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# Note

## Synthesis, crystal structure and thermal stability of the $MgCl_2$ formamide adduct

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### Abstract

The reaction of $\alpha$-$MgCl_2$ with formamide affords the $MgCl_2(HCONH_2)_6$ adduct which was obtained as crystals suitable for X-ray analysis. $M_r = 730.91$, monoclinic, space group $P2_1/a$ with $a = 9.199(4)$, $b = 7.413(2)$, $c = 12.227(6)$ Å, $\alpha = 90.00$, $\beta = 91.5(1)$, $\gamma = 90.00°$, $V = 833.5(6)$ Å$^3$, $D_x = 1.46$ g cm$^{-3}$, $\lambda$(Mo K$\alpha$) = 0.71069 Å, $\mu = 4.17$ cm$^{-1}$, $F(000) = 380$, $T = 298$ K; observed reflections 1198, $R = 0.048$, $R_w = 0.047$. Such adduct shows a three-dimensional polymeric structure formed through hydrogen bonds between the $-NH_2$ groups and the chloride ions Each magnesium atom appears to be octahedrally coordinated by six formamide molecules through the carbonyl oxygen atom. The thermal stability of the adduct has also been investigated by thermogravimetric analysis and the obtained TG curve shows that the thermal elimination of the coordinated Lewis base appears to be the result of more than one step.

*Key words:* Crystal structures; Magnesium complexes, Formamide complexes

### Introduction

The interaction between anhydrous $\alpha$-$MgCl_2$ and electron-donor compounds is at present the subject of several investigations, especially in order to prepare activated $\delta$-$MgCl_2$ usable as a support for the Ziegler-Natta type catalysts for the $\alpha$-olefin polymerization processes.

The treatment of $\alpha$-$MgCl_2$ with Lewis bases yields well defined adducts. The successive thermal elimination of the coordinated bases carried out under controlled conditions produces polycrystalline $\delta$-$MgCl_2$ formed by disordered $MgCl_2$ covalently bonded chains having a large number of uncoordinated Mg atoms. This compound was found to be a useful material for the preparation of high yield supported catalysts for the commercial $\alpha$-olefin polymerization. The $MgCl_2$ supports so obtained, especially by treatment with aromatic esters [1] or ethanol [2], are claimed in several patents. Considering that the performance of the supported Ziegler-Natta catalysts can be related to both structural and chemical features of the supporting materials we have investigated the role of the Lewis base used for the $\alpha$-$MgCl_2$ activation. We have recently reported the synthesis and characterization of some $MgCl_2$–Lewis base adducts, such as $MgCl_2$–ethyl formate [3], $MgCl_2$–benzyl alcohol [4], $MgCl_2$–ethyl acetate [5], $MgCl_2$–ethyl alcohol [6] and a study of the thermal elimination of the coordinated base from these adducts [7]. We now report here the preparation and single crystal structure determination of the $MgCl_2(HCONH_2)_6$ adduct, together with an investigation of the coordinated base elimination carried out by means of thermogravimetric measurements.

### Experimental

#### *Preparation of the $MgCl_2(HCONH_2)_6$ adduct*

70 ml of formamide (Aldrich A.C.S. reagent), previously purified and dried by standard methods, were added drop by drop at 0 °C to 4 g of anhydrous $\alpha$-$MgCl_2$ (reagent grade, supplied by Himont Italia S.p.A). $\alpha$-$MgCl_2$ was weighed and manipulated inside a Braun MB-150 I/II dry box under a strictly controlled inert atmosphere. The obtained mixture was heated at room temperature and stirred for *ca.* 30 min and then filtered. The clear solution obtained was warmed under vacuum at 40 °C for 12 h. After cooling at room temperature thin strip-like crystals were formed.

#### *X-ray analysis*

A diffraction quality crystal with dimensions $0.3 \times 0.3 \times 0.5$ mm was transferred, inside a dry-box, to a quartz capillary previously filled with dry and oxygen free vaseline. The data were collected at room temperature on a Philips PW 1100 four-circle automatic diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å), and a $\theta$–$2\theta$ scan modem up to $2\theta = 56°$. The cell parameters were determined by

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25 reflections in the range 8–12° A total of 1357 independent reflections was collected for $-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 9$ and $0 \leqslant l \leqslant 16$. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structure was solved by direct methods using SHELX86 [8] programs and it was refined by full-matrix least-squares methods using anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were located on a DF map and isotropically refined. The atomic scattering factors for the Mg atom were taken from the International Tables for X-ray Crystallography [9], while the other factors together with all the computations were performed using the SHELX76 [10] program. The full-matrix least-squares refinement, based on $F$ using weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, where $g = 2.46 \times 10^{-3}$, gave final values of $R = 0.048$, $R_w = 0.047$, $S = 1.048$ for 134 variables and 1198 observed reflections having $F_o > 7\sigma(F_o)$; $(\Delta/\sigma)_{max} = 0.237$. The final maximum residual electron density is $\Delta\rho = 0.469$ e Å$^{-3}$. The high value $7\sigma$ is due to the need to carry out the data collection with adequate high speed, because the crystal undergoes decay.

TABLE 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å$^2$)[a, b]

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cl(1) | 0.4930(1) | 0.1664(1) | 0.13308(7) | 0.0309(2) |
| Mg(1) | 1.000000 | 0.500000 | 0.000000 | 0.0279(4) |
| O(1) | 0.7866(3) | 0.4210(4) | −0.0192(2) | 0.0342(8) |
| O(2) | 0.9391(3) | 0.7692(3) | 0.0101(3) | 0.0422(3) |
| O(3) | 1.0146(3) | 0.5252(5) | −0.1677(2) | 0.051(1) |
| N(1) | 0.5853(4) | 0.3244(5) | −0.1074(3) | 0.043(3) |
| N(2) | 0.8025(4) | 0.0093(5) | 0.0515(3) | 0.043(1) |
| N(3) | 1.2439(4) | 0.5253(6) | −0.2242(3) | 0.054(1) |
| C(1) | 0.7086(4) | 0.4078(5) | −0.1023(3) | 0.034(1) |
| C(2) | 0.8236(4) | 0.8370(5) | 0.0389(3) | 0.038(1) |
| C(3) | 1.1081(5) | 0.4941(7) | −0.2349(3) | 0.048(1) |

[a] In this and following tables standard deviations in the least significant digit(s) are given in parentheses [b] The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $(1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

TABLE 2 Fractional coordinates for H atoms

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(1)C(1) | 0.724(5) | 0.473(7) | −0.172(4) |
| H(1)N(1) | 0.550(5) | 0.272(7) | −0.037(4) |
| H(2)N(1) | 0.539(5) | 0.312(6) | −0.162(4) |
| H(1)C(2) | 0.738(4) | 0.762(6) | 0.051(3) |
| H(1)N(2) | 0.720(5) | 0.043(5) | 0.066(3) |
| H(2)N(2) | 0.865(6) | 0.089(9) | 0.048(5) |
| H(1)C(3) | 1.1121(7) | 0.424(9) | −0.302(6) |
| H(1)N(3) | 1.280(5) | 0.582(7) | −0.162(4) |
| H(2)N(3) | 1.312(9) | 0.46(1) | −0.287(7) |

TABLE 3 Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Mg(1)–O(1) | 2.056(3) | Mg(1)–O(2) | 2.077(3) |
| Mg(1)–O(3) | 2.067(3) | O(1)–C(1) | 1.233(4) |
| O(2)–C(2) | 1.235(5) | O(3)–C(3) | 1.226(5) |
| N(1)–C(1) | 1.292(5) | N(3)–C(3) | 1.273(6) |
| O(2)–Mg(1)–O(3) | 89.8(1) | O(1)–Mg(1)–O(3) | 90.0(1) |
| O(1)–Mg(1)–O(2) | 91.3(1) | Mg(1)–O(1)–C(1) | 130.5(2) |
| Mg(1)–O(2)–C(2) | 130.0(3) | Mg(1)–O(3)–C(3) | 135.4(3) |
| O(1)–C(1)–N(1) | 124.6(3) | O(3)–C(3)–N(3) | 126.9(4) |

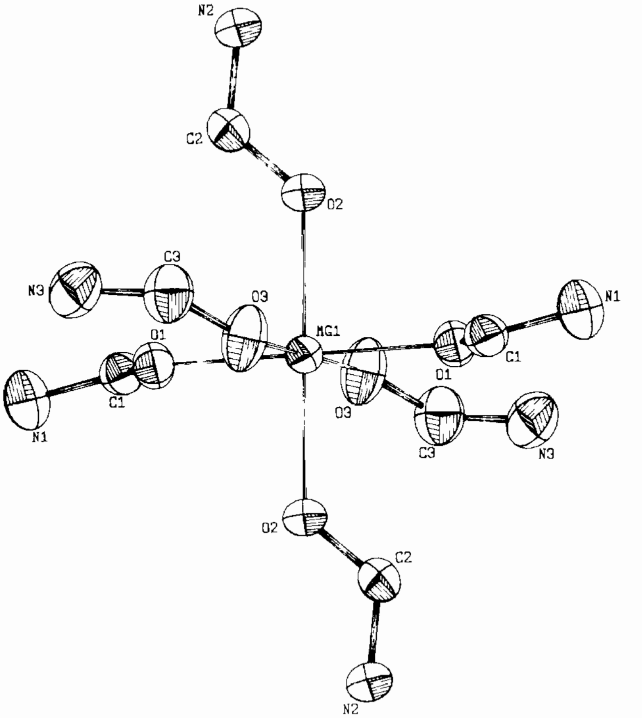

Fig 1. A perspective view showing the coordination around the magnesium atom with the atomic numbering scheme.

The powder X-ray diffraction patterns were scanned in the transmission technique with a GD-2000 diffractometer (Ital Structures, Riva del Garda, Italy) operating in the Seemann-Bohlin geometry and equipped with a quartz-curved crystal monochromator of the Johansson type aligned on the primary beam. Cu K$\alpha_1$ radiation ($\lambda = 1.5406$ Å) was employed, and an instrumental $2\theta$ step of 0.1° every 10 s was selected.

### *Thermogravimetric analysis*

The thermogravimetric analysis was carried out with a Perkin-Elmer TGS-2 thermobalance and the TG data were collected and processed by a Perkin-Elmer 3700 data station, under a nitrogen flow of 60 ml min$^{-1}$, with a heating rate of 20 °C min$^{-1}$ in the temperature range 30–600 °C.

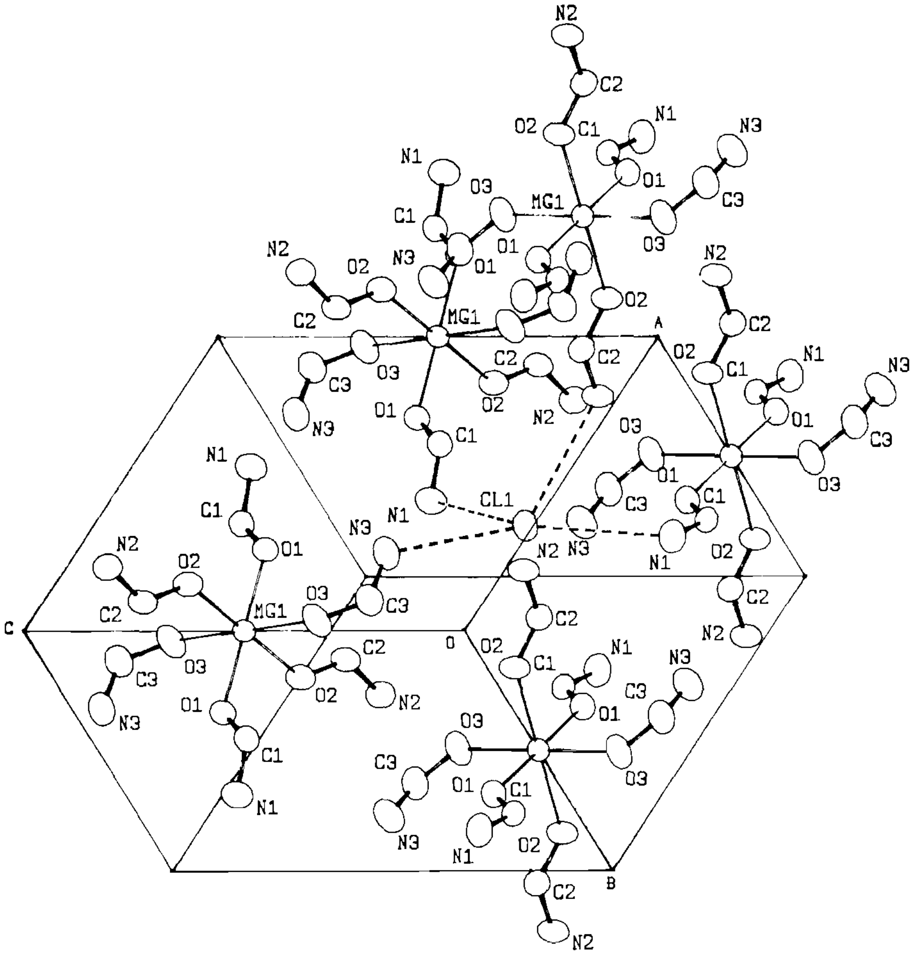

Fig. 2. Unit cell projection and hydrogen bonds between amidic groups and chloride ions.

TABLE 4. Geometry of hydrogen bonds

| | N–H (Å) | H–Cl (Å) | N---Cl (Å) | N–H---Cl (°) |
|---|---|---|---|---|
| C(1)–N(1)–H(1)---Cl | 1.002 | 2 299 | 3.296 | 173 64 |
| C(2)–N(2)–H(1)---Cl | 0 822 | 2.441 | 3 256 | 171 52 |
| C(1)–N(1)–H(2)---Cl | 0.786 | 2.538 | 3.265 | 154.45 |
| C(3)–N(3)–H(2)---Cl | 1.129 | 2 152 | 3 245 | 162 28 |

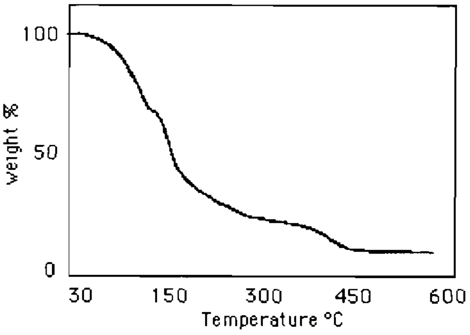

Fig. 3. Thermogram of the formamide elimination reaction from the $MgCl_2(HCONH_2)_6$ adduct (heating rate 20 °C min$^{-1}$)

## Discussion

Tables 1 and 2 give the fractional atomic coordinates with equivalent isotropic thermal parameters. Selected bond lengths and angles are listed in Table 3. The crystal analysis of $MgCl_2(HCONH_2)_6$ shows an ionic structure in which the magnesium ion is octahedrally coordinated by six formamide moieties through the oxygen atoms of the carbonyl groups as shown in Fig. 1. Bond lengths and angles of this compound resemble those reported for $[MgCl_2(C_7H_7OH)_6]$ and $[MgCl_2(C_2H_5OH)_6]$ [4, 6]. In particular the average values of the Mg–O and O–C distances fall into the expected values. The crystallographic data (see Table 4 and Fig. 2) are in agreement with a structure in which each chloride ion is bonded to four formamide amidic groups through hydrogen bonds so forming in the solid state a tridimensional network.

Figure 3 shows the thermogram recorded in the temperature range 30–600 °C. The overall weight loss

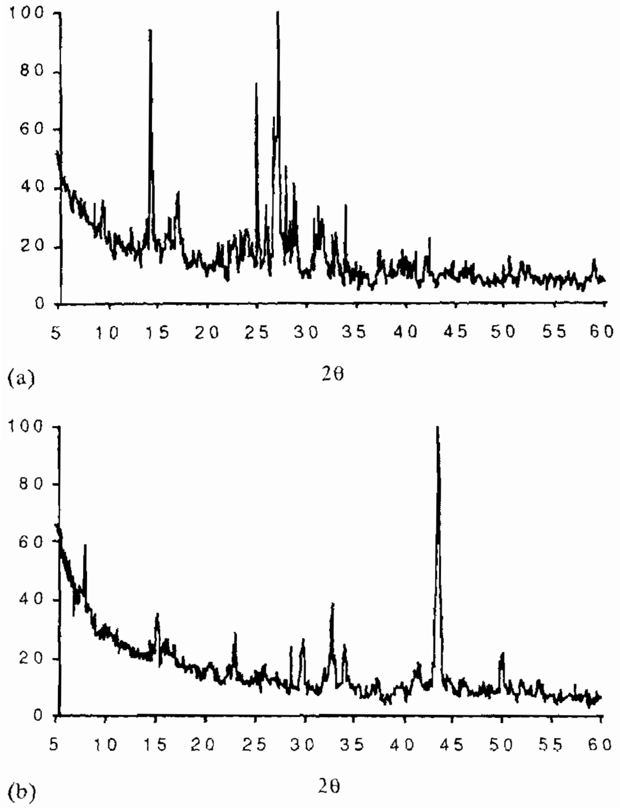

Fig 4 Powder XRD patterns of (a) $MgCl_2(HCONH_2)_6$; (b) $MgCl_2(HCONH_2)_2$ (intensities in arbitrary units).

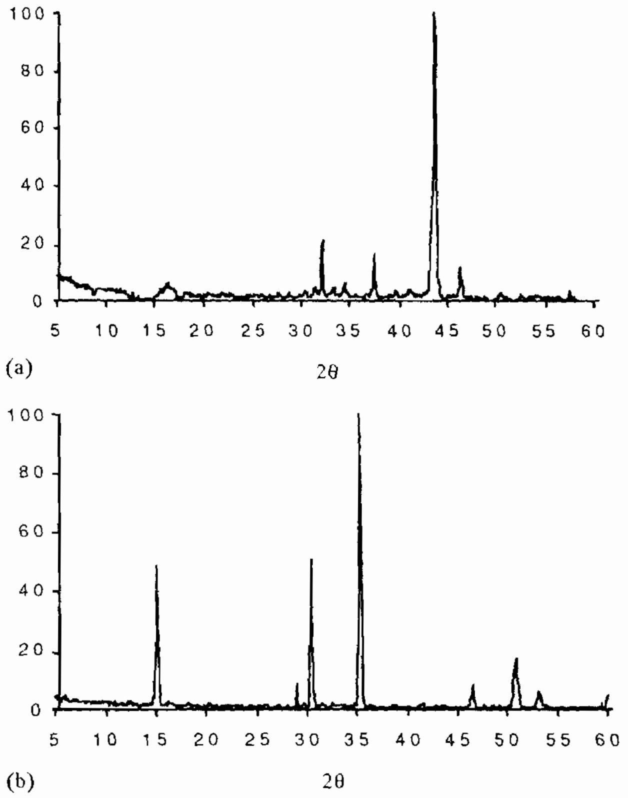

Fig 5 Powder XRD patterns of (a) $MgCl_2(HCONH_2)_6$ adduct after treatment at 220 °C and reduced pressure for 160 h; (b) $\alpha$-$MgCl_2$ (*intensities in arbitrary units*)

is equal to 75%, corresponding to the elimination of all of the six-coordinated molecules of formamide from the $MgCl_2(HCONH_2)_6$ adduct (the theoretical value is 73.95%). The elimination of the coordinated Lewis base appears to be the result of three successive steps. This behaviour is due to both steric and electronic factors. In particular, it should be noted that the elimination of the donor molecules occurs at temperatures progressively higher as the elimination goes on. In fact, with the decrease in the number of coordinated donors the electrophilicity of the metal centre increases and so also the activation energy of the elimination reaction [7].

By gradual slow elimination we were also able to obtain an adduct having the composition $MgCl_2(HCONH_2)_2$. Figure 4(a) and (b) shows the powder XRD spectra of the adducts $MgCl_2(HCONH_2)_6$ and $MgCl_2(HCONH_2)_2$, respectively.

Finally the compound $MgCl_2(HCONH_2)_6$ was subjected to thermal treatment at 220 °C and $10^{-2}$ mmHg for 160 h. The resulting material still contains 2% wt./wt. of residue base. Therefore, the $MgCl_2$ adduct with formamide appears more thermally stable than those with ethanol, ethyl acetate or benzoate [11] as donor ligands. In fact, the coordinated formamide molecules appear to be not easily removed and therefore a fully disordered $MgCl_2$ species cannot be obtained in this way. The XRD pattern of the thermally treated product (Fig. 5(a)) looks more like a discrete compound rather than a disordered species. On the other hand it is to be noted that the characteristic peaks shown by the $\alpha-MgCl_2$ XRD spectrum (Fig. 5(b)) are totally absent in the spectrum of the product obtained after prolonged heating. In particular, the disappearance of the 003 peak centred at $2\theta = 15°$ should be noted. This peak, shown by $\alpha$-$MgCl_2$, may be associated with the stacking of the Cl–Mg–Cl triple layers along the *c* crystallographic direction [2].

Experiments are now in progress in order to evaluate the effectiveness of this material to act as a catalyst support in propene polymerization.

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