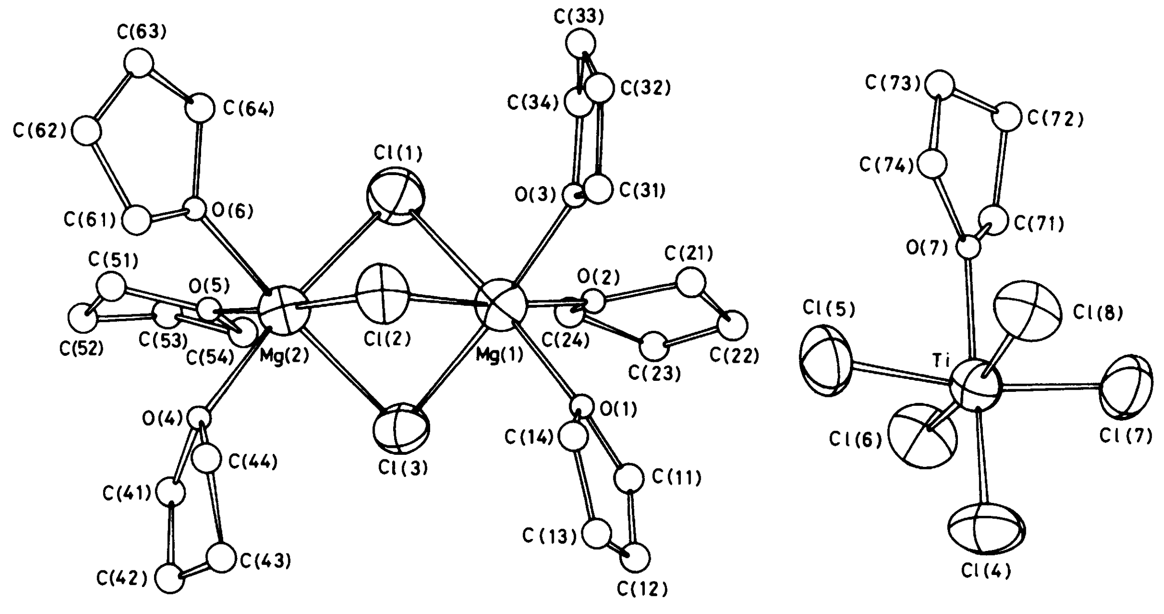

Figure. Structure of the $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3]^+$ cation and the $[TiCl_5(thf)]^-$ anion

Table 1. Atomic positional parameters for $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3][TiCl_5(thf)]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti	0.064 1(1)	0.276 1(2)	0.116 4(1)	C(22)	0.292 6(7)	0.522 9(9)	0.049 3(6)
Mg(1)	0.495 0(2)	0.305 9(3)	0.156 9(2)	C(23)	0.367 0(7)	0.587 1(8)	0.064 8(6)
Mg(2)	0.694 9(2)	0.308 4(2)	0.212 0(2)	C(24)	0.440 1(7)	0.518 0(8)	0.079 1(6)
Cl(1)	0.587 5(2)	0.326 5(2)	0.089 3(2)	C(31)	0.390 8(7)	0.099 3(9)	0.106 1(5)
~~Cl(2)~~	~~0.598 3(2)~~	~~0.167 3(2)~~	~~0.220 6(2)~~	~~C(32)~~	~~0.381 8(13)~~	~~0.030 4(11)~~	~~0.048 6(8)~~
Cl(3)	0.597 3(2)	0.429 5(2)	0.239 8(2)	C(33)	0.399 4(14)	0.084 9(13)	0.000 8(9)
Cl(4)	0.061 3(2)	0.289 1(2)	0.223 2(2)	C(34)	0.407 4(10)	0.180 8(11)	0.016 5(6)
Cl(5)	0.198 1(2)	0.203 4(3)	0.155 1(2)	C(41)	0.811 5(6)	0.408 5(7)	0.351 7(5)
Cl(6)	0.122 7(2)	0.437 6(2)	0.119 2(2)	C(42)	0.815 6(8)	0.398 6(8)	0.424 7(6)
Cl(7)	−0.068 9(2)	0.345 6(3)	0.060 8(2)	C(43)	0.763 3(7)	0.308 2(8)	0.424 2(5)
Cl(8)	0.008 0(2)	0.109 7(2)	0.098 5(2)	C(44)	0.770 0(6)	0.240 7(8)	0.369 6(5)
O(1)	0.425 5(4)	0.298 8(4)	0.219 7(3)	C(51)	0.856 0(6)	0.408 5(8)	0.203 2(5)
O(2)	0.413 7(4)	0.418 5(5)	0.096 2(3)	C(52)	0.888 1(7)	0.5156 (8)	0.201 8(6)
O(3)	0.417 3(4)	0.195 8(5)	0.086 9(3)	C(53)	0.812 8(7)	0.575 9(8)	0.158 9(5)
O(4)	0.777 5(4)	0.310 6(4)	0.317 4(3)	C(54)	0.741 4(7)	0.527 2(7)	0.172 0(5)
O(5)	0.768 4(4)	0.421 8(5)	0.195 4(3)	C(61)	0.755 7(8)	0.160 8(9)	0.119 4(5)
O(6)	0.767 2(4)	0.196 8(5)	0.188 0(3)	C(62)	0.805 5(8)	0.068 8(10)	0.126 1(6)
O(7)	0.064 0(4)	0.260 7(4)	0.013 1(3)	C(63)	0.856 6(9)	0.057 1(10)	0.196 3(6)
C(11)	0.388 9(8)	0.389 7(8)	0.236 9(6)	C(64)	0.818 2(7)	0.119 8(8)	0.235 7(5)
C(12)	0.386 5(10)	0.369 4(10)	0.305 5(7)	C(71)	0.043 9(7)	0.342 0(7)	−0.039 9(5)
C(13)	0.415 9(9)	0.268 0(9)	0.327 3(6)	C(72)	0.024 9(7)	0.284 1(8)	−0.105 8(5)
C(14)	0.431 7(7)	0.219 2(8)	0.270 8(6)	C(73)	0.079 9(7)	0.193 0(9)	−0.086 9(5)
C(21)	0.324 5(7)	0.414 5(9)	0.058 8(6)	C(74)	0.090 3(7)	0.168 4(8)	−0.014 8(5)

most probably because of the loss of thf. Intensities were measured only for reflections above background using a 2θ–ω scan technique. The intensities of two standard reflections, which were monitored after every 50 intensity scans, decreased continuously approximately 11% over the period of the data collection. Scans of other reflections indicated that the decomposition was essentially isotropic. 3 218 Reflections were collected, of which 2 424 [$I > 3\sigma(I)$] were used for the structure analysis. The data were corrected for background attenuation and Lorentz and polarisation effects, only.

Structure determination and refinement. The structure was solved by use of MULTAN programs. The *E* map corresponding to the solution with the best figure of merit showed the Ti, Mg, Cl, and O atoms. The C atoms were found from difference-Fourier maps. All H atoms were included in geometrically calculated positions with d(C–H) = 1.0 Å. Blockdiagonal least-squares refinements were carried out on the positional and anisotropic thermal parameters of all the non-hydrogen atoms. Least-squares refinement converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.044$ and $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.044$, where $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors were taken from ref. 10. The Ti, Mg, Cl, O, and C scattering factors were corrected for real and imaginary components. All calculations were performed on a NOVA 1200 computer with Syntex XTL/XTLE programs.[11] Thermal parameters for C(12), C(32), C(33), and C(34) were rather high suggesting disorder of these atoms. The final difference-Fourier synthesis was featureless.

Table 2. Selected bond lengths (Å) and angles (°) for the complex $[(thf)_3Mg(\mu\text{-}Cl)_3Mg(thf)_3][TiCl_5(thf)]$

Mg(1)–Cl(1)	2.511(4)	Mg(2)–Cl(1)	2.515(3)
Mg(1)–Cl(2)	2.499(4)	Mg(2)–Cl(2)	2.510(4)
Mg(1)–Cl(3)	2.497(4)	Mg(2)–Cl(3)	2.512(4)
Mg(1)–O(1)	2.085(7)	Mg(2)–O(4)	2.102(5)
Mg(1)–O(2)	2.066(6)	Mg(2)–O(5)	2.041(6)
Mg(1)–O(3)	2.096(6)	Mg(2)–O(6)	2.079(6)
Ti–Cl(4)	2.249(3)	Ti–Cl(7)	2.301(3)
Ti–Cl(5)	2.318(3)	Ti–Cl(8)	2.314(3)
Ti–Cl(6)	2.296(3)	Ti–O(7)	2.158(5)
O–C	1.42—1.47(2)	C–C	1.27—1.50(2)
Cl(1)–Mg(1)–Cl(2)	84.3(2)	Cl(1)–Mg(2)–Cl(2)	84.0(2)
Cl(1)–Mg(1)–Cl(3)	83.8(2)	Cl(1)–Mg(2)–Cl(3)	83.4(2)
Cl(2)–Mg(1)–Cl(3)	85.5(2)	Cl(2)–Mg(2)–Cl(3)	85.0(2)
O(1)–Mg(1)–O(2)	90.0(3)	O(4)–Mg(2)–O(5)	87.5(3)
O(1)–Mg(1)–O(3)	92.5(3)	O(4)–Mg(2)–O(6)	92.1(3)
O(2)–Mg(1)–O(3)	87.2(3)	O(5)–Mg(2)–O(6)	89.2(3)
O(1)–Mg(1)–Cl(1)	174.6(3)	O(4)–Mg(2)–Cl(1)	172.6(3)
O(1)–Mg(1)–Cl(2)	95.5(2)	O(4)–Mg(2)–Cl(2)	97.6(2)
O(1)–Mg(1)–Cl(3)	90.8(2)	O(4)–Mg(2)–Cl(3)	89.5(2)
O(2)–Mg(1)–Cl(1)	90.4(2)	O(5)–Mg(2)–Cl(1)	91.2(3)
O(2)–Mg(1)–Cl(2)	174.3(3)	O(5)–Mg(2)–Cl(2)	174.8(3)
O(2)–Mg(1)–Cl(3)	96.0(2)	O(5)–Mg(2)–Cl(3)	96.2(2)
O(3)–Mg(1)–Cl(1)	93.0(2)	O(6)–Mg(2)–Cl(1)	95.2(2)
O(3)–Mg(1)–Cl(2)	91.1(2)	O(6)–Mg(2)–Cl(2)	89.5(2)
O(3)–Mg(1)–Cl(3)	175.5(3)	O(6)–Mg(2)–Cl(3)	174.4(3)
Mg(1)–Cl(1)–Mg(2)	78.2(2)	Mg(1)–Cl(3)–Mg(2)	78.5(2)
Mg(1)–Cl(2)–Mg(2)	78.5(2)		
Cl(4)–Ti–Cl(5)	94.9(2)	Cl(4)–Ti–Cl(6)	94.9(2)
Cl(4)–Ti–Cl(7)	94.1(2)	Cl(4)–Ti–Cl(8)	93.5(2)
Cl(5)–Ti–Cl(6)	89.4(2)	Cl(5)–Ti–Cl(7)	171.0(2)
Cl(5)–Ti–Cl(8)	88.7(2)	Cl(6)–Ti–Cl(7)	90.1(2)
Cl(6)–Ti–Cl(8)	171.6(2)	Cl(7)–Ti–Cl(8)	90.5(2)
O(7)–Ti–Cl(4)	178.5(2)	O(7)–Ti–Cl(5)	85.8(2)
O(7)–Ti–Cl(6)	86.5(2)	O(7)–Ti–Cl(7)	85.2(2)
O(7)–Ti–Cl(8)	85.1(2)		

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