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Synthesis, characterisation and properties of magnesium di(ε-caprolactamate)

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Abstract

The various synthetic routes to the magnesium di(ε-caprolactamate), CL_2Mg, were investigated, primarily to establish reproducibility of the route and purity of the products. The reactions of ε-caprolactam, CL, with diethylmagnesium, Et_2Mg, in diethyl ether have proved to be the most favourable preparative method. The products, primarily CL_2Mg and CL_nMg, the later representing CL_2Mg solvated with $(n-2)$ CL, were characterised by IR, Raman, mass and NMR spectroscopies, including methods of thermal analysis (TGA and DSC), and colligative properties of their benzene solutions were studied as well. A particular attention was paid to the reactions of the products with water. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Magnesium salts of lactams are known as initiators of the anionic polymerisation of ε-caprolactam, CL, [1,2]. Magnesium di(ε-caprolactamate), CL_2Mg, elucidated earlier as a less active initiator of the CL polymerisation [3–5], has received only insignificant attention in comparison with a commercial product ε-caprolactam magnesium bromide, CLMgBr [6]. However, a commercial-scale production of the CL_2Mg [7] makes it possible to produce the above CLMgX initiators by reaction of CL_2Mg with HX, where X = Cl, Br, I [4]. Combinations of CL_2Mg with others inorganic halides, like $SiCl_4$, PCl_{3-5} or $TiCl_4$ etc. or organic acylhalides, like RCOCl, appear as interesting catalytic systems for CL polymerisation, even the latest one represent an extremely powerful one [7].

While an activity of CL_2Mg used as an initiator of the non-activated anionic CL polymerisation was evaluated elsewhere [8], a serious characterisation of CL_2Mg as a chemical species has not yet been done. Only indistinct IR spectra in solid phase and in solution were published [9]. An oligomeric structure was proposed for CL_2Mg, the dissociation degree of which depended on the type of solvent and decreased with the solvent polarity.

Several synthetic routes were evaluated regarding their feasibility to provide CL_2Mg as a chemical individual or products of reproducible stoichiometry and yields as well. The products were differentiated by elemental analyses and primarily those meeting the requirements of reproducible preparation were characterised by spectroscopic methods and thermal analysis.

CL_2Mg represents a compound of an extreme sensitivity to hydrolysis. For this reason a particular attention was paid to reaction of CL_2Mg with water. There is another reason for such a study. A controlled hydrolysis of CL_2Mg in melt CL, followed by condensation of the hydrolysis product, presumably CLMgOH, might produce an inorganic oxopolymer, like [Mg–O–Mg]n.

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Subsequent polymerisation of CL in situ with this inorganic part seems to be an interesting way leading to new type of reinforced composites.

2. Experimental part

ε-Caprolactam (Spolana Neratovice) was purified by vacuum distillation. Toluene, benzene, diethyl ether, diisopropyl ether, 1,2-dimethoxyethane, and 1,4-dioxane (Fluka) were absolutized by distillation with Synhydrid (sodium bis-2-methoxyethoxodihydrido aluminate; product of Synthesia Kolín). The used alcohols (ethanol, isopropyl alcohol, sec-butanol) were predried with $MgSO_4$ or CaH_2 and absolutized by distillation from the corresponding aluminum alkoxide.

Magnesium (purity 99.9%, Fluka), magnesium chloride and bromide (Fluka) were used as obtained.

All reactions were carried out in flamed apparatuses in the atmosphere of dry nitrogen or argon freed of oxygen traces.

2.1. Syntheses of magnesium lactamates

Several synthetic routes were considered for the preparation of CL_2Mg, namely:

(i) the reaction between CL and $Mg(OR)_2$, where R = ethyl or isopropyl, analogously to the preparation of alkaline salts of lactams from alkoxides [10];
(ii) condensation of the alkali metal ε-caprolactamate (e.g. sodium, CLNa), with $MgCL_2$ in a suitable aromatic solvent or ether or in the CL melt, analogously to process in [2];
(iii) reaction of dialkylmagnesium with CL in the medium of ether [11].

Two first methods (i) and (ii) included initial heterogeneous reactions resulting thus in products of poor reproducibility and indefinite compositions as well. Both methods represented thus the least effective ways for preparation of CL_2Mg.

A detailed attention has been paid to the method (iii) involving reactions of CL with various dialkylmagnesiums, R_2Mg, where R = i–Bu, s–Bu, Et, in diethylether. In course of the preparations based on the butyl derivatives of R_2Mg, heterogeneous systems invariably occur. The solid and soluble fractions are about of the same composition, however, the quantitative ratio of these fractions was entirely uncertain even under apparently the same conditions of the preparations. The solid fractions are entirely insoluble in aromatic and ethereal solvents.

The only quite homogeneous course of syntheses was based on R = Et which gives products of both reproducible compositions and yields as well. At a typical synthetic route to products of $CL/Et_2Mg = 2$, the ethereal solution of diethylmagnesium, Et_2Mg, (18.5 g, 0.096 mol, prepared according to [12]), is dropwise added within 15 min to 21.5 g CL (0.19 mol) overlaid with 200 ml of ether. The reaction was completed by refluxing for 2 h. After the next 12 h, the clear reaction mixture was freed of ether by distillation and the fine powdery product was dried for 10 h at 80°C/30 Pa giving the yield of 23.7 g. Analytical composition of products (average values of two parallel experiments): Mg 9.2% (theor. 9.79), N 10.3% (11.28) C/N 6.2 (6), CL/Mg 2.0 (2).

In addition to reactions with the primary molar ratio $CL/Mg \cong 2$, this route easily provides products with higher molar ratios, CL_nMg, $n > 2$, resulting initial molar ratio $CL/Et_2Mg > 2$. These products exhibit essentially faster solubility in CL melt or in other solvents, such as toluene and benzene, at lower temperature. A maximum value of n, an effective solvation of the central metal in CL_2Mg with CL, was not established. A comparison with $MgBr_2$ which is solvated by 6 CL in solid state [Z. Černý, private communication.] indicates that a maximum of n value would not be lower than six. The maximum value of n in products examined in the paper was about ca. 3.6.

2.2. Characterisation of lactamates

Mg in products was determined by chelatometric titration according to [13].

The ^{25}Mg-NMR spectra were recorded at 24.49 MHz on Bruker spectrometer AM 400, the ^{13}C-NMR spectra on Varian Spectrometer Unity 500 at 125.697 MHz.

Mass spectra were recorded on Magnum GC-MS ion trap system (Finnigan MAT, US), equipped with heated inlet developed by Spectronex AG, Basle (Switzerland). Measuring conditions: temperature program from 35 to 300°C by the rate 10°C min^{-1}; scanning rate 1 scan s^{-1}.

The IR spectra of lactamates in the form of suspension in dry Nujol and Raman spectra of solid substances were recorded in the protecting atmosphere of dry Ar on Bruker IFS-55 FT-IR spectrometer equipped with the Raman module FRA-106.

Thermogravimetric analysis was performed with thermogravimetric analyzer, DuPont Instruments, modulus 951 at heating rate 20°C min^{-1} at atmospheric pressure in 50 cm^3 min^{-1} stream of N_2 or at reduced pressure 130 Pa. Water sorption was followed in the stream of wet nitrogen, saturated by H_2O at 20°C.

The DSC analysis was scanned with the modulus 910 Differential Scanning Calorimeter, DuPont Instruments; heating rate 10°C min^{-1}, nitrogen flow rate 50 cm^3 min^{-1}. The samples were dosed into sealed capsules under strictly inert conditions.

The apparatus and procedure for the ebullioscopic determination of molar masses of moisture and oxygen sensitive substances were described elsewhere [14].

Table 1
Dependence of apparent molar masses (*m.m.*) on molar fraction ***x*** of $CL_{2.7}Mg$ and $CL_{2.3}Mg$ in benzene

$CL_{2.7}Mg$	*x*.(10^2)	***m.m.***	$CL_{2.3}Mg$	*x*.(10^2)	***m.m.***
	0,8	455		—	—
	1,34	472		1.2	533
	2,10	484		2.5	503
	3,21	478		3.8	530

3. Results and discussion

3.1. Determination of molar masses

The colligative properties of benzene solution of $CL_{2.3}Mg$ and $CL_{2.7}Mg$, were determined by means of ebulliscopy, Table 1. Apparent molar masses of the solutes decreased with increasing number of ‘overstoichiometric’ CL content and exhibit an insignificant variation in a given concentration range. These findings correspond to association of the solute where increasing number of solvating CL decrease the degree of the association.

3.2. Thermal properties of magnesium di(ε-caprolactamate)

The thermal stability of CL_2Mg has not been evaluated so far. DSC measurement of CL_2Mg is presented in Fig. 1, record (***a***). The substance shows an endotherm at about 67–72°C, which apparently corresponds to the melting region of pure CL. This process is, however, irreversible and does not occur with any change in mass or apparent morphology of the samples. In case of CL_nMg products the peak area, thermal response, cannot be simply related to *n*, i.e. to the compositions of the products. This indicates that the endothermic phenomena could be attributed to an allotropic transformation of the products. The next more or less noticeable exotherm in the region over 300°C can be assigned (in agreement with the TGA measurements showing weight loss of samples, see below Fig. 2) to the decomposition of the products.

A typical TGA record of the CL_2Mg is shown in Fig. 2*A*. Decomposition at atmospheric pressure, record (***a***), occurred in a single step; the incombustible residue corresponds to the theoretical MgO. In the TGA run

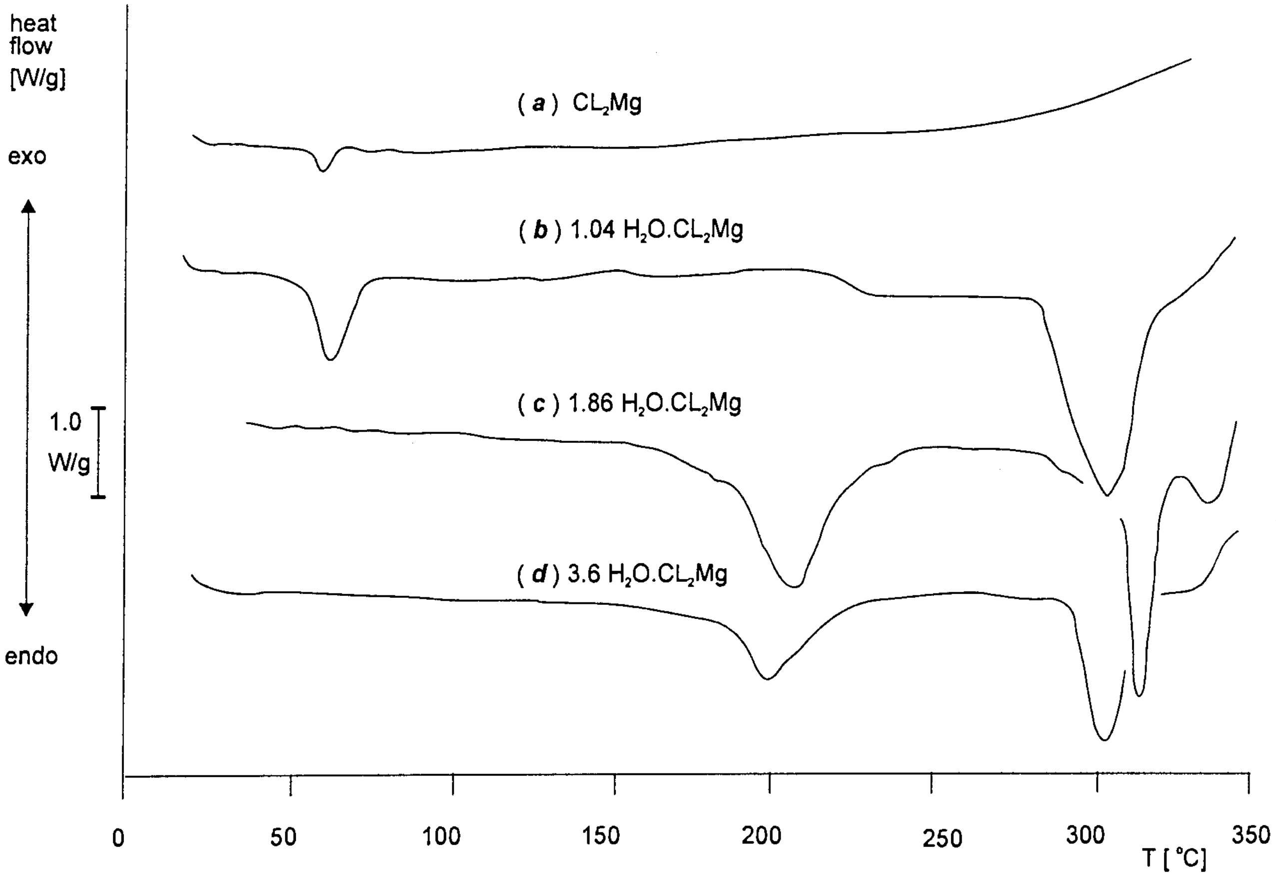


Fig. 1. DSC analysis of CL_2Mg (***a***) and CL_2Mg treated with different amount of water: H_2O/CL_2Mg ca. 1.04 (***b***); 1.86 (***c***) and 3.6 (***d***). (Note: open capsule for DSC with CL_2Mg were exposed in thew tube of TG analyzer in the stream of wet N_2 (saturated by H_2O at 20°C). The content of sorbed H_2O was obtained as a weight difference.)

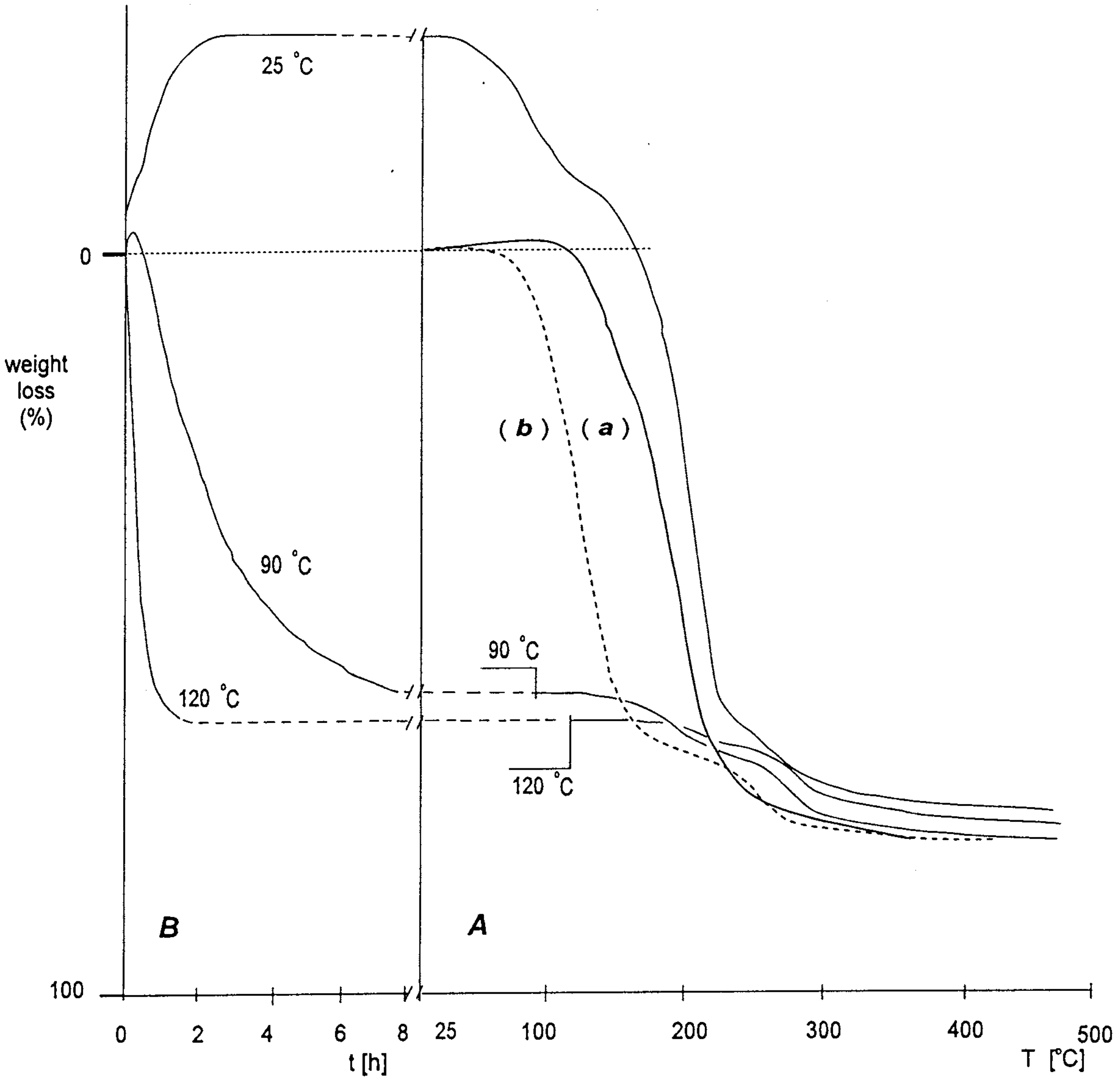
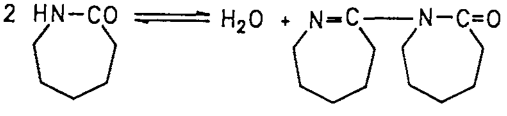


Fig. 2. TG analysis of CL_2Mg at atmospheric pressure (***a***) and reduced pressure 130 Pa (***b***). TGA analyses of hydrolysis of CL_2Mg: dependence of sample mass (%) on time of interaction with wet N_2, (saturated at 20°C) at different temperatures (*A*) and the subsequent dynamic decomposition at 20°C min^{-1} (***B***). N_2 flow rate in both cases 50 cm^3 min^{-1}.

carried out at reduced pressure, record (***b***), the decomposition curve was shifted to lower temperatures by 70°C and a two-stage decomposition became distinct. The second decomposition stage probably corresponds to the liberation of H_2O from $Mg(OH)_2$ resulting in MgO.

The final formation of MgO could be explained by either the presence of moisture traces in inert gas, or by formation of H_2O in course of dehydration of the ε-caprolactam in Scheme 1, giving rise to iminolactam [15].



Scheme 1.

The later hypothesis was tested in a particular experiment in which volatile residues were collected in course of 1 h of the thermal decomposition of CL_2Mg in a sealed tube up to 300°C. Mass spectra of the residues do not confirm any presence of molecular ions corresponding to N-iminolactam but exclusively CL molecular ions were observed. This probably indicates that under apparently strictly inert conditions used in TGA long term experimental runs the traces of water are sufficient for gradual decomposition of samples. The increase of mass (ca. 3%) of samples in TGA experiments corresponds to this process, see Fig. 2*A*, record *(a)*.

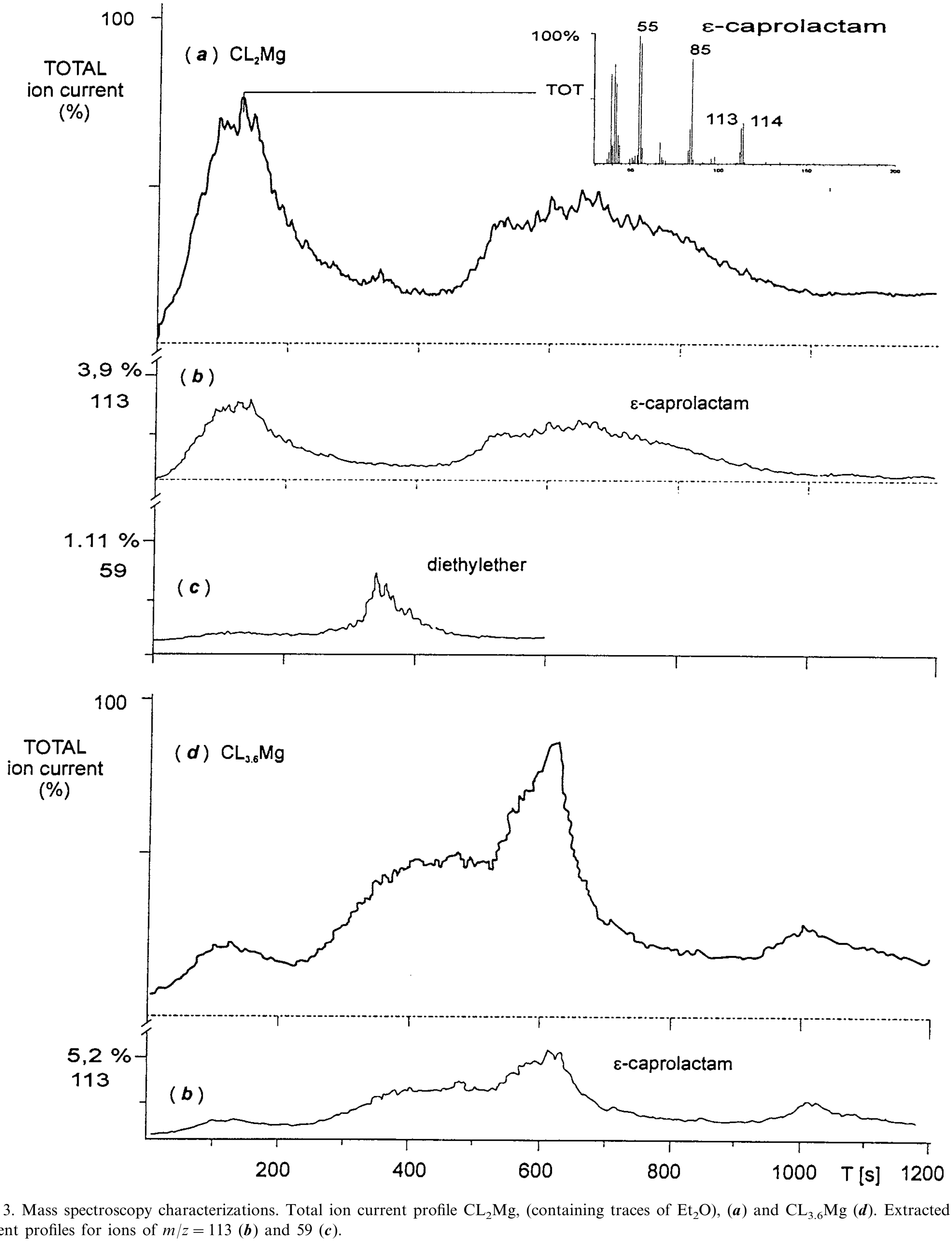


Fig. 3. Mass spectroscopy characterizations. Total ion current profile CL_2Mg, (containing traces of Et_2O), (*a*) and $CL_{3.6}Mg$ (*d*). Extracted ion current profiles for ions of $m/z = 113$ (*b*) and 59 (*c*).

The TGA records did not exhibit any distinct loss of solvating ether proposed in the products. Release of the ether was assumed to be involved in course of the first stage of thermal decomposition. Other facts were revealed by mass spectrometry. The 'evaporation curves' of two products CL_2Mg and $CL_{3.6}Mg$, obtained via

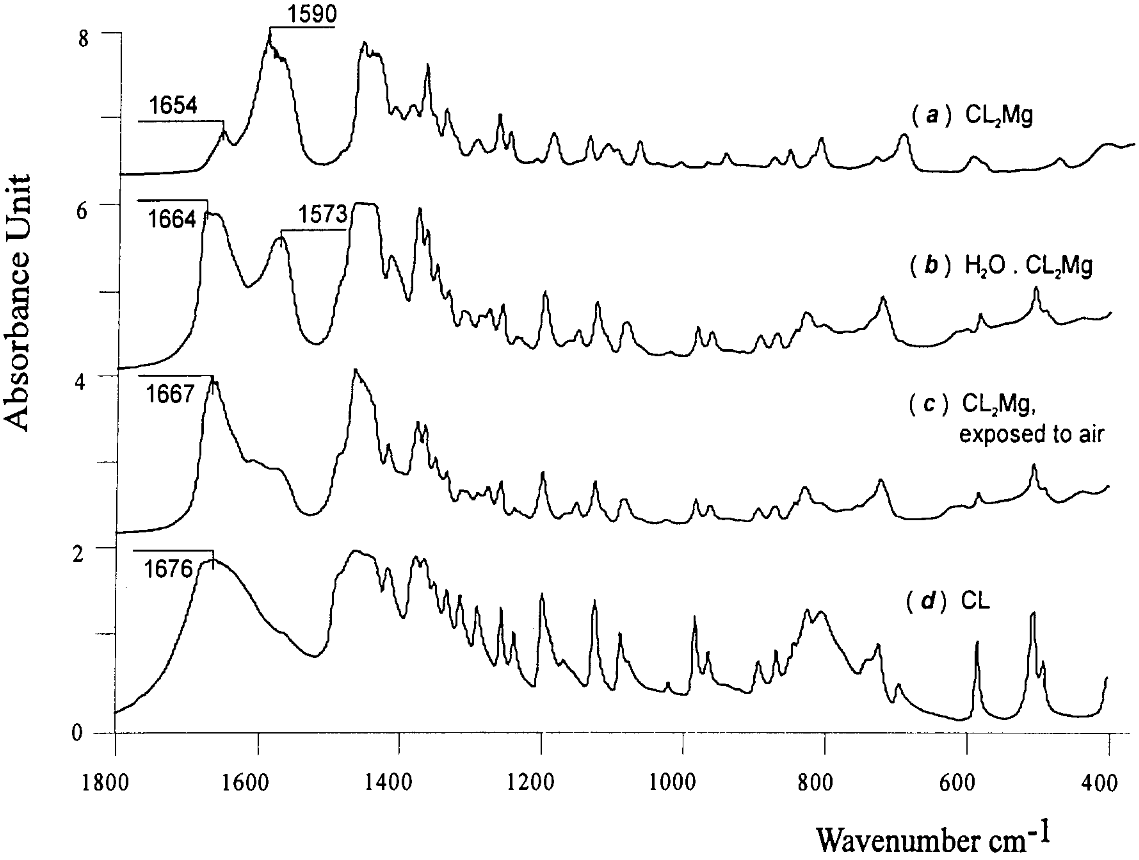


Fig. 4. IR spectra of CL_2Mg and products of interaction of CL_2Mg with water and air in dry nujol: initial CL_2Mg (***a***), reaction product of CL_2Mg with H_2O, H_2O/CL_2Mg ca. 1 (***b***); CL_2Mg exposed for 10 min to air (***c***) and ε-caprolactam, (CL) (***d***).

direct inlet of spectrometer, are shown in Fig. 3. In the former case CL is released in agreement with above TGA results, (see Fig. 2, record (***b***)), in two stages and the solvating diethyl ether is liberated even after splitting of the first CL. In the latter case, the decomposition profile of the product is much more complicated and comprises at least four distinct stages. Any liberation of the ether solvent was not reliably documented. It seems that content of solvating ethers in CL_nMg products, where $n > 3$, can be reasonably reduced.

3.3. Spectral analysis of magnesium lactamates

3.3.1. IR and Raman spectroscopy

The IR spectra of CL_2Mg exhibit no bands in the region of valence vibrations N–H and the vibration band amide I at 1590 cm^{-1} strongly differs from $\nu(C{=}O)$ of initial pure CL (1676 cm^{-1}), Fig. 4, spectra (***a***) and (***d***) respectively. This confirms that CL anions are bonded with Mg.

The amide I band ($\nu(C{=}O)$) of free CL, Fig. 5*A*, spectrum (***a***), occurs in Raman spectrum at 1636 cm^{-1} while that in CL_2Mg is shifted to 1610 cm^{-1}, spectrum (***b***). The shift is considerable smaller than that observed in above IR spectra. The same conclusions indicate spectra in the region of valence vibration $\nu(N–H)$, Fig. 5***B***. This vibration is missing in pure CL_2Mg, spectrum (***b***), while a strong band at 3189 cm^{-1} in CL is observed, spectrum (***a***).

In the case of CL_nMg, $n = 3.6$, an asymmetric doublet in the region of amide I vibration at 1590 and 1602 cm^{-1}, Fig. 5*A*, spectrum (***c***), corresponds to two unequally bonded CL. The more complex region related closely to the above $\nu(C(O)$ vibration of free CL, contains the bands at 1646 and 1660 cm^{-1} assignable to solvating CL. The same conclusion, i.e. solvating character of the 'overstoichiometric' $(n - 2)$ CL, can be drawn from valence vibration $\nu(N–H)$, Fig. 5***B***, spectrum (***c***), where vibrations of solvating CL differ from that of the free compound, spectrum (***a***).

3.3.2. NMR measurement

The ^{25}Mg-NMR spectrum of 0.4 M solution of CL_2Mg in THF shows a single signal at $\delta = 8$ ppm, $w_{1/2} = 2000$ Hz (relatively to Mg^{2+} aqueous solution for which $\delta = 0$ ppm). The chemical shift corresponds to a region of hexacoordinate species which indicate additional solvatation of central metal with THF [16].

Fig. 6 shows the ^{13}C-NMR spectra of benzene solutions of $CL_{3.6}Mg$ and CL, spectra (***a***) and (***b***), respec-

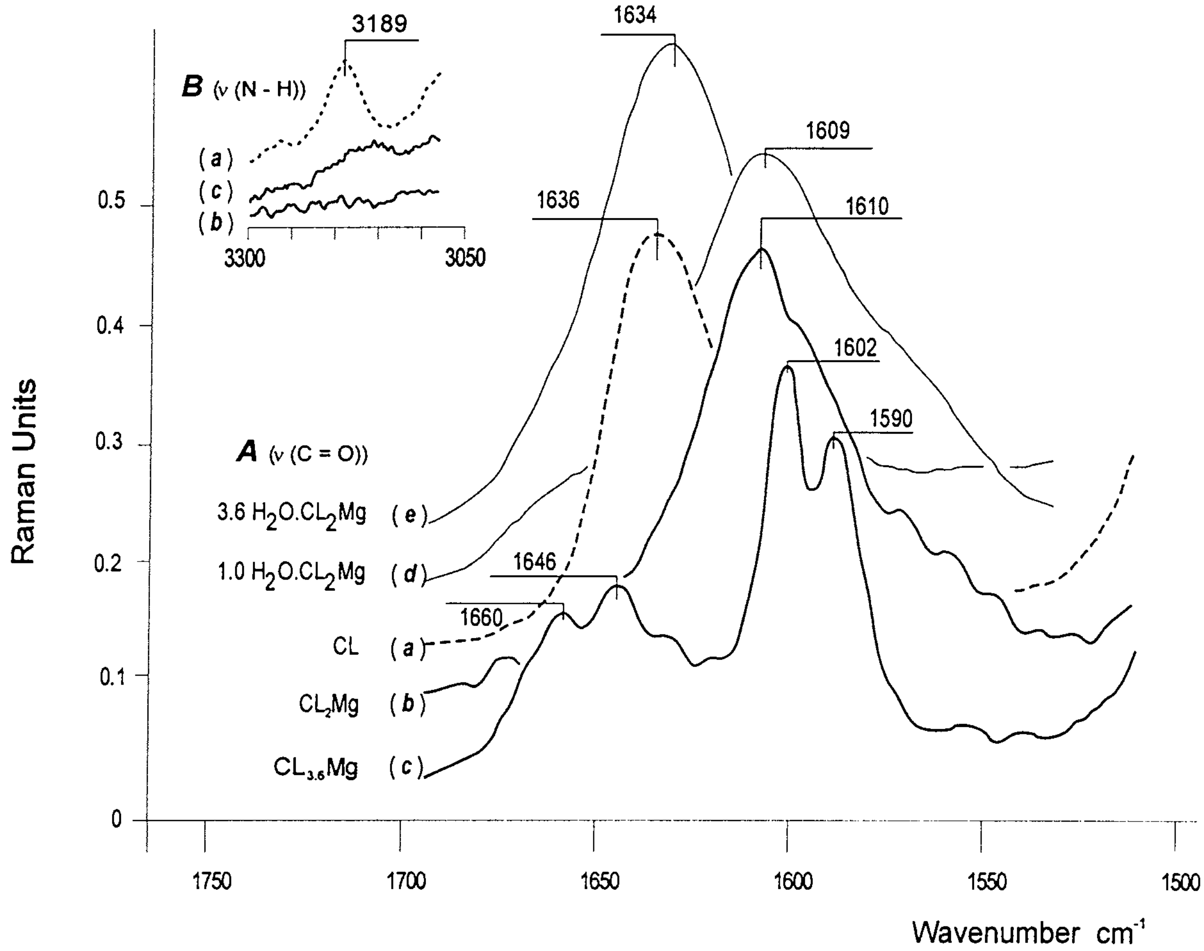
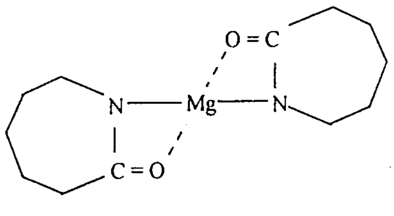


Fig. 5. Raman spectra of ε-caprolactam, (CL) (*a*), CL_2Mg (*b*) and $CL_{3.6}Mg$ (*c*). Products of interaction of CL_2Mg with H_2O in molar ratio H_2O/CL_2Mg ca. 1 (*d*) and 3.6 (*e*).

tively. A rather complex spectrum (*a*) displays six signals along with a set of six broad ones, some of which are notably shifted to lower field, spectrum (*c*). The former set of narrow signals can be assigned to solvating CL, compared with the narrow signals of free CL standard that are slightly shifted to higher field, spectrum (*b*). The deconvoluted broad signals in spectrum (*c*) were assigned to carbons in lactamate anions in CL_2Mg. The most distinct shift to lower field is observed for C(5) atom in neighbourhood of N atom. Surprisingly, this is in contrast with predicted changes in δ of carbonyl carbon, for which reorganisation of s + p population on sp^2–C could be expected on going from CL to lactamate anion. In fact, almost negligible changes in δ of C=O were observed. The anomalous downfield shift of C(5) could be interpreted in terms of different conformation rigidity of the lactamate anion and free CL. The increase of the rigidity of the CL anion can be reasonably explained by participation of carbonyl groups in intramolecular coordination of central Mg atom, Scheme 2, (solvating CL are not involved and a monomeric form is presented).

3.4. Reaction of CL_2Mg with water

The reaction of solid CL_2Mg with water was observed by thermal methods TGA and DSC and by Raman and IR spectroscopy. The samples for these studies, except IR spectroscopy, were prepared by exposition of finely powdered CL_2Mg to deliberately moisturised inert gas, N_2 saturated by H_2O at 20°C, directly on the sample pan (capsule) of the TG analyser. In course of the exposition increase in mass of the samples and resulting ratio H_2O/CL_2Mg were calculated from the difference of initial and final weights. Samples for IR spectroscopy was prepared by the mixing (48 h) of CL_2Mg with water directly in dry Nujol at



Scheme 2.

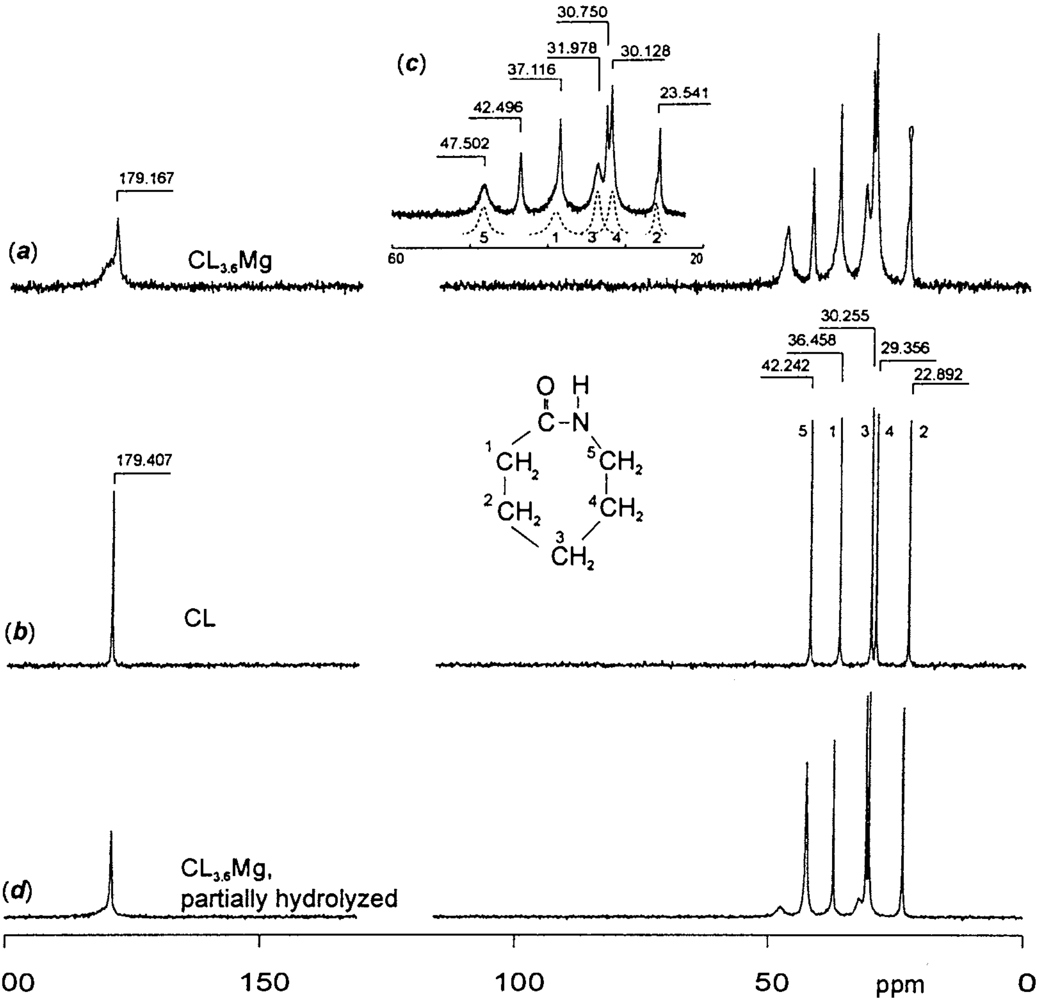


Fig. 6. ^{13}C-NMR spectra of 0.4 M solution of $CL_{3.6}Mg$ in benzene (*a*), ε-caprolactam, (CL) (*b*) and (*d*) partially hydrolysed $CL_{3.6}Mg$ in benzene, molar ratio of H_2O/Mg ca. 0.5; spectrum (*c*) deconvoluted part of the spectrum (*a*).

laboratory temperature and a sample for NMR spectroscopy was prepared directly from a benzene solution of $CL_{3.6}Mg$.

3.4.1. TGA

Within of 7 h at ambient temperature the mass of CL_2Mg exposed to moistened inert gas at 25°C increased by 30.7 wt%, which corresponds to about 4 mol H_2O/mol of lactamate, Fig. 2*B*. At the subsequent decomposition, Fig. 2*A*, the mass of the reaction products decreased during heating to 140°C interestingly by the value apparently corresponding to the water previously bound.

Next, reactions of CL_2Mg with H_2O were observed at higher temperatures in an isothermal arrangement, Fig. 2*B*. At 90°C the mass increased initially only by 3%. At 120°C, the feature of isothermal decomposition was ceasing at 33% of the original mass in course of 8 h, however without any introductory increase in mass. The following dynamic decomposition proceeds in three distinct stages in all the cases and ends with practically the identical content of ashes $\approx 20\%$ corresponding to MgO, (16% theoretical value), Fig. 2*A*.

3.4.2. DSC

DSC data are shown in Fig. 1. DSC records of products of H_2O/CL_2Mg from 0.4 to 1 are nearly identical with that of pure CL_2Mg in the positions of bands and thermal response, compare records (*a*) and (*b*), respectively. Beyond of an equimolar content of water, i.e. $H_2O/CL_2Mg > 2$, the DSC, records (*c*) and (*d*), are quite different containing again two bands, the first of which, however, is shifted to ca. 200 and second at ca. 300°C. The latter band corresponds to the decomposition of the product, shifts of the former band documents fundamental reorganisation of the hydrolysed product.

3.4.3. Raman spectroscopy

In accordance with the DSC record for sample of $H_2O/CL_2Mg \leq 1$, Raman spectrum (*c*) in Fig. 5*A* do not exhibit significant differences from that of initial CL_2Mg. Hydrolysis changes are practically indistinct till $H_2O/CL_2Mg \geq 2$, see spectrum (***e***).

3.4.4. IR spectroscopy

Fig. 4 shows IR spectra of the hydrolysed product obtained from the reaction of CL_2Mg with water in molar ratio 1:1 directly in Nujol, spectrum (***b***). In contrast to results from the above methods, the IR spectroscopy exhibits significant changes in the spectrum of the product from that of initial CL_2Mg even with $H_2O/CL_2Mg < 1$. The spectrum in the region of the amide I vibration exhibits two distinct intense bands which can be assigned both to the bound, 1573 cm^{-1}, and to solvating CL, 1664 cm^{-1}, near to free CL at 1676 cm^{-1}. The bound Mg–OH in hydrolysis product can be well documented by a sharp band at 3698 cm^{-1}.

3.4.5. ^{13}C- and ^{25}Mg-NMR

In process of hydrolysis of $CL_{3.6}Mg$ intensity of the ^{13}C-NMR signals of solvating CL apparently increases relative to signals of lactamate anion, spectrum (***d***) in Fig. 6. An absence of new signals, i.e. signals of the lactamate anion of proposed CLMgOH species, indicates low solubility of polymerisation and/or condensation products of CLMgOH in benzene. The same conclusions were obtained from ^{25}Mg spectra, in course of hydrolysis of CL_2Mg in THF or $CL_{3.6}Mg$ in benzene; invariant decay of initial ^{25}Mg-NMR signals was observed till H_2O/CL_2Mg ca. 1.5–1.8.

4. Conclusion

The above results show that interaction of H_2O with products depends strongly on reaction pathway including physical forms of samples. A contrast between the results of IR and NMR spectroscopies and the other methods can be explained by the different physical forms of examined samples. While the samples were hydrolysed in heterogeneous form in the case of TGA, DSC and Raman methods those examined by the former methods were hydrolysed in form of fine suspension in Nujol and directly in homogenous solutions. The sensitivity of CL_2Mg in fine suspension to water can be well demonstrated by an extremely fast hydrolysis of CL_2Mg in Nujol by exposing for 10 min to air simply in an open tube, Fig. 4, spectrum (***c***).

The hydrolysis pathway clearly determines the characteristics of hydrolysis products. For example, when 0.4 M benzene solution of $CL_{3.6}Mg$ is rapidly hydrolysed directly by H_2O in molar ratio $H_2O/CL_{3.6}Mg$ ca. 1, mostly non-reversible white precipitation occurs, probably containing insoluble $Mg(OH)_2$. On the other hand, hydrolysis under gentle conditions, e.g. via N_2 saturated by H_2O at ambient temperature and vigorous mixing, results in apparently homogenous products till ratio H_2OH/Mg ca. 1. In course of a few days a transparent gel occurs in this system. Characterisation and utilisation of the gel represents scope of continued investigation.

Hydrolysis in the solid phase exhibits many interesting features as well. It seems that hydrolysis starts with sorption of H_2O, however, distinct bands in Raman spectra of such occluded water are not present [17]. This phase represents interestingly a reversible interaction of solid CL_2Mg with H_2O for $H_2O/CL_2Mg \leq 2$. Only a notable excess of H_2O, leads to irreversible decomposition of products.

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