

A STUDY OF THE MgCl_2 -TETRAHYDROFURANE SYSTEM

Karel HANDLÍŘ, Jaroslav HOLEČEK and Ludvík BENEŠ

*Department of General and Inorganic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice*

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The solid phase-solution equilibrium has been studied in the MgCl_2 -tetrahydrofuran system. Below 28°C the saturated solution of magnesium chloride is in equilibrium with the solid phase composed of $\text{MgCl}_2 \cdot 4\text{C}_4\text{H}_8\text{O}$, whereas at higher temperatures the equilibrium solvate has the composition of $\text{MgCl}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$. The solvate $\text{MgCl}_2 \cdot 4\text{C}_4\text{H}_8\text{O}$ forms tetragonal crystals composed of molecules of *trans*-dichloro-tetrakis(tetrahydrofuran)magnesium(II) complex. The solvate $\text{MgCl}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$ most probably represents a polymeric catena-di- μ -dichloro-*trans*-bis(tetrahydrofuran)magnesium(II) complex.

Precursors of highly efficient and stereospecific catalysts for polymerization of 1-olefins, and especially the so-called 3rd generation catalysts, are very often composed of compounds or mixtures isolated from the systems MgCl_2 - $\text{TiCl}_4(\text{TiCl}_3)$ -the Lewis base. The catalytic precursors very often mentioned¹ include products of interactions in the system MgCl_2 - TiCl_4 -tetrahydrofuran. Although catalysts based on this system have found practical applications, the system itself is not sufficiently studied. Only recently three different chemical individua were isolated from this system²⁻⁴, and crystal and molecular structure of one of them is only known³. Basic information is available^{5,6} on the binary system TiCl_4 -tetrahydrofuran, whereas the system MgCl_2 -tetrahydrofuran has not been studied in more detail so far. The existence of various solvates $\text{MgCl}_2 \cdot x \text{C}_4\text{H}_8\text{O}$ ($x = 2, 4, \text{ or } 1.5$) can be inferred from some remarks in papers or patents^{3,7-12}. The present paper deals with a detailed study of solutions of magnesium chloride in tetrahydrofuran and of the solvates which can be isolated from these solutions.

EXPERIMENTAL

Reagents and Analytical Procedures

Magnesium (Reachim, SSSR) of 99.4% purity in the form of fine shavings was washed with 1% solution of hydrogen chloride in tetrahydrofuran for a short time before use. Tetrahydrofuran pure (Laborchemie Apolda, DDR) was freed from peroxides by means of CuCl , dried with sodium metal, and distilled with lithium aluminium hydride before use. The other reagents were of "pure" or "p.a." purity grades. All the procedures were carried out in inert atmosphere of dry

argon. Magnesium and chlorine analyses were carried out by usual volumetric methods, the tetrahydrofurane content was calculated and checked by means of ¹H NMR spectra¹³.

Apparatus

The IR spectra were measured with a Perkin-Elmer 684 apparatus in KBr cells (1400–400 cm⁻¹) or in polyethylene cells (600–200 cm⁻¹). The powder diffractograms were measured with an X-ray diffractometer HZG 4B (Freiberger Präzisionsmechanik, DDR) equipped with a lamp with copper anode, nickel K_β filter, and proportional detector. The samples were measured in a special sample carrier and were protected with a polyethylene film against air humidity.

MgCl₂·4C₄H₈O Solvate

A) A mixture of 8.1 g (0.33 mol) magnesium, 15 g (0.055 mol) HgCl₂ and 400 ml tetrahydrofurane was heated to boiling for 12 h, and then it was left to stand at room temperature 16 h. After filtration, the solution was concentrated to the volume of 70 ml. It deposited 8.4 g (40%) solvate on standing at 0–5°C for 24 h. Complete removal of traces of mercury necessitated three crystallizations.

B) A mixture of 8.5 g (0.35 mol) magnesium and 250 ml tetrahydrofurane was stirred and cooled at 18 ± 2°C, and 50 g (0.65 mol) allyl chloride was added slowly thereto. After 14 h reaction, the whole amount of magnesium dissolved. The solution was filtered with suction and concentrated under reduced pressure to the volume of 100 ml, the further treatment being the same as sub A). Yield 112 g (84%) solvate.

C) The filtered solution of butylmagnesium chloride prepared from 8.5 g (0.35 mol) magnesium, 40 ml (0.38 mol) butyl chloride, and 100 ml tetrahydrofurane was mixed portionwise with equimolar amount of solution of hydrogen chloride in tetrahydrofurane (*c* ~ 5–6 mol l⁻¹). After 3 h standing at 0–5°C, the crystalline slurry was filtered and washed with 30 ml cold tetrahydrofurane. The mother liquor gave another portion of crystals on evaporation to a quarter volume. Total yield about 100 g (75%).

D) A solution of hydrogen chloride in tetrahydrofurane (120 ml, *c* = 6 mol l⁻¹) was added gradually to a suspension of 8.5 g (0.35 mol) magnesium in 150 ml tetrahydrofurane. The temperature was maintained at 25–30°C. After dissolution of magnesium, the mixture was "neutralized" by stirring with about 2 g magnesium band whose residue was then removed mechanically. The crystalline product was cooled at 0–5° and filtered, the further treatment being the same as sub C). Yield about 100 g (75%).

The solvates MgCl₂·4C₄H₈O prepared by the above methods had, within experimental error, the same analytical composition corresponding to the formula MgCl_{1.98–2.02}·3.96 to 4.08 C₄H₈O. The powder diffractograms (see below) were identical, too.

MgCl₂·2C₄H₈O Solvate

E) A suspension of 42 g solvate MgCl₂·4C₄H₈O in 100 ml tetrahydrofurane was stirred at 45–50°C 1 h. The coarse crystalline MgCl₂·4C₄H₈O solvate was transformed rapidly into fine fibrous to gelatinous MgCl₂·2C₄H₈O solvate which was filtered on a tempered funnel and dried in a stream of inert gas. Yield 13.7 g (52%). Composition MgCl_{1.97}·2.04 C₄H₈O.

F) A suspension of 19.2 g MgCl₂·4C₄H₈O in 100 ml dichloromethane was gently boiled for 1 h. The suspension was filtered, washed with 20 ml dichloromethane, and dried. Yield 11.2 g (93%). Composition MgCl_{2.02}·1.98 C₄H₈O.

The $\text{MgCl}_2 \cdot 2 \text{C}_4\text{H}_8\text{O}$ solvates prepared by both the procedures exhibit identical powder diffractograms.

Powder Diffractograms

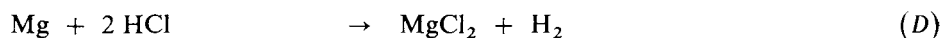
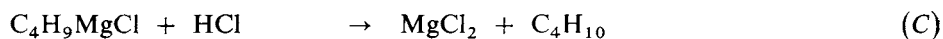
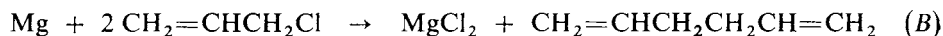
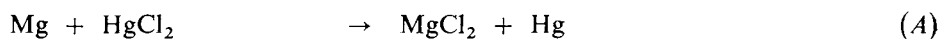
(d , nm/relative intensity): $\text{MgCl}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$ (0.867/10, 0.776/7, 0.531/3, 0.470/2, 0.436/2, 0.427/2, 0.400/1, 0.383/1, 0.382/1, 0.377/1, 0.367/1, 0.351/1, 0.339/1, 0.325/1, 0.316/1, 0.298/1, 0.288/2, 0.284/1, 0.279/1, 0.223/1, 0.185/1); $\text{MgCl}_2 \cdot 2 \text{C}_4\text{H}_8\text{O}$ (1.150/10, 1.070/6, 0.929/4, 0.682/2, 0.622/5, 0.499/10, 0.455/7, 0.380/5, 0.350/7, 0.326/3, 0.316/3, 0.296/1, 0.285/7, 0.278/7, 0.266/1, 0.261/1, 0.231/3).

RESULTS AND DISCUSSION

Dissolution of anhydrous magnesium chloride in tetrahydrofuran is difficult and very lengthy (after 50 h boiling of the two components the concentration of the solution did not exceed about 0.02 mol l^{-1}). The reason is obviously in that solvation energy of the not very firm adducts of the two components of the solution cannot surpass the barrier of lattice energy of polymeric arrangement of crystals of anhydrous magnesium chloride. Therefore, the solutions of magnesium chloride in tetrahydrofuran and the solvates formed thereof had to be prepared by indirect way, *i.e.* by reactions producing magnesium chloride in the solution "*in situ*".

Preparation of Magnesium Chloride Solution in Tetrahydrofuran

Four procedures were used for preparation of solutions of relatively high concentrations ($\sim 0.7 \text{ mol l}^{-1}$) of magnesium chloride in tetrahydrofuran, and the corresponding solvates were prepared from them, too. The syntheses used are described by the following equations:



The first two preparation procedures of the solution and subsequent isolation of the solvate $\text{MgCl}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$ represent modifications of the methods described in literature for other solvates of magnesium halogenides^{14,15}. Both the methods give products which are considerably impure and contain either the starting substances (HgCl_2) or by-products (1,5-hexadiene). The first method gives relatively low yields and is lengthy. The drawbacks of both the procedures are considerably

less in the procedures (C) and (D) which give high yields of pure solvates. The procedure (C) involves two steps, whereas in (D) it is necessary to carefully "neutralize" a possible excess of hydrogen chloride, because the by-product of the reaction of hydrogen chloride with tetrahydrofuran, 4-chloro-1-butanol, can cause additional contamination of the solutions or solvates.

Solubility of Magnesium Chloride in Tetrahydrofuran

The found large concentration differences between the solutions prepared by the above-described methods (A–D) and those prepared from anhydrous magnesium chloride, as well as a possibility to evaluate the solid phase–solution equilibrium led us to measure the temperature dependence of solubility of magnesium chloride in tetrahydrofuran. Sets of samples of pure tetrahydrofuran with excess MgCl₂·4 C₄H₈O solvate were tempered at least 72 h, whereupon both the solid phase and the saturated solutions were analyzed. The solubility curve is given in Fig. 1. The analysis of the solid phase showed that up to the temperature of 28°C the MgCl₂·4 C₄H₈O solvate stands in equilibrium with the saturated solution, whereas above this temperature composition of the solid phase corresponds to the MgCl₂·2 C₄H₈O solvate. The magnesium chloride solutions tend to supersaturation and remain in a metastable state for a longer period. The fact that the transition MgCl₂·4 C₄H₈O → MgCl₂·2 C₄H₈O is connected with a deep structural change (see below), which needs a certain time, has the consequence that a quick heating of a mixture of MgCl₂·4 C₄H₈O with tetrahydrofuran produces saturated solutions of 1.5 mol l⁻¹ or even higher concentrations.

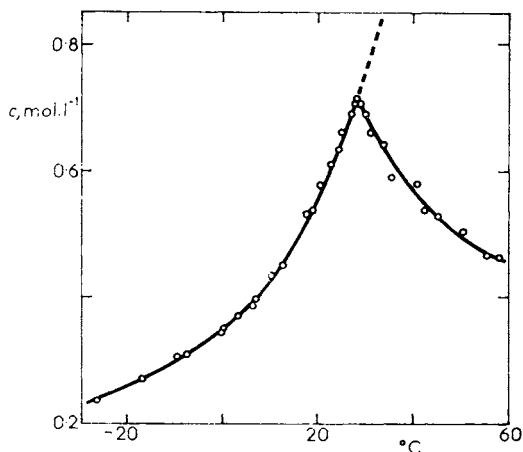


FIG. 1
Solubility of magnesium chloride in tetrahydrofuran

Isolation of the MgCl₂·4 C₄H₈O and MgCl₂·2 C₄H₈O Solvates

The MgCl₂·4 C₄H₈O solvate can be obtained by crystallization of solutions of magnesium chloride in tetrahydrofuran at temperatures below 28°C. As a part of the solvent molecules are bound in the solvate by labile bonds, it proved useful to rapidly collect the product by suction and dry it for a short time in a stream of inert gas at room temperature until it is loose. Under these conditions the product forms colourless prismatic crystals with the composition MgCl_{1.98-2.02}·3.96-4.08 C₄H₈O.

The MgCl₂·2 C₄H₈O solvate is somewhat more stable than the tetrasolvate. It can be obtained by heating MgCl₂·4 C₄H₈O suspension in tetrahydrofuran above 28°C or by desolvation of the same solvate by action of an inert solvent (dichloromethane, hexane, Nujol *etc.*), and it forms very fine fibrous crystals like cotton wool.

Powder Diffractograms of MgCl₂·4 C₄H₈O and MgCl₂·2 C₄H₈O

The powder diffractograms of the two solvates sufficiently differ in both magnitude of the diffraction angles (interlayer distances) and intensities of lines, and they are also different from the diffraction lines of two modifications of anhydrous magnesium chloride¹⁶. All these findings prove chemical individuality of the solvates isolated.

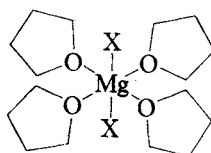
Most diffraction lines of the MgCl₂·4 C₄H₈O solvate agree in their diffraction angles values (interlayer distances) and intensities with those found by Pérucaud and Lebihan^{17,18} and Schröder and Spandau¹⁹ from powder diffractograms of the homologous compound MgBr₂·4 C₄H₈O. Hence, both the homologous compounds obviously form crystals of the same tetragonal structure. The same result also follows from comparison of the data given in Table I. The almost perfect agreement of the lattice parameters of MgCl₂·4 C₄H₈O and MgBr₂·4 C₄H₈O, and agreement of the

TABLE I
Comparison of crystal parameters of MgCl₂·4 C₄H₈O and MgBr₂·4 C₄H₈O

Parameter	MgCl ₂ ·4 C ₄ H ₈ O	MgBr ₂ ·4 C ₄ H ₈ O ^a
Crystal system	tetragonal	tetragonal
Space group		P 4 ₂ 2 ₁ 2
Z	2	2
a = b, nm	0.78 ₂	0.779 ± 0.002
c, nm	1.73 ₄	1.732 ± 0.003
ρ, kg m ⁻³ (calculated)	1 206	1 484
ρ, kg m ⁻³ (found) ^b	1 194	1 500

^a Ref.¹³; ^b by the flotation method in tetrachloromethane-hexane mixture.

lattice parameters of MgBr₂·4 C₄H₈O obtained from the powder diffractograms with results of complete structural analysis of the compound (with the single crystal)¹³ led to the conclusion that also the molecular structure of MgCl₂·4 C₄H₈O is analogous to that of MgBr₂·4 C₄H₈O. Crystals of the two compounds, consequently, are constructed from isolated units [Mg(C₄H₈O)₄X₂] (X = Cl or Br) with *trans*-octahedral coordination around the magnesium atom (I). This is a reasonable conclusion,



I

if we consider that space filling of the crystal lattice of the two compounds is predominantly determined by dimensions of the bulky pseudo-planar unit [Mg(C₄H₈O)₄]. Dimensions of the halogen atoms play quite a subsidiary role¹³. Thus with respect to these considerations, the MgCl₂·4 C₄H₈O solvate must be formulated as *trans*-dichloro-tetrakis(tetrahydrofurane)magnesium(II) complex. The results of IR spectral analysis (given below) do not contradict this presumption.

The powder diffractogram of the MgCl₂·2 C₄H₈O solvate differs markedly from that of the orthorhombic MgBr₂·2 C₄H₈O (ref.¹³). The total number of lines is higher, hence an even lower symmetry of the crystal can be expected.

Infrared Spectra of the MgCl₂·4 C₄H₈O and MgCl₂·2 C₄H₈O Solvates

Especially two spectral regions are immediately related to structure of the two solvates, *viz.* the region due to ether group of the tetrahydrofurane molecule (1 050 to 850 cm⁻¹) and that of valence vibrations of Mg-Cl and Mg-O bonds (below 400 cm⁻¹). Therefore, we focused our attention to the region of 1 400–200 cm⁻¹. The IR spectra of the two solvates in this region were measured in Nujol suspension, those of the MgCl₂·4 C₄H₈O solvate, in addition, in saturated tetrahydrofurane solution and in solid state itself. The results are summarized in Table II. The relatively low stability of the MgCl₂·4 C₄H₈O solvate, which was manifested by partial desolvation by action of the inert Nujol and of thermal radiation, resulted in formation of new bands and, hence, lowering of quality of the spectral record. Useful results were obtained mainly with saturated solutions of the compound in which the particles MgCl₂·4 C₄H₈O are stable at room temperature.

In the spectrum of saturated solution of MgCl₂·4 C₄H₈O it is possible to find both the components of vibration of C—O—C group of the tetrahydrofurane molecule at 1 039 cm⁻¹ (ν_a) and 887 cm⁻¹ (ν_s). They are both shifted (by 29 and 21 cm⁻¹,

resp.) towards lower wavenumbers as compared with the values obtained with free tetrahydrofuran molecule, which confirms the existence of O–Mg bond between tetrahydrofuran and magnesium atom. Shifts of the two vibrations, however, are somewhat smaller than those of the homologous compound $\text{MgBr}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$ (39 and 25 cm^{-1} , resp.)²⁰, which probably corresponds to a weaker bond of the tetrahydrofuran molecule in the magnesium chloride solvate as compared with the bromide analogue. The long-wave spectral region includes a medium band at 408 cm^{-1} and a strong one at 348 cm^{-1} . For the $\text{MgBr}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$ compound similarly found were two intensive bands²⁰ at 342 and 312 cm^{-1} . The existence of the two pairs of bands corresponds precisely to the idea of *trans*-octahedral arrangement of the particles $[\text{Mg}(\text{C}_4\text{H}_8\text{O})_4\text{X}_2]$, where $X = \text{Cl}$ or Br , with D_{4h} symmetry, each involving one IR active vibration $\nu(\text{MgX})$ and $\nu(\text{MgO})$. Hence, the bands at 348 and 342 cm^{-1} are obviously due to the $\nu(\text{MgO})$ vibrations, whereas the bands

TABLE II

The infrared spectra (cm^{-1}) of $\text{MgCl}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$ and $\text{MgCl}_2 \cdot 2 \text{C}_4\text{H}_8\text{O}$

$\text{MgCl}_2 \cdot 4 \text{C}_4\text{H}_8\text{O}$			$\text{MgCl}_2 \cdot 2 \text{C}_4\text{H}_8\text{O}$	Assignment
Nujol	solid phase	solution	Nujol	
1 364 vw	1 365 vw		1 365 sh	$\delta(\text{CH}_2)$, wagg.
1 342 vw	1 345 vw	1 340 vw	1 344 w	$\delta(\text{CH}_2)$, wagg.
1 290 vw	1 292 w	1 292 vw	1 295 vw	$\delta(\text{CH}_2)$, wagg.
1 240 vw	1 243 vw	1 243 vw	1 244 vw	$\delta(\text{CH}_2)$, wagg.
1 182 vw	1 180 m	1 180 m	1 175 w	$\nu(\text{CC})$
1 070 s	1 068 vs		1 068 sh	$\nu_a(\text{COC})$ free
1 039 vs	1 038 vs	1 039 vs	1 037 vs	$\nu_a(\text{COC})$ bonded
915 s	912 s		917 sh	$\nu_s(\text{COC})$ free
889 s	887 s	887 s	883 vs	$\nu_s(\text{COC})$ bonded
870 sh			846 sh	
675 w	674 w	672 m	676 w	$\rho(\text{CH}_2)$, rock.
590 vw	590 vw	590 vw	590 vw	δ (ring)
		445 vw	455 vw	δ (ring)
408 sh	405 w	408 m		$\nu(\text{MgCl})$
350 sh	346 sh	348 s	340 sh	$\nu(\text{MgO})$
315 vs	315 s	310 sh	312 vs } 305 vs }	$\nu(\text{MgClMg})$
305 vs	305 s			
	290 sh			
	280 sh	270 w	270 sh }	
260 vs	255 s	250 sh	255 vs }	$\nu(\text{MgClMg})$
242 vs	240 sh		243 sh }	
225 sh		225 sh	225 sh }	

at 408 and 312 cm⁻¹ are due to $\nu(\text{MgCl})$ and $\nu(\text{MgBr})$ vibrations, respectively. This assignment is consistent with the observation²¹ that the ratio $\nu(\text{MgCl}) : \nu(\text{MgBr})$ is usually about 4 : 3 in analogous compounds. Besides the intensive bands discussed spectra of the saturated solutions also contain groups of weak bands in the region of 250–270 cm⁻¹. This finding is ascribed to the presence of a small amount of the MgCl₂·2 C₄H₈O solvate formed during recording of the spectrum. This explanation is supported by their increase in spectra of the Nujol suspension and in solid phase (Table II) as well as by the fact that a short-term heating of the saturated solution of the compound at 50°C distinctly increased the intensity of the bands at 250–270 cm⁻¹ with simultaneous decrease of the band at 408 cm⁻¹.

The IR spectrum of the MgCl₂·2 C₄H₈O solvate contains the $\nu(\text{COC})$ vibration bands at 1 037 and 883 cm⁻¹. Hence, shifts of these bands towards lower wavenumbers are slightly higher than with MgCl₂·4 C₄H₈O. In the region below 400 cm⁻¹ there are two broad bands having obviously complex structure, *viz.* one at about 310 cm⁻¹ with a distinct shoulder at 340 cm⁻¹ and the other at about 250 cm⁻¹ with shoulders at both the sides (similar bands are found in spectra of partially desolvated MgCl₂·4 C₄H₈O, the desolvation being due to action of Nujol or heat radiation). As to molecular structure, the MgCl₂·2 C₄H₈O solvate can be expected to form either the tetrahedral monomer with C_{2v} symmetry or the octahedral polymer with chlorine bridge atoms and local symmetry D_{2h} similar to the analogous compound MgBr₂·2 C₄H₈O (ref.¹³). Character of the IR spectra rather supports the second possibility (not only by number of the bands found, but mainly by the absence of any band corresponding to the terminal Mg–Cl bond). Generally, chlorine atom as a bridge ligand makes itself felt always at distinctly lower wavenumber than the same atom as a terminal ligand. For Mg₂Cl₄ dimer in argon matrix²², *e.g.*, the vibration $\nu(\text{MgCl})$ was found at 514 cm⁻¹, whereas the vibrations of the bridge link $\nu(\text{MgClMg})$ are found at 372 and 260 cm⁻¹. Hence, the bands at 310 and 260 cm⁻¹ are assigned to the Mg–Cl–Mg bonds of the MgCl₂·2 C₄H₈O solvate, whereas the band at about 340 cm⁻¹ is ascribed to Mg–O bond vibration. With respect to appearance of the crystals and results of IR spectra, the solvate itself could form polymeric chains of catena-di- μ -chloro-*trans*-bis(tetrahydrofurane)magnesium(II) complex in analogy to its homologue MgBr₂·2 C₄H₈O.

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