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Magnesium chloride – ethanol adducts

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Some 60 addition compounds of the type $MgCl_2 \cdot n$EtOH ($6 \leqslant n \leqslant 1.4$), formed between magnesium chloride and ethanol, have been prepared and were characterized by means of X-ray powder diffraction. The spectra were interpreted on the basis of a subset of nine characteristic diffraction patterns, and a range of (partially) new products, $MgCl_2 \cdot n$EtOH with $n = 6$, 4.5, 4, 3.33, 2.5, 1.67, 1.50 and 1.25, is described. $MgCl_2$ adducts with alcohols can be converted to active olefin polymerization catalyst supports through the elimination of the alcohol molecules from the adducts by thermal desolvation.

1. Introduction

The drying process of bischofite, $MgCl_2 \cdot 6H_2O$, to obtain pure anhydrous $MgCl_2$, has been given ample attention [1–7] and it has been shown [8] that by chlorination of partially dried bischofite with HCl gas at 400 °C, a practically pure and dry $MgCl_2$ is obtained with only traces of MgO and H_2O. Efficient removal of water is also achieved by reaction with silanes [9] or by utilizing a magnesium chloride solvent, such as an alcohol, in a distillation zone whereby an azeotropic mixture of alcohol and water is removed overhead [2]. For the purpose of preparation of highly disperse (active) $MgCl_2$-based supports for polyolefin Ziegler–Natta catalysts, there is considerable interest in the properties of $MgCl_2 \cdot$electron-donor (Lewis-base) complexes [10–13], such as $MgCl_2 \cdot n$THF [14, 15], $MgCl_2 \cdot n$EB [16–19], $MgCl_2 \cdot n$EtOAc [17, 19] and $MgCl_2 \cdot 2$B [19] (THF, tetrahydrofuran; EB, ethylbenzoate; EtOAc, ethylacetate; B, monoesters, alcohols and ketones). Thermal or extractive desolvation of $MgCl_2 \cdot$Lewis-base adducts provides very active supports. In the case of $MgCl_2 \cdot 4$THF, this process appears to proceed as follows: $MgCl_2 \cdot 4\text{THF} \rightarrow MgCl_2 \cdot 2\text{THF}, \rightarrow MgCl_2 \cdot 1.5\text{THF} \rightarrow MgCl_2 \cdot \text{THF} \rightarrow \beta MgCl_2$ [15]. It is considered to be important that the interaction between $MgCl_2$ and the solvate is weak so that easy removal of these moieties (chemical activation) may form a very disordered $MgCl_2$ material, suitable as a Ziegler–Natta support [20].

Magnesium chloride-supported catalysts are increasingly made from magnesium chloride alcoholates (Mitsui–Himont technology) or by reacting magnesium alkyls and alkoxides with other halogenated materials. Procatalysts for the (co)polymerization of ethylene or propylene (and α-olefin), obtained by alcoholation of $MgCl_2$ powder, have been described [9–12, 21, 22]. On the other hand, magnesium chloride supports may also be formed by spray-drying ethanol solutions of the salt [11, 23]. Recently, various aspects of the thermal desolvation of $MgCl_2$ adducts with alcohols and ethers were reported [20, 24]. The results of complete desolvation of $MgCl_2 \cdot 6$ROH are controversial. While it has been stated [25] that free $MgCl_2$ is obtained by desolvation of $MgCl_2 \cdot 6$ROH, Multani [26] obtained ClMgOEt by heating $MgCl_2 \cdot$EtOH to 180 °C at $p = 0.1$ mm. Other workers have reported alkoxymagnesium chlorides as being the reaction products [24, 27]. We have also shown interest in the dealcoholation of ethanol associates of magnesium chloride. In order to gain insight into the parameters controlling this process, it was felt to be worthwhile to examine the $MgCl_2$–ethylalcohol adduct compositions. Some 60 $MgCl_2 \cdot n$EtOH solvates ($6 \leqslant n < 1.4$) were synthesized using various preparative routes.

2. Experimental procedure

$MgCl_2 \cdot n$EtOH ($6 \leqslant n < 1.4$) adducts were prepared as white powders according to one of the synthetic routes detailed below.

2.1. Liquid-phase quenching of fused emulsified adducts (controlled turbulence emulsion method, CTEM)

Commercial $MgCl_2$ and a calculated amount of dry EtOH were loaded in an autoclave together with excess of paraffin oil (ROL–OB/30) and heated at 120–150 °C for 1–3 h under continuous stirring in a nitrogen atmosphere. The emulsion was then ejected from the reaction vessel through a tube (length, l 2 m; diameter 2 mm) with a 1 mm exit by means of a nitrogen stream with a flow rate of about 4–5 ms^{-1} at a constant pressure of 10 atm and the liquid phase was quenched in stirred n-heptane kept at − 30 °C. The suspension was held at this temperature for 1 h under stirring and after decanting for 15 min a microspheroidal product with mean particle size in the

30–50 μm range was collected in a nitrogen atmosphere. The solid was repeatedly washed with *n*-heptane to remove paraffin oil, filtered, dried at room temperature in vacuum and subjected to ultrasonics for further particle segregation.

2.2. Fluid-bed dealcoholation

$MgCl_2 \cdot n$EtOH, obtained according to preparative methods given in Sections 2.1, 2.5 or 2.7, was packed into a fluidized bed reactor (length, *l* 270 mm; diameter 25 mm) and evacuated to 0.1 torr (1 torr = 133.322 Pa) isothermally at temperatures ranging from 40–90 °C. A nitrogen-stream (flow rate $2\,l\,h^{-1}$, corresponding to 4–5 mm Hg) was then passed through the packed reactor maintained at this temperature and calculated amounts of EtOH were collected in cold traps. After 15 min, about 2 cm^3 were collected from 5.6 $MgCl_2 \cdot 6$EtOH, evacuated at 60 °C, indicating the formation of $MgCl_2 \cdot 2.85$EtOH. The method was equally well used as a post-treatment of $MgCl_2 \cdot n$EtOH ($n < 6$) adducts prepared according to the aforementioned different experimental procedures.

2.3. Azeotropic distillation

$MgCl_2 \cdot 6$EtOH was prepared at room temperature by slow evaporation under exclusion of humidity of a highly saturated $MgCl_2$ solution in ethanol. The product (23 g), obtained as (poor quality) colourless crystals, which are efflorescent and hygroscopic, was subjected to azeotropic distillation with 0.5 l dry *n*-hexane in a 30 cm column packed with Fenske rings. The distillation was continued at total reflux until a constant temperature was achieved at the top of the column. The product was filtered in a nitrogen stream and vacuum dried at room temperature.

2.4. Vacuum-drying

$MgCl_2 \cdot 6$EtOH, obtained according to Di Noto *et al.* [20], was vacuum dried in a flask at 0.1–0.2 torr on a thermostatic bath at 60 °C for the time necessary to reach a desired composition. After 1 h outgassing, $MgCl_2 \cdot 3.85$EtOH was obtained.

2.5. Recrystallization

$MgCl_2 \cdot n$EtOH was prepared by adding *n* mol ethanol to 1 mol commercial anhydrous $MgCl_2$ under cooling to 0 °C in nitrogen atmosphere. Subsequently, the reaction tube was closed and heated until fusion of the contents under magnetic stirring. After cooling to room temperature, the desired product was obtained.

2.6. Reaction with HCl

A 80–125 μm fraction of metallic magnesium (C. Erba) was dissolved in *n*-heptane containing a stoichiometric amount of C_2H_5OH and anhydrous HCl was passed through the mixture for 4 h at $T < 15$ °C. After additional heating at 70 °C for 3 h in a stream of HCl, a white product was isolated.

2.7. Spray drying

$MgCl_2$ and dry EtOH were loaded in an autoclave at 12 atm and melted by heating at 120 °C for 1–3 h under continuous stirring. The product was then ejected from the reaction vessel through a tube (length, *l* 2 m; diameter 2 mm) with a 1 mm exit by means of a nitrogen stream at a pressure of 10 atm and the liquid phase was spray-cooled (by Niro Atomizer equipment) at 15–50 °C in a turbulent nitrogen atmosphere. The adducts were obtained in microspheroidal form with average particle diameter less than about 40 μm.

The following standard analytical techniques were used to verify the chemical composition of the white reaction products: magnesium, complexation with EDTA using Eriocromo T as an indicator; chlorine, potentiometric methods; EtOH [28]; H_2O, Karl Fischer.

X-ray powder spectra were recorded on a Philips PW 1050/1070 diffractometer using nickel-filtered CuK_α radiation ($\lambda = 0.15418$ nm) at 40 kV, 20 mA. Like most $MgCl_2 \cdot n$ROH adducts, the $MgCl_2 \cdot n$EtOH complexes are unstable, hygroscopic, deliquescent in an atmosphere saturated with alcohol vapour, and easily loose ethanol in an atmosphere in which the partial pressure is lower than the saturated vapour pressure. Therefore, the specimens were protected from the atmosphere by Nujol and were packed as a slurry into the X-ray diffractometer holder (paraffin oil shows up in the X-ray spectra as a broad band centred at 18° in 2θ). The characteristic *d*-values and peak intensities of the various $MgCl_2 \cdot n$EtOH phases identified, on the basis of which the 60 XRD spectra could be interpreted, were obtained from diffractometer charts recorded with a scanning speed of 1/4° and 1° $2\theta\,min^{-1}$, after careful calibration of the goniometer with α-Al_2O_3. Given the instability of the products, great care was taken in ensuring the reproducibility of both diffraction positions and intensities. Decomposition and transformation temperatures were recorded on a Mettler TA2 thermobalance equipped with a low-temperature furnace using α-Al_2O_3 (DTA) as a reference sample. Temperatures were measured using a Pt/Pt–Rh thermocouple and heating rates of 1–3 °C min^{-1} were used. Heating curves were run in controlled atmospheric conditions.

3. Results and discussion

3.1. Solvation

The solvation behaviour of magnesium chloride in mixed aqueous organic solvents (amongst which is EtOH) has widely been studied and sets the background scene. Whereas $MgCl_2$ in the solid state consists of the hard Lewis-acid Mg^{2+} coordinated to six neighbouring Cl^- ligands in a typical layer structure (Fig. 1), in aqueous solution preferentially the more stable complexes with the harder H_2O base are expected [29, 30]. If we consider the order of decreasing electronegativities (F, O, Cl, N, Br, S, I, C) then it is understood that in various coordinations, chlorine ions may easily displace oxygen atoms. Therefore, other factors, such as steric encumbrance, may play a role in determining the final structural type.

In $MgCl_2/H_2O$ solutions the existence of hexa-aqua complexes of the Mg^{2+} ion has been clearly demonstrated by diffraction measurements [31–37], molecular dynamics [36, 38], neutron inelastic scattering [39], Raman [40] and ^{25}Mg nuclear magnetic resonance (NMR) spectroscopy [41, 42]; the coordination number of eight obtained by Albright [33] is doubtful. Concentrated aqueous solutions of $MgCl_2$ have a (local) quasi-crystalline structure, a liquid-type quasi-close-packing in the vicinity of the Mg^{2+} cation [34, 37]. In very concentrated solutions of chloride ions in water, hard ions such as Mg^{2+} and Ca^{2+} will bind to H_2O, whereas softer ions such as Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} will bind to Cl^- [43]; the $NiX_2 \cdot nEtOH$ systems (X = Cl, Br) have been studied to some extent and various compounds were identified ($n = 4, 2$) [44]. In formulating structural hypotheses for the $MgCl_2 \cdot nEtOH$ complexes subject of this paper, it is therefore most appropriate to make comparisons to calcium halide solvates, some of which have been the subject of past studies (Table I). In this respect it is noticed that $MgI_2 \cdot 6MeOH$ is isomorphous with $CaX_2 \cdot 6MeOH$ (X = Br, I). Alkyl substituents, such as in alcohols, reduce the hardness in proportion to the size of the alkyl groups. In an ethylalcoholic $MgCl_2$ solution, chlorine atoms are therefore not expected to belong to the first solvation sphere of magnesium, i.e. $[Mg(EtOH)_6]^{2+} \cdot 2Cl^-$. Indeed, in a 1.44 M $MgCl_2/MeOH$ solution the cationic solvate shell consists of an octahedral arrangement of OH groups (with the methyl groups having much less tendency to occupy symmetrical positions), [45]. The observed Mg–O distance (0.2068(3) nm) is here somewhat less than usually found in aqueous solution (0.210–0.212 nm) [35], which is physically significant. On the basis of bond valence analysis [46] a value of 0.209 nm is expected. The distance shortening has been ascribed to the different electrostatic interactions between Mg^{2+} and CH_3OH molecules as compared to Mg^{2+} and H_2O due to the difference in the dipole moments in magnitude and in position relative to the lone pair. Raman and ^{25}Mg NMR studies of $MgCl_2$ in MeOH and $MeOH/H_2O$ mixtures denote preferential hydration of Mg^{2+} in $MeOH–H_2O$ mixtures; nevertheless, cation–methanol interactions were also detected even with low methanol contents [47, 48]. In the $MgCl_2–H_2O–MeOH$ system, the solid phases existing successively as the methanol content increases are $MgCl_2 \cdot 6H_2O$, $MgCl_2 \cdot 4H_2O \cdot 2CH_3OH$ and $MgCl_2 \cdot 6CH_3OH$ [49]. In the solid state, the structure

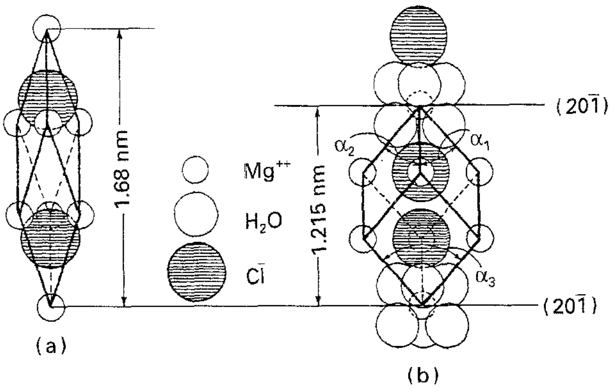


Figure 1 (a) Rhombohedral elementary unit cell of $MgCl_2$ and (b) pseudorhombohedral elementary unit cell of $Mg(H_2O)_6Cl_2$ [52].

TABLE I Structural data of $MX_2 \cdot nROH$ complexes

Compound	Structural type	Reference
$MgCl_2 \cdot 6MeOH$[a]	Discrete octahedral $[M(MeOH)_6]^{2+}$ groups (ionic)	[53]
$MgBr_2 \cdot 6MeOH$[a]	Id.	[53]
$NiBr_2 \cdot 6MeOH$[b]	Id.	[73]
$CoBr_2 \cdot 6MeOH$[b]	Id.	[53, 73]
$CaBr_2 \cdot 6MeOH$[b]	Id.	[53, 73]
$CaI_2 \cdot 6MeOH$[b]	Id.	[53, 74]
$MgI_2 \cdot 6MeOH$[b]	Id.	[53, 74]
$MgCl_2 \cdot 6EtOH$	Discrete octahedral $[M(EtOH)_6]^{2+}$ groups (ionic)	[75]
$CaCl_2 \cdot 4MeOH$[c]	Discrete octahedral M[*trans*$X_2(ROH)_4$] groups (molecular)	[62]
$CaBr_2 \cdot 4MeOH$	Id.	[55]
$CoCl_2 \cdot 4MeOH$[c]	Id.	[76]
$CaBr_2 \cdot 4EtOH$	Id.	[55]
$NiBr_2 \cdot 4EtOH$	Dinuclear $[(EtOH)_4NiBr_2Ni(EtOH)_4]^{2+}$ ion	[63]
$CoBr_2 \cdot 3EtOH$	$(CoBr_4)^{2-}$ and $[Co(EtOH)_6]^{2+}$ions	[68]
$5MnCl_2 \cdot 14EtOH$	Complex polymeric chains MX_2L_4, MX_4L_2, MX_3L_3	[77]
$CoCl_2 \cdot 2.5EtOH$	$[Co(EtOH)_6]^{2+}$ and trinuclear $[Cl_3Co–Cl–Co\ (EtOH)_4–Cl–CoCl_3]^{2-}$ ions	[69]
$CaCl_2 \cdot 2MeOH$	$[M(Cl_4O_2)]_\infty$ chains; doubly chlorine bridged octahedra	[78]
$MgCl_2 \cdot 2EtOH$	Id.	[19]
$HgCl_2 \cdot 2MeOH$	Id., highly deformed octahedra	[79]
$CoCl_2 \cdot 2MeOH$	O_h(IR, VIS, magnetic)	[80]
$CoCl_2 \cdot 2EtOH$	C_{3v} (IR, VIS, magnetic)	[80, 81]
$NiCl_2 \cdot 2EtOH$	Polynuclear zig-zag chain of $Ni(Cl_4O_2)$ octahdera	[81]
$2MnCl_2 \cdot 3EtOH$	Complex polymeric chains MX_4L_2, MX_5L	[82]
$NiCl_2 \cdot MeOH$	Pseudooctahedral	[83]

[a,b,c] Isomorphous

of $MgCl_2\cdot 6H_2O$ can be considered as an arrangement of discrete $Cl\text{-}(H_2O)_3\ Mg^{2+}\ (H_2O)_3Cl^-$ groups (molecular lattice structure type) [50]; the relation to the $MgCl_2$ structure is given in Fig. 1. Partin and O'Keeffe [51] have recently discussed the relationship of $MgCl_2$ to the fluorite structure within the framework of a simple Born–Mayer model. $MgCl_2\cdot 6H_2O$ can even more appropriately be compared to a highly deformed fluorite-type lattice with its sizeable $Mg(H_2O)_6^{2+}$ pseudocations but with only two instead of four close contacts between each H_2O ligand and Cl^- ions [52]. The isomorphous $MgX_2\cdot 6MeOH$ ($X = Cl, Br$) structures are built up of discrete octahedral $[Mg(MeOH)_6]^{2+}$ groups; the halogens are again excluded from the coordination sphere of the metal [53]. This is the usual arrangement for hexaalcoholates (Table I). If we consider cations replacing the oxygen octahedra around magnesium and anions occupying the tetrahedral interstices, the structure of $MgX_2\cdot 6MeOH$ can be described as a distorted fluorite lattice (though less distorted than in the case of $MgCl_2\cdot 6H_2O$), now with three hydrogen bonds between each halogen and hydroxyl groups [53]. $MgCl_2\cdot 6EtOH$ is not isomorphous with the methanol solvate [54], as indeed would be unexpected (cf. similar absence of isomorphism between $CaBr_2\cdot 4MeOH$ and $CaBr_2\cdot 4EtOH$ [55]). In $MgBr_2\cdot 6C_5H_5N$, bromine is included in the magnesium sphere contrary to the case of $MgBr_2\cdot 6H_2O$ [56]. This is explained by the hard and soft acid concept [29, 30]. Apart from the nature of the metal, factors which determine the structure of an adduct are, therefore, polarity, steric factors and the number and kind (soft/hard) of ligands available.

3.2. Dealcoholation

The results of the phase analysis of some 60 preparations of $MgCl_2\cdot n$EtOH adducts are collected in Table II. X-ray powder spectra could readily be interpreted on the basis of nine characteristic sets of d and I/I_0 values (Table III). It then appears that most of the preparations are admixtures of two adducts with different $EtOH/MgCl_2$ ratio. Although this interpretation is fairly straightforward, assignment of the correct stoichiometry to each of the new phases is considerably more difficult. The interpretation given (Table II) is the one which at present best accounts for the observed diffraction data.

The occasional observation of more than two phases in several preparations denotes the absence of equilibrium conditions. As our preparative conditions do not necessarily just lead to stable adducts in the $MgCl_2$–EtOH phase diagram, the interpretation of the experimental data might be less reliable in the occurrence of metastable phases. It should also be underscored that the relevance of thermal decomposition data (Fig. 1) to the findings of Table II is limited due to the great differences in preparative conditions. Moreover, our experiments do not necessarily lead to the detection of *all* $MgCl_2\cdot n$EtOH adducts within the interval ($6 \leqslant n < 1.4$) studied. Finally, no cases of isomorphism were detected between any of our $MgCl_2\cdot n$EtOH adducts with similar solvates which could facilitate structural attributions.

The thermal behaviour of $MgCl_2\cdot 6EtOH$ (at a heating rate of 3 °C min^{-1}) shows a steady loss of ethanol with decompositions (peak temperatures) at 92, 120, 163, 168 and 201 °C (Fig. 2). At lower heating rates (1 and 2 °C min^{-1}) the observed thermal effects indicate an even more complex pattern (Table IV), at variance to the rather smooth degradation suggested by Fig. 1 of [27]. Peak shapes denote the occurrence of multiple processes at various stages (12.4% weight loss corresponds to 1 mol ethanol). The results appear to be more complex than the thermal decomposition of $MgCl_2\cdot 6H_2O$, which proceeds as follows [57]

$$\begin{aligned} MgCl_2\cdot 6H_2O &\xrightarrow{117-160\,^{\circ}C} MgCl_2\cdot 4H_2O \\ &\xrightarrow{190\,^{\circ}C} MgCl_2\cdot 2H_2O \\ &\xrightarrow{240\,^{\circ}C} MgCl_2\cdot H_2O \\ &\xrightarrow{285\,^{\circ}C} Mg(OH)Cl \\ &\xrightarrow{520\,^{\circ}C} MgCl_2 + MgO \end{aligned} \tag{1}$$

By general dehydration processes it is possible to remove about four molecules of water without securing undesirable side reactions. However, the evolution of molecular water of crystallization is not the only possible chemical process, and alternative reactions may proceed through intracrystalline interactions of lattice water with other constituents of the salt. This is particularly important upon further dehydration of $MgCl_2\cdot 2H_2O$ to $MgCl_2$, where various undesired side reactions do occur, such as the formation of $Mg(OH)Cl$, MgO and HCl [58]. This inconvenience can be avoided using a magnesium chloride entraining solvent (e.g. a higher alcohol) in the extraction–azeotropic zone [2] or by other procedures based on the use of HCl [3], derouting via a magnesium chloride (hex) ammoniate product [2, 6] or those indicated in the experimental section. At reduced pressures (< 6.666 kN m^{-2}) magnesium basic chloride was not observed by Pribylov and Krasherinnikova [59].

Other stable hydrates, namely $MgCl_2\cdot 12H_2O$ and $MgCl_2\cdot 8H_2O$ (in α and β modification) [60] do not find analogues in the alcoholates (Tables I and V) and other adducts. This is not surprising both for steric reasons and in view of the fact that $MgCl_2\cdot 6EtOH$ has a high vapour pressure.

On the basis of the foregoing it should be pointed out that the name "magnesium chloride hydrate" used for $MgCl_2\cdot nH_2O$ is misleading. These substances are true hydroxides, differing in structure from $MgCl_2$ (Fig. 1), not species in which water molecules as such have been taken up into the magnesium dichloride lattice, though the chloride has a strong affinity for water and for other polar molecules. The same applies to the "alcohol adducts".

As indicated above, when "hydrates" or "alcoholates" are heated strongly, they lose water or alcohol

TABLE II Phase distribution of $MgCl_2 \cdot n$EtOH preparations

Sample	Experimental method[a]	EtOH/$MgCl_2$ ratio[b]	Phase distribution[c]
1	2.5	5.85	6
2	2.5	(6.0)	6
3	2.7	5.25	$6 > 4.5$
4	2.5	5.25	6
5	2.7	5.15	$6 > 4.5$
6	2.7	5.15	$6 \simeq 4.5$
7	2.7	(5.0)	6, 4
8	2.7	(5.0)	6, 4
9	2.7	5.0	4.5, some 6
10	2.7	4.87	6, some 3.33
11	2.6	4.80	6, some 4.5
12	2.7	4.75	4.5, some 6
13	2.7	4.56	4.5, some 6
14	2.4	4.0	3.33, some 4.5
15	2.5	3.87	4, some 6, some 3.33
16	2.1	3.60	3.33, some 6, unknown
17	2.1	3.49	3.33
18	2.1	3.27	3.33
19	2.1	3.25	3.33
20	2.1	3.21	3.33
21	2.4	3.20	3.33, 2.5, unknown
22	2.1	3.13	3.33, some 2.5
23	2.1	3.08	3.33, 2.5
24	2.1	3.04	3.33, 2.5
25	2.1	3.00	3.33, some 2.5
26	2.7 + 2.2	(3.00)	3.33, 2.5
27	2.7 + 2.2	(3.00)	3.33, 2.5 (?), some 4
28	2.5	2.90	3.33, 2.5
29	2.1	2.95	3.33, some 2.5
30	2.1	2.86	2.5
31	2.1	2.85	2.5, some 3.33
32	2.1	2.80	2.5
33	2.1	2.68	2.5, some 1.67
34	2.6	2.0[f]	$MgCl_2 \cdot 2EtOH \cdot 0.5H_2O$
35	2.1	2.63	2.5, unknown (traces)
36	2.1	2.60	2.5, some 1.67
37	2.1	2.53	2.5, some 1.67
38	2.1	2.51	2.5, some 1.67
39	2.1	2.50	2.5, unknown (traces)
40	2.1	2.49	2.5, some 1.67
41	2.1	2.45	2.5, some 1.67
42	2.1	2.40	2.5, some 1.67, some 1.50
43	2.1	2.36	2.5, some 1.67
44	2.1	2.36	2.5
45	2.1	2.28	2.5, some 1.67
46	2.1	2.27	largely 2.5
47	2.1	2.18	2.5, some 1.5
48[d]	2.1	~ 2.10	2.5, some unknown
49	2.1	2.09	2.5, some unknown
50[e]	2.1	2.09	2.5, some 1.67
51	2.1	1.77	1.67
52	2.1	1.72	1.67
53	2.1	1.69	1.67
54	2.1	1.66	1.67
55	2.5 + 2.2	1.60	1.25, amorphous
56	2.1	1.60	1.67
57	2.1	1.58	1.67
58	2.3	1.50	1.5
59	2.1 + 2.2	(3.0 →)1.48	1.25, some unknown
60	2.1 + 2.2	1.39	1.25, amorphous

[a] Cf. Section 2.

[b] Values given in parentheses are nominal compositions.

[c] n of $MgCl_2 \cdot n$EtOH.

[d] After heating of sample 50 at 85 °C for 10 min.

[e] Shows irreversible exothermal transition at 82 °C in nitrogen.

[f] $[H_2O] = 4.47\%$.

TABLE III Interplanar distances of $MgCl_2 \cdot n$EtOH adducts

$MgCl_2 \cdot 6EtOH$[a]		$MgCl_2 \cdot 6EtOH$[b]			$MgCl_2 \cdot 4.5EtOH$[a]		$MgCl_2 \cdot 4EtOH$[c]		$MgCl_2 \cdot 3.33EtOH$[a]		$MgCl_2 \cdot 2.5EtOH$[a]		$MgCl_2 \cdot 2EtOH \cdot 0.5H_2O$[c]		$3MgCl_2 \cdot 5EtOH$[a]		$MgCl_2 \cdot 1.5EtOH$[c]		$MgCl_2 \cdot 1.25EtOH$[c]	
d(nm)	(I/I_0)	*d*(nm)	*h k l*	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0	*d*(nm)	I/I_0
0.988	> 100	0.995	0 0 1	100	0.918	100	1.016	49	0.966	15	1.403	27	1.119	35	1.449	9	1.046	100	1.163	100
0.674	3	0.688	1 0 0	64	0.776	10	0.876	73	0.937	> 100	0.977	100	1.040	> 100	1.323	100	0.741	48	0.720	25
0.568	5	0.566	1 0 1	36	0.708	24	0.842	100	0.745	15	0.890	70	0.912	26	0.987	50	0.624	46	0.595	8
0.491	39	0.498	0 0 2	2	0.684	32	0.750	58	0.686	27	0.757	11	0.783	100	0.895	33	0.442	12	0.359	8
0.399	26	0.403	1 0 2	1	0.621	20	0.572	42	0.557	11	0.717	6	0.703	11	0.750	8	0.344	17	0.347	16
0.366	22	0.398	1 1 0	16	0.592	6	0.377	21	0.529	15	0.595	6	0.658	12	0.720	33	0.336	14	0.334	8
0.365	30	0.369	1 1 1	66	0.532	19	0.345	79	0.488	19	0.522	14	0.537	21	0.611	13	0.314	38	0.323	7
0.341	5	0.344	2 0 0	2	0.499	13	0.314	17	0.470	18	0.478	10	0.516	24	0.601	4	0.300	68	0.307	16
0.323	4	0.332	0 0 3	< 1	0.458	11	0.2840	30	0.465	19	0.456	15	0.480	30	0.556	8	0.265	26	0.288	49
0.308	14	0.325	2 0 1	2	0.394	57	0.2522	26	0.456	19	0.432	5	0.442	30	0.528	4	0.255	20	0.278	16
0.2967	53	0.311	1 1 2	7	0.385	33			0.447	19	0.407	8	0.422	36	0.504	12	0.240	19	0.242	28
0.2810	5				0.358	80			0.4031	7	0.392	14	0.394	43	0.456	8	0.223	16	0.232	7
0.2532	4				0.346	19			0.3826	36	0.378	25	0.379	19	0.427	4	0.219	21	0.228	16
0.2475	100				0.343	23			0.3663	100	0.364	8	0.375	12	0.417	6	0.213	18	0.221	9
0.2377	6				0.334	24			0.3520	16	0.353	11	0.363	10	0.399	4			0.206	16
0.2334	20				0.324	27			0.3401	44	0.334	26	0.360	19	0.394	8			0.190	11
0.2330	25				0.312	20			0.3317	16	0.319	18	0.351	30	0.380	8			0.181	12
0.2300	8				0.309	13			0.3226	39	0.313	8	0.345	24	0.355	6				
0.2100	1				0.300	19			0.3081	27	0.2998	14	0.336	16	0.345	6				
0.2038	10				0.296	11			0.2912	24	0.2950	5	0.323	31	0.340	12				
0.2010	6				0.2865	27			0.2879	20	0.2891	11	0.314	31	0.335	10				
0.1985	7				0.2650	8			0.2788	51	0.2770	10	0.308	33	0.322	20				
0.1907	5				0.2539	15			0.2714	26	0.2736	22	0.303	26	0.311	22				
0.1792	9				0.2383	9			0.2679	46	0.2684	20	0.294	8	0.300	3				
0.1774	7				0.2356	10			0.2484	34	0.2632	5	0.276	23	0.2940	17				
0.1720	3				0.2278	10					0.2569	16	0.267	43	0.2907	25				
0.1606	5				0.2202	12					0.2471	8	0.260	15	0.2872	26				
0.1578	6				0.2145	9					0.2442	5	0.253	15	0.2814	30				
					0.2115	6					0.2404	8	0.247	20	0.2790	12				
					0.2015	7					0.2383	11	0.245	39	0.2741	9				
					0.1984	6							0.219	25	0.2692	10				
													0.197	6	0.2550	6				
													0.190	11	0.2456	18				
															0.2420	5				
															0.2361	10				
															0.2328	7				
															0.2222	15				
															0.2142	3				
															0.2101	4				
															0.2083	5				

TABLE III (Continued)

$MgCl_2 \cdot 6EtOH$[a]		$MgCl_2 \cdot 6EtOH$[b]			$MgCl_2 \cdot 4.5EtOH$[a]		$MgCl_2 \cdot 4EtOH$[c]		$MgCl_2 \cdot 3.33EtOH$[a]		$MgCl_2 \cdot 2.5EtOH$[a]		$MgCl_2 \cdot 2EtOH \cdot 0.5H_2O$[c]		$3MgCl_2 \cdot 5EtOH$[a]		$MgCl_2 \cdot 1.5EtOH$[c]		$MgCl_2 \cdot 1.25EtOH$[c]	
d(nm)	(I/I_0)	d(nm)	hkl	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0	d(nm)	I/I_0
															0.2038	5				
															0.1979	5				
															0.1903	8				
															0.1831	4				
															0.1807	9				
															0.1794	8				
															0.1705	5				
															0.1687	8				

[a] Recorded at 1/4° 2θ min^{-1} chart speed.
[b] Calculated on the basis of trigonal space group $P\bar{3}$, $a = 0.795$ nm, $c = 0.995$ nm, atomic parameters from [75].
[c] Recorded at 1° 2θ min^{-1} chart speed.

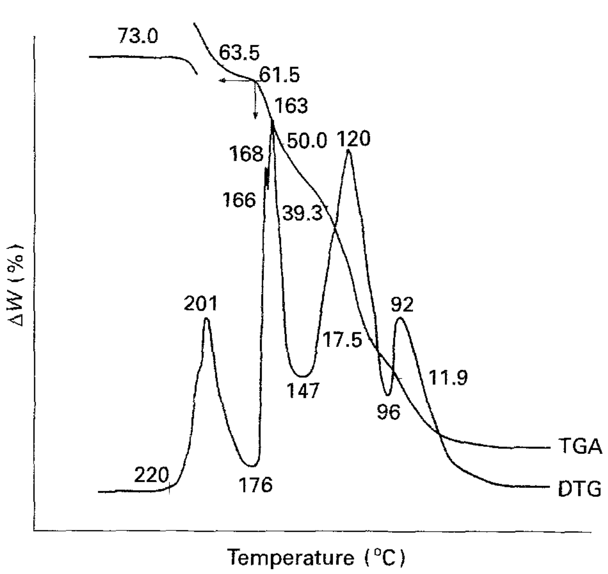


Figure 2 Thermal decomposition of $MgCl_2 \cdot 6EtOH$ in a nitrogen atmosphere at a heating rate of 3 °C min^{-1}.

and are converted ultimately into the chloride, $MgCl_2$, by way of a series of intermediate phases recognizable as structurally distinct by means of their X-ray powder diffraction patterns. The intermediate phases encountered in a particular (de)solvation experiment depend critically on the starting material and experimental conditions used [11, 22]. In addition to our experimental techniques, adducts have also been prepared by grinding a mixture of magnesium dihalide with the desired amount of organic electron-donor compound or by spray-drying [11]. Also treatment of $MgCl_2$–alcohol complexes with $SiCl_4$ or organoaluminium compounds results in partial removal of alcohol, causing further collapse of the $MgCl_2$ crystal aggregates [11, 12]. Slow elimination of ethanol from $MgCl_2 \cdot 6EtOH$ at 50 °C and 0.1 atm (i.e. in conditions close to our experimental procedure in Section 2.4) has recently been reported over the full composition range [20]. For $2 < n \leqslant 6$ ionic Mg–Cl bonds prevail in the structure of the adducts. For $n \leqslant 2$, covalent bonds are observed among chlorine and magnesium atoms, which give rise to chain compounds through chlorine bridges among the magnesium atoms. This conforms schematically to a process $MgCl_2 \cdot nB \rightarrow MgCl_2 \cdot 2B \rightarrow$ activated $MgCl_2$, as observed for many electron donors.

In our experimental conditions the most frequently encountered phases of dealcoholation of $MgCl_2 \cdot 6EtOH$ are $MgCl_2 \cdot 3.33EtOH$, $MgCl_2 \cdot 2.5$ EtOH and $MgCl_2 \cdot 1.67$ EtOH. It is interesting to notice the absence of $MgCl_2 \cdot 3EtOH$, a jet-crystallized product mentioned by Neste Oy (61) and of $MgCl_2 \cdot 2EtOH$, described by Di Noto *et al.* [19].

(Sub)solvated dimetal halogenides exhibit a great variety of structural types with variation in stereochemical metal coordination and the formation of either discrete structure units or condensed species (from short to infinite polymeric chains). Essentially three structural types may be distinguished:

(a) structures composed of only one discrete mononuclear species, either ionic (when charged) as in

TABLE IV TGA and DTA of $MgCl_2 \cdot 6EtOH$ in a nitrogen atmosphere

Heating rate 1 °C min^{-1}		2 °C min^{-1}		3 °C min^{-1}	
T interval (°C)	$-\Delta W$ (%)	T interval (°C)	$-\Delta W$ (%)	T interval (°C)	$-\Delta W$ (%)
25–35	2.96[a]	25–35	1.75	25–90	11.9
35–82	13.4	35–105	20.55	90–107	5.6
82–102	20.4	105–133	14.34	107–131	21.8
102–105	2.08	133–158	12.4	131–158	10.7
105–123	3.51	158–163	12.3	158–169	11.5
123–128	3.4	163–195	3.58	169–192	2.0
128–131	0.99	195–220	7.5	192–210	9.5
131–134	1.42		$\Delta W_{tot} = -72.4\%$		$\Delta W_{tot} = -73.0\%$
134–140	4.06				
140–150	4.5				
150–156	4.5				
156–193	8.3				
193–210	2.19				
	$\Delta W_{tot} = -71.7\%$				

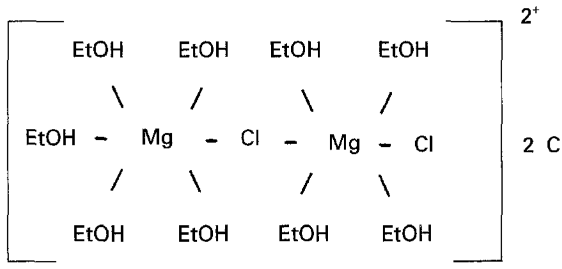
[a] Weight losses are referred to inflection points of TG curve.

$CoBr_2 \cdot 6MeOH$ and $MgCl_2 \cdot 6EtOH$, or molecular (uncharged) as in $CoCl_2 \cdot 4MeOH$ and $CoCl_2 \cdot 6H_2O$;

(b) polymeric polynuclear structures, such as $NiBr_2 \cdot 4EtOH$, $CaCl_2 \cdot 2MeOH$, $HgCl_2 \cdot 2MeOH$ and $2MnCl_2 \cdot 3EtOH$, resulting from one- to three-dimensional association of octahedra;

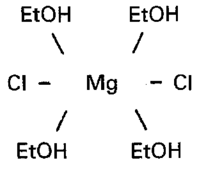
(c) intermediate structures with complex mononuclear and/or polynuclear species (e.g. $CoCl_2 \cdot 2.5EtOH$ and $CoBr_2 \cdot 3EtOH$).

As may be seen from Table II, two solvates are observed in the intermediate range of $MgCl_2 \cdot 6EtOH$ and $MgCl_2 \cdot 3.33EtOH$. One of these is present in the range $5.25 < n < 4.0$ and is provisionally assigned as $MgCl_2 \cdot 4.75EtOH$ or $MgCl_2 \cdot 4.5EtOH$. The latter compound could display the following structure (I)



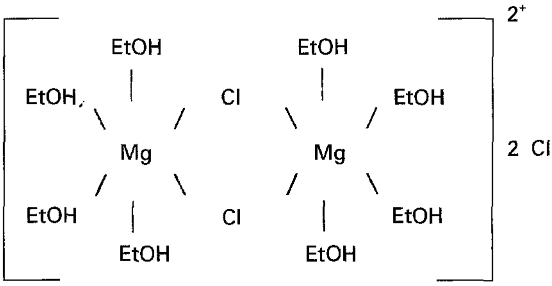
(I)

The second species was occasionally present in the $5.0 < n < 3.0$ range and, like $MgCl_2 \cdot 4.5EtOH$, was never found as a single-phase product but always in admixture. The best possible hypothesis is $MgCl_2 \cdot 4EtOH$, which is most simply represented as (II)



(II)

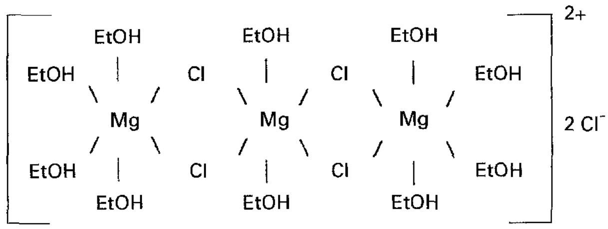
with *trans* arrangement of the halides in a deformed octahedral structure, in accordance with other metal halides solvated with four molecules of a monodentate solvent (Table I); usually, the O_h symmetry around the metal is slightly deformed [62]. Alternatively, the existence of a binuclear ion (III)



(III)

could also be admitted, as found in $NiBr_2 \cdot 4EtOH$ [63] or in α-$CaCl_2 \cdot 4H_2O$ [64] though with a different structural unit. Infinite chains of doubly halogen bridged $Cd(4X, 2H_2O)$ octahedra are reported in $CdX_2 \cdot 4H_2O$ (X = Cl, Br), which are actually both better described as $[CdX_2 \cdot 2H_2O] \cdot 2H_2O$, i.e. hydrated $CdX_2 \cdot 2H_2O$ with two water molecules by insertion [65, 66]. The latter examples illustrate that EtOH in $MgCl_2 \cdot n$EtOH may, in principle, be either chemically bound as a ligand or physically built into the crystal lattice as a true solvate. $MgBr_2 \cdot 6C_5H_5N$ is another example in case [56].

$MgCl_2 \cdot 3.33EtOH$ or $3MgCl_2 \cdot 10EtOH$ is observed for $4.0 > EtOH/MgCl_2 > 2.9$ and appears as the only phase in samples with $n = 3.21, 3.25, 3.27$ and 3.49 (Table II). Reasonable structural hypotheses for this phase are ionic or molecular trinuclear structures such as IV or V



(IV)

TABLE V Structural data of addition products of magnesium halides

Adduct[a]	Ligand set	Coordination	Bond distances (nm)		Reference
			Mg–X	Mg–O	
$MgCl_2\cdot 12H_2O$	$O_6\,(H_2O)$	Octahedral	–	[0.2059, 0.2061, 0.2065 (7)] 2x	[84]
$MgCl_2\cdot 2CdCl_2\cdot 12H_2O$	$O_6\,(H_2O)$	Octahedral	–	[0.2052(5)] 4x, [0.2081(4)] 2x	[85]
$2MgCl_2\cdot CdCl_2\cdot 12H_2O$	$O_6\,(H_2O)$	Octahedral	–	[0.2041, 0.2096(4)] 3x; [0.2071(4)] 6x	[86]
$MgCl_2\cdot 10H_2O\cdot 2(CH_2)_6N_4$	$O_6\,(H_2O)$	Octahedral	–	0.210 (–) 6x	[87]
$MgCl_2\cdot 6H_2O\cdot dx$	$O_6\,(H_2O)$	Octahedral	–	[0.2057, 0.2060, 0.2073(4)] 2x	[88]
$MgCl_2\cdot 6H_2O$[b,c]	$O_6\,(H_2O)$	Octahedral	–	[0.2057, 0.2062(1)] 3x	[50]
$MgClBr\cdot 6H_2O$[c]	$O_6\,(H_2O)$	Octahedral	[d]	n.d.	[89]
$MgBr_2\cdot 6H_2O$[c]	$O_6\,(H_2O)$	Octahedral	–	n.d.	[52]
$MgCl_2\cdot KCl\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.2028, 0.2042, 0.2042, 0.2045, 0.2053, 0.2053(2); 0.2040, 0.2041, 0.2042, 0.2049 ,0.2050, 0.2056(2)	[90]
$MgCl_2\cdot RbCl\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.1991, 0.2020, 0.2062, 0.2071, 0.2078, 0.2115(14); 0.1982, 0.2007, 0.2016, 0.2027, 0.2088, 0.2097(14)	[91]
$MgCl_2\cdot CsCl\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.2035, 0.2041, 0.2062, 0.2062, 0.2076, 0.2080(9)	[92]
$MgCl_2\cdot NH_4Cl\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.198, 0.200, 0.202, 0.210, 0.210, 0.213(1); 0.196, 0.199, 0.204, 0.209, 0.212, 0.214(1)	[93]
$MgX_2\cdot 2HgX_2\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.2019, 0.2038(2x), 0.2087, 0.2139(26) (2x)	[94]
$MgCl_2\cdot toc\cdot 6H_2O$	$O_6\,(H_2O)$	Octahedral	–	0.2054, 0.2057, 0.2059(2x), 0.2082(2) (2x)	[95]
$MgCl_2\cdot 6C_2H_5OH$	O_6	Octahedral	–	0.2069(3) 6x	[75]
$MgX_2\cdot 6CH_3OH$ (X = Cl, Br)[c]	O_6	Octahedral	–	(Br:) 0.207(1) 6x	[53, 74]
$[Mg(CH_3COOC_2H_5)_6][AlCl_4]_2$	O_6	Octahedral	–	0.2053(4) 6x	[96]
$MgBr_2\cdot 4THF\cdot 2H_2O$	O_6[e]	Octahedral	–	[0.2042, 0.2117, 0.2164(7)] (2x)	[97]
$MgCl_2\cdot C_6H_{12}O_6\cdot 4H_2O$	$O_6(4H_2O + 2OH)$	Octahedral	–	0.2032, 0.2038, 0.2051, 0.2079, 0.2094, 0.2143(4)	[98]
$[MgBr_2\cdot 4C_5H_5N]\cdot 2C_5H_5N$	*trans* Br_2N_4	Octahedral	[0.2767(8)] 2x	–	[56]
$MgX_2\cdot 4THF$ (X = Cl, Br)	*trans* X_2O_4	Octahedral	Br: [0.2625(25)] 2x	0.2165(15) 4x	[14, 97, 99]
$MgBr_2\cdot 3THF$[f]	Br_2O_3	Trigonal bipyramid	–	–	[97]
$MgX_2\cdot 2THF$ (X = Cl, Br)	X_4O_2[g]	Octahedral	Br: [0.2633, 0.2799(14)] 2x	0.2126(13) 2x	[14, 97]
$MgBr_2\cdot 2(CH_3CH_2)_2O$	Br_2O_2	Tetrahedral	0.318, 0.332 (–); 0.274, 0.302 (–)	0.213, 0.216 (–); 0.209, 0.214 (–)	[100]
$MgCl_2\cdot 2HCOOC_2H_5$	Cl_4O_2	Octahedral	[0.2494(10)] 4x	[0.2077(20)] 2x	[72]
$MgCl_2(CH_3COOC_2H_5)_2\cdot 1/2CH_3COOC_2H_5$	Cl_4O_2	Octahedral	0.2477, 0.2496, 0.2515, 0.2516(2)	0.2101, 0.2107(3)	[71]

[a] dx, dioxan; THF, tetrahydrofuran; toc, 1,4,7,10-tetraoxacyclodecane.

[b] Bischofite, ND.

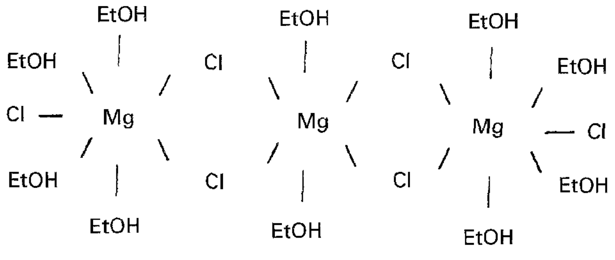
[c] Isomorphous.

[d] Random occupancy of anion sites by chlorine and bromine atoms.

[e] $2H_2O$ (*trans*) + 4THF.

[f] Only powder data.

[g] Polymeric structures with two *trans* THF groups, two interformula unit *cis* Mg–X bonds and two intraformula unit *cis* Mg–X bonds.



(V)

The second structural type with triangular prisms linked by two Cl bridges is found (in dimeric form) in α-$CaCl_2 \cdot 4H_2O$ [64]. A seven coordination around magnesium is less likely, the reason why the first option is preferred. We did not find evidence for the existence of $MgCl_2 \cdot 3EtOH$. Whereas the corresponding $CaBr_2$ adduct has been reported, though without much detail [67], it appears that only the crystal structure of one triethanolate ($CoBr_2 \cdot 3EtOH$) has been determined [68].

In the range of low ethanol contents, $MgCl_2 \cdot 2.5EtOH$ is found extensively for $3.20 < n < 2.09$ with excess of $MgCl_2 \cdot 3.33EtOH$ at high $EtOH/MgCl_2$ ratios and of $MgCl_2 \cdot 1.67EtOH$ at low ratios. The X-ray powder spectrum (Table III) is recognizable in the bar diagram of an unidentified $MgCl_2 \cdot n$EtOH adduct in the $3.08 \leqslant n \leqslant 2.24$ range (Fig. 4 of [20]), prepared according to a method closely similar to our experimental procedure in Section 2.4. On the basis of the only known compounds with a similar monodentate solvate/MX_2 ratio, $CoCl_2 \cdot 2.5EtOH$ and $CdCl_2 \cdot 2.5H_2O$, it is difficult to make any structural assignment. $MgCl_2 \cdot 2.5EtOH$ does not seem to be isomorphous with $CoCl_2 \cdot 2.5EtOH$, which is composed of trinuclear $[Cl_3Co{-}Cl{-}Co(EtOH)_4{-}Cl{-}CoCl_3]^{2-}$ and $[Co(EtOH)_6]^{2+}$ ions [69]. In $CdCl_2 \cdot 2.5H_2O$, one H_2O molecule is physically bound as crystal water; the structure exhibits a complicated framework structure [70].

$MX_2 \cdot 2ROH$ adducts have been found in various MX_2–ROH systems (Tables I and VI), but we failed to observe this stoichiometry in our experiments. These compounds are usually built up of infinite planar chains of doubly halogen bridged octahedra with a 4X,2O coordination, i.e. $[MgCl_2(EtOH)_x]_n$, as also suggested for $MgCl_2 \cdot 2EtOH$ [19]. $MgCl_2 \cdot 2$ ethylacetate [71] and $MgCl_2 \cdot 2EB$ [18] exhibit a similar structure at variance to $MgCl_2 \cdot 2$ethylformate [72].

It is of interest to notice that Di Noto *et al.* [19] report that $MgCl_2 \cdot 2B$ adducts may be obtained by direct synthesis, except for $MgCl_2 \cdot 2EtOH$ for which slow elimination of alcohol from $MgCl_2 \cdot 6EtOH$ is necessary (reflux time of 20 min at 150 °C). Fig. 4 of [20] and Table II of the present study suggest that the experimental methods play a crucial role with regard to the nature of the reaction product(s) obtained.

Further dealcoholation in the approximate $EtOH/MgCl_2$ range of $2.0 < n < 1.5$ leads to a compound which is best described as $MgCl_2 \cdot 1.67EtOH$ or $3MgCl_2 \cdot 5EtOH$. At even lower analytical $EtOH/MgCl_2$ ratios (approximately 1.5) our data are scarce but X-ray diffraction spectra indicate that at least two more compounds are formed. One of the spectra appears to correspond rather closely to the poorly resolved X-ray diagrams of $MgCl_2 \cdot n$EtOH ($2.10 \leqslant n \leqslant 1.06$) of [20]. The stoichiometry $MgCl_2 \cdot 1.25EtOH$ is provisionally assigned as being best in accordance with the now available evidence.

As opposed to work by Di Noto *et al.* [20] dealcoholation below $EtOH/MgCl_2 \simeq 1.5$ was not investigated systematically in this study but was observed to lead to δ-$MgCl_2$ or more complicated structures, in agreement with this reference.

Summarizing the results, we obtain the following (sequence of) phases: $MgCl_2 \cdot 6EtOH \rightarrow MgCl_2 \cdot 4.5 EtOH \rightarrow MgCl_2 \cdot 4EtOH \rightarrow MgCl_2 \cdot 3.33EtOH \rightarrow MgCl_2 \cdot 2.5EtOH \rightarrow MgCl_2 \cdot 1.67EtOH \rightarrow MgCl_2 \cdot 1.5EtOH \rightarrow MgCl_2 \cdot 1.25EtOH \rightarrow \delta MgCl_2$, whereas $MgCl_2 \cdot 2EtOH$ was not observed in this study; the existence of $MgCl_2 \cdot 3EtOH$, as a well-defined compound, has not been proven.

Using quite a different desolvation route (heating in argon in a glass tube at 250–400 °C for 2.5–6 h)

TABLE VI Structural data of some sub-solvate MX_2 adducts.

Adduct	Coordination	Structural type	Reference
$\alpha CaCl_2 \cdot 4H_2O$	Triangular prismatic	Dimeric $Ca(Cl_3O_4)$; double chlorine bridge	[64]
$MgCl_2 \cdot 4H_2O$	D_{4h}	$Mg(Cl_2O_4)$	[101]
$MnCl_2 \cdot 4H_2O^a$	D_{4h}	$Mn(Cl_2O_4)$	[102]
$MnBr_2 \cdot 4H_2O^a$	D_{4h}	$Mn(Br_2O_4)$	[103, 104]
$[CdCl_2 \cdot 2H_2O] \cdot 2H_2O^b$	D_{2h}	$M(X_4O_2)$ infinite chains; double halogen bridge	[66]
$[CdBr_2 \cdot 2H_2O] \cdot 2H_2O^b$	D_{2h}	id.	[65]
$[CdCl_2 \cdot 1.5H_2O] \cdot H_2O$	MX_4L_2, MX_5L	$Cd_4(Cl_5O)_2(Cl_4O_2)_2$ framework	[70]
$CaCl_2 \cdot 2H_2O$	D_{2h}	$M(X_4O_2)$ infinite chains; double halogen bridge	[105]
$CdCl_2 \cdot 2HCONH_2$	D_{2h}	id.	[106]
$MgCl_2 \cdot 2H_2O$	D_{2h}	id.	[101]
$CuCl_2 \cdot 2H_2O$	Coplanar	$Cu(Cl_2O_2)$	[107, 108]
$MnCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 2H_2O^a$	D_{2h}	$M(Cl_4O_2)$	[109–111]
$CdCl_2 \cdot H_2O$	Octahedral	Double $Cd(Cl_5O)$ chains	[112]

[a] Isostructural
[b] Not isostructural

Taveira Magalhães *et al.* [24] have given evidence for the following processes

$$MgCl_2\cdot 6C_2H_5OH \xrightarrow{250\,°C/6\ h} MgCl_{1.90}(OC_2H_5)_{0.10} + 0.10\,HCl + 5.90\,C_2H_5OH \quad (2)$$

$$MgCl_2\cdot 6C_2H_5OH \xrightarrow{400\,°C/2.5\ h} MgCl_{1.85}(OC_2H_5)_{0.15} + 0.15\,HCl + 5.85\,C_2H_5OH \quad (3)$$

Comparison of Fig. 2 of [24] and Table II shows that no similar alkoxymagnesium chlorides were formed in our case. In analogy to [24], Turova *et al.* [27] established that heating of $MgCl_2\cdot 6ROH$ in the temperature range 20–350 °C yields products of the composition $MgCl_{1.75}\,(OMe)_{0.25}$ and $MgCl_{1.80}(OEt)_{0.20}$. Experimental reaction conditions play a major role in the nature of the decomposition process. These results are complementary to the experiments described in this paper.

4. Conclusion

The carefully controlled decomposition of $MgCl_2\cdot nEtOH$ adducts has allowed us to establish the influence of various CTEM process parameters (such as time, pressure, temperatures, concentration, dimensions of the ejection tube, $EtOH/MgCl_2$ ratio, presence of ethylbenzoate, nature of the quenching medium, etc.) on the morphology and consistency of the microsphere particles, suitable as catalyst supports in gas-phase Ziegler–Natta α-olefin polymerization.

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