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***N,N*-Dimethylcarbamato derivatives of magnesium starting  
from the metal oxide**

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Received 2 December 2003; accepted 6 April 2004

Available online 12 August 2004

#### Abstract

Magnesium oxide reacts with dimethylammonium dimethylcarbamate,  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ , in toluene yielding the carbonato-carbamato complex  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$  **1**, which gradually loses  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  upon mild heating or by lowering the carbon dioxide pressure to give products of intermediate composition  $[\text{Me}_2\text{NH}_2]_n[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12+n}]$  with  $n$  ranging from 3 to 0, the neutral complex  $[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12}]$ , **2**, being obtained upon exhaustive treatment in vacuo. The equilibria may be shifted back from **2** to **1** by using an excess of  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ . The same products were obtained in low yields by reacting magnesium with  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ : in this case the reaction proceeds slowly, being presumably promoted by the presence of some MgO and/or  $\text{H}_2\text{O}$ . The crystal and molecular structure of **1** has been studied by single-crystal X-ray diffraction methods, the anion containing a ring of eight edge- or apex-sharing  $\{\text{MgO}_6\}$  distorted octahedra, with Mg–O distances in the range from 1.921 to 2.313 Å. The framework is kept together by two  $\mu_6$ -carbonato ligands and by the fifteen carbamato ligands. The ionic aggregates  $[\text{NH}_2\text{Me}_2]_n[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$  are alternated in the crystal with heptane molecules and only weak van der Waals interactions are present between adjacent octanuclear aggregates, in agreement with the solubility of the substance in toluene. **To cite this article:** *D. Belli Dell'Amico et al., C. R. Chimie 7 (2004).*

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#### Résumé

L'oxyde de magnésium réagit avec le diméthylcarbamate de diméthylammonium,  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ , dans le toluène, donnant le complexe  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$ , **1**, qui, progressivement, dans des conditions de chauffage doux ou de pression faible de dioxyde de carbone, perd  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  pour donner des produits de composition  $[\text{Me}_2\text{NH}_2]_n[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12+n}]$  avec  $n$  compris entre 3 et 0, le complexe neutre  $[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12}]$ , **2**, étant obtenu sous condition de vide prolongé. L'équilibre peut être déplacé de **2** à **1** grâce à un excès de  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ . Les mêmes produits sont obtenus à faibles rendements en faisant réagir le magnésium avec  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ : dans ce cas, la réaction a lieu lentement, probablement facilitée par la présence de MgO et/ou de  $\text{H}_2\text{O}$ . La structure cristalline et moléculaire de **1** a été étudiée par diffraction des rayons X, l'anion contenant un cycle à huit octaédres distordus  $\{\text{MgO}_6\}$ , partageant des

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sommets ou des côtés, avec des distances Mg–O de l'ordre de 1.921 à 2.313 Å. L'ossature est maintenue par deux ligands  $\mu_6$ -carbonato et par les quinze ligands carbamato. Les agrégats ioniques  $[\text{NH}_2\text{Me}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{OCONMe}_2)_{15}]$  alternent dans le cristal avec des molécules d'heptane et seules des interactions de van der Waals faibles sont présentes entre les agrégats octanucléaires adjacents, en accord avec la solubilité de la substance dans le toluène. *Pour citer cet article : D. Belli Dell'Amico et al., C. R. Chimie 7 (2004).*

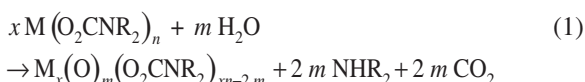
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**Keywords:** Carbamato complexes; Magnesium; Metal oxide

**Mots-clés :** Complexes carbamato ; Magnésium ; Oxyde métallique

## 1. Introduction

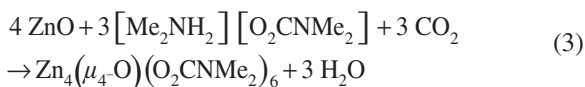
The *N,N*-dialkylcarbamato ligand is versatile, forming complexes with many elements within the Periodic Table [1]. *N,N*-dialkylcarbamato complexes have unique properties, and protic reagents [2] promptly displace coordinated carbon dioxide. The reactivity of *N,N*-dialkylcarbamato complexes has been extensively exploited in our laboratories for: (i) controlled hydrolysis in various M/H<sub>2</sub>O molar ratios [3]; (ii) exhaustive hydrolysis; (iii) implanting metal cations on inorganic surfaces, mainly silica [4]. The well-established hydrolysis experienced by homoleptic *N,N*-dialkylcarbamato metal complexes of formula  $\text{M}(\text{O}_2\text{CNR}_2)_n$ , leads to  $\mu$ -oxo derivatives (see Eq. (1)), the degree of oxide formation depending on the M/H<sub>2</sub>O ratio, and on the nature of M.



In apparent contrast with this reactivity, some metal oxides have been used in the past as synthetic precursors to *N,N*-dialkylcarbamato metal derivatives. Not only silver oxide [5], characterized by a low value, of the free energy of formation ( $\text{Ag}_2\text{O}$ ,  $\Delta G_f^\circ = -11.2 \text{ kJ mol}^{-1}$ , i.e.  $-5.6 \text{ kJ mol}^{-1}$  per mol of silver) [6], but also ZnO [7] ( $\Delta G_f^\circ = -320.5 \text{ kJ mol}^{-1}$  [6]) react according to Eqs. (2) and (3), respectively:



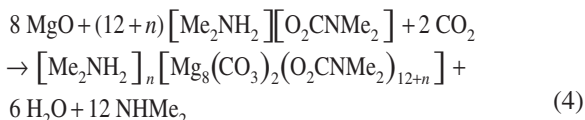
$R = \text{Me}$ ,  $n = \infty$ ;  $R = \text{Et}$ ,  $n = 2$



This paper reports some new results on the synthesis and characterization of new *N,N*-dialkylcarbamato complexes of magnesium, as obtained from the metal oxide. The synthesis of magnesium carbamato complexes has been recently reported by four different groups [8–11], the interest on this subject being justified by the probable presence of these systems in the active site of Rubisco [12], an enzyme involved in the carbon dioxide metabolism in living organisms. We therefore reckoned that the extension of the metal-oxide-based synthetic methodology to  $\mu_n$ -O– or to homoleptic metal–dialkylcarbamato complexes of magnesium could represent an important acquisition in general terms and an even more challenging proposition in view of the higher stability of magnesium oxide ( $\Delta G_f^\circ = -569.4 \text{ kJ mol}^{-1}$ ) [6].

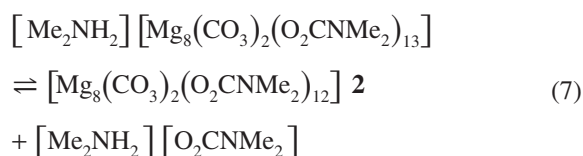
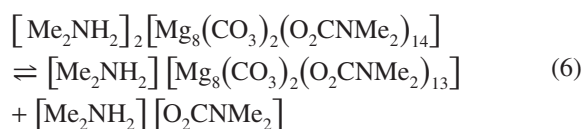
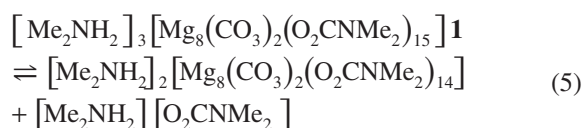
## 2. Results and discussion

The reaction of MgO with  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  in toluene resulted in a relatively fast (1 d for the conversion of 2 g of MgO at room temperature) and substantially complete conversion to products of formula  $[\text{Me}_2\text{NH}_2]_n[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12+n}]$ , with  $n$  ranging from 3 to 0 (see Eq. (4)).



Product composition was found to depend on work-up conditions, especially temperature and time during the recovery, the solid being treated in vacuo before analysis. Products of the two limiting compositions,  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$ , **1**, and  $\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12}$ , **2**, were obtained by approx-

priate work-up, see *Experimental Section*. The latter compound was obtained from **1** by gradual releasing of  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ , as confirmed by the weight loss experienced by a sample of **1** when heated in vacuo. The  $\text{CO}_2/\text{Mg}$  molar ratio varies consistently from 2.06 to 1.74, the theoretical values being 2.12 and 1.75 for **1** and **2**, respectively.



We propose the presence in solution of equilibria (5)–(7). This is substantiated by the observation that **2** has been converted back into **1** by treatment in toluene with an excess of dimethylammonium *N,N*-dimethylcarbamate under a carbon dioxide atmosphere. Addition of heptane to the toluene solution of the primary products in the presence of  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  will precipitate the ionic products (**1** was recrystallized at 4 °C in a satisfactory yield), while removing the volatiles in vacuo at 60 °C will form **2**, that is sparingly soluble in organic solvents. A similar release of  $[\text{R}_2\text{NH}_2][\text{O}_2\text{CNR}_2]$  was observed for  $[\text{NH}_2^i\text{Pr}_2][\text{Ti}_2(\text{O}_2\text{CN}^i\text{Pr}_2)_7]$  giving  $\text{Ti}_2(\text{O}_2\text{CN}^i\text{Pr}_2)_6$  [13].

The analysis of the IR and NMR spectra of **1** is complicated by the high number of non-equivalent carbamate ligands. A broad strong band is present in the nujol IR spectrum in the range 1640–1450  $\text{cm}^{-1}$ , attributable to a number of slightly different C–O and C–N stretching vibrations of the carbamate and carbonate ligands, suggesting various coordination modes. Carbamate [1] and carbonate [14] derivatives are reported to show stretching vibrations in the range 1680–1450  $\text{cm}^{-1}$ .

In the  $^1\text{H}$ -NMR spectra of product **1**, signals due to carbamate methyl groups coalesce in a broad band centred at 2.8 ppm, while a broad signal at about 2.4 ppm is due to the ammonium methyl groups. Broad  $^{13}\text{C}$ -NMR signals are also present for the methyl carbons (36.2 ppm) and for the carbamate/carbonate  $\text{CO}_2$  moieties at 162.8 ppm. As the signals are rather broad, it is reasonable that those due to the  $\text{CO}_2$  moieties of the carbonate and carbamate groups overlap. They are in fact expected to be quite close: for instance in  $\text{Mg}_5(\text{CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_8(\text{HMPA})_2$  [11], the resonances are at 162.49 and 163.85 ppm for the carbamate and carbonate groups, respectively. Signals of low intensity attributable to crystallization solvents (toluene and heptane) are present even in samples extensively dried in vacuo at room temperature. Unfortunately, the low solubility of **2** prevents its NMR spectra to be recorded.

As already observed in the case of ZnO [7], dimethylamine is unique in reacting with MgO under absorption of  $\text{CO}_2$  to give the carbamate complexes. As a matter of fact, no products were obtained with  $\text{NHET}_2$ ,  $\text{NH}^i\text{Pr}_2$  and  $\text{NHBu}_2$ .

Attempts have also been made to obtain *N,N*-dimethylcarbamate complexes starting from magnesium metal and  $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$ . As magnesium has a low standard reduction potential, this appeared to be a practicable route, similar to what already established for sodium [15]. A preliminary unsuccessful attempt was carried out between magnesium and  $\text{NH}^i\text{Pr}_2/\text{CO}_2$  [8]. However, since we had already shown that the reactivity of the  $\text{NHMe}_2/\text{CO}_2$  system, as compared with other  $\text{NHR}_2/\text{CO}_2$  systems, is somehow special [7], this unsuccessful first attempt did not discourage us from trying with dimethylamine. We have found that magnesium reacts quite slowly with  $\text{NHMe}_2/\text{CO}_2$  in toluene *with di-hydrogen evolution* affording **1**, albeit in low yields. Thus, we assume that the direct reaction between Mg and  $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$  is exceedingly slow and MgO impurities on the surface of the metal and accidental presence of water may promote the process. In fact, yields increase when commercial magnesium turnings (99.0%) or commercial  $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$  are used instead of high-purity magnesium (99.9%) or freshly prepared  $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$ .

The slow and incomplete reaction of magnesium with  $[\text{NH}_2\text{Me}_2][\text{O}_2\text{CNMe}_2]$  agrees with the previous observation [16] that zinc of the highest available pu-

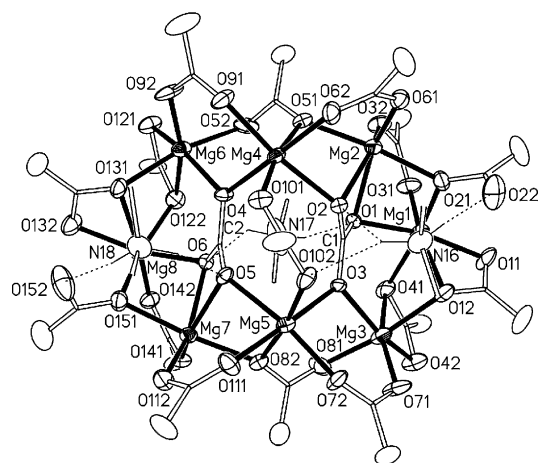


Fig. 1. View of the structure of the ionic  $[\text{NH}_2\text{Me}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$  heptane, **1**. The thermal ellipsoids of the C atoms have been omitted for clarity, those of the Mg, O and N atoms have been represented at 30% probability. The dotted lines represent the main H-interactions.

rity (99.999%) fails to react with the  $\text{NHMe}_2/\text{CO}_2$  system, while zinc of a lower purity led to the corresponding homoleptic carbamato derivative of zinc(II)  $[\text{NH}_2\text{Me}_2][\text{Zn}_2(\text{O}_2\text{CNMe}_2)_3]\cdot\text{CH}_3\text{CN}$ .

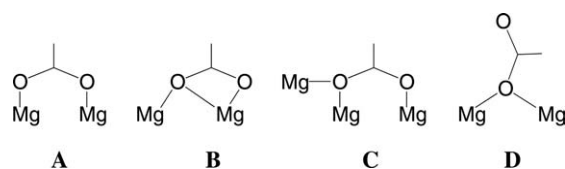
Product **1**, as recrystallized from hot heptane under a carbon dioxide atmosphere, was studied by single crystal X-ray diffraction methods. In the octanuclear aggregate, containing lattice heptane,  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]\cdot\text{C}_7\text{H}_{16}$ , each magnesium atom is hexacoordinated in an octahedral geometry to the oxygen atoms of the carbamato and carbonate groups. A similar octahedral  $\text{MgO}_6$  core is encountered in the Rubisco enzymes, whose catalytic activity towards carboxylation is believed to rely on the formation of a magnesium carbamato complex resulting from the interaction of  $\text{CO}_2$  with an amino group of lysine at the active site of the enzyme [12].

Fig. 1 displays a view of the octanuclear ionic aggregates  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$  of **1**, while the Mg–O bond distances, shown in the figure as filled sticks, are reported in Table 1. The anion contains a ring of eight edge- or apex-sharing  $[\text{MgO}_6]$  distorted octahedra, where the Mg–O distances span a rather large range of values from 1.921 to 2.313 Å. Also the O–Mg–O angles are rather far from the ideal octahedral values, e.g.  $58.2^\circ$  for O1–Mg2–O2 and  $174.8^\circ$  for O111–Mg5–O3. The framework is kept together by

Table 1  
Co-ordination distances (Å) of Mg in the structure of  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]\cdot\text{heptane}$ , **1**

Mg1–O31	1.945(10)	Mg5–O72	1.921(9)
Mg1–O11	1.996(10)	Mg5–O102	2.021(10)
Mg1–O1	2.068(9)	Mg5–O111	2.043(10)
Mg1–O41	2.093(10)	Mg5–O5	2.104(9)
Mg1–O21	2.070(10)	Mg5–O82	2.108(9)
Mg1–O12	2.251(9)	Mg5–O3	2.195(9)
Mg2–O32	1.967(10)	Mg6–O92	1.944(10)
Mg2–O61	2.007(10)	Mg6–O52	2.045(11)
Mg2–O51	2.031(9)	Mg6–O131	2.056(10)
Mg2–O21	2.046(10)	Mg6–O121	2.102(10)
Mg2–O1	2.187(9)	Mg6–O4	2.139(9)
Mg2–O2	2.252(9)	Mg6–O122	2.300(10)
Mg3–O71	1.963(11)	Mg7–O112	1.979(10)
Mg3–O81	1.990(11)	Mg7–O141	1.985(9)
Mg3–O42	2.070(10)	Mg7–O82	2.025(9)
Mg3–O12	2.107(11)	Mg7–O151	2.082(10)
Mg3–O3	2.177(9)	Mg7–O6	2.179(9)
Mg3–O41	2.313(10)	Mg7–O5	2.244(9)
Mg4–O91	1.983(10)	Mg8–O142	1.973(10)
Mg4–O62	1.989(10)	Mg8–O6	2.030(9)
Mg4–O101	2.030(10)	Mg8–O132	2.032(10)
Mg4–O2	2.128(9)	Mg8–O122	2.044(10)
Mg4–O51	2.153(9)	Mg8–O151	2.072(10)
Mg4–O4	2.169(9)	Mg8–O131	2.248(10)

two  $\mu_6$  carbonato ligands and by the fifteen carbamato ligands. The latter adopt four different ligation types. Scheme 1 shows the four types arranged in the decreasing order of frequency.



Scheme 1.

While ligation types **A**, **B** and **C** have been encountered previously [1], the bridging type **D** has never been observed before. It is interesting to note that the Mg–O bond distances longer than 2.30 Å are related to the carbamato groups 4 and 12, both adopting the ligation type **B**. The octanuclear aggregate is completed by three dimethylammonium cations, whose nitrogen atoms are labelled N16, N17 and N18, which are disposed around the anion through both ionic bonds and a number of N–H···O interactions shown in the figure by dotted lines. The parameters of the main H-interactions are listed in Table 2.

As it can be seen in both Figs. 1 and 2, the dimethylammonium cation containing the N16 nitrogen atom presents a multiple interaction through one of its hydrogen atoms. Moreover, the carbamato ligation of type **D** (see Scheme 1), which is not found in homoleptic metal carbamates [1], is present in **1**, because the oxygens O22 and O152 accept the strongest hydrogen bonds.

The octanuclear aggregate has approximate  $C_2$  symmetry, with the twofold axis passing through N17 and the carbamato group 10. This feature is easily recognized in Fig. 1, which is projected almost exactly in this direction. The octanuclear ionic aggregates  $[\text{NH}_2\text{Me}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{OCONMe}_2)_{15}]$  are packed in

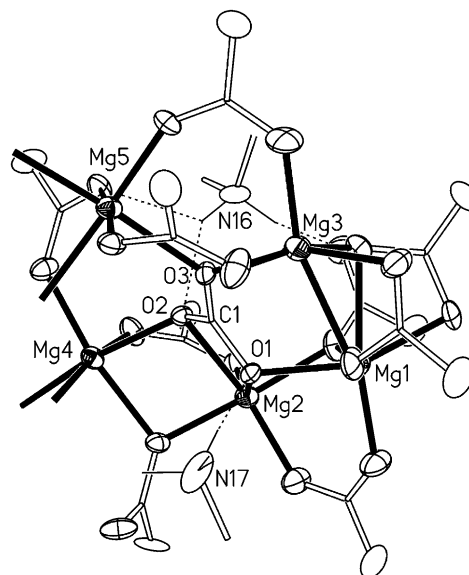


Fig. 2. Detailed view of the coordination of the carbonato ligand in **1** (C1, O1, O2, O3).

the crystal alternated with heptane molecules, and only van der Waals interactions are present between adjacent octanuclear aggregates. The strong ionic and hydrogen interactions that connect the components of each aggregate probably survive in solvents of low polarity, which explains the solubility of this substance in toluene.

Fig. 2 shows the coordination of the carbonato group containing the carbon atom labelled C1. We have taken advantage of the presence of the pseudo  $C_2$  symmetry to simplify the drawing and to represent only one half of the aggregate, the other half being almost equivalent. As shown in Fig. 2, the O3 atom of the substantially planar carbonato ligand is coordinated to C1, Mg3 and Mg5, being only 0.009 Å out of the plane defined by these three atoms. On the contrary, the oxygen atoms O1 and O2 are co-ordinated to C1,

Table 2

Main H-interactions in the ion quartet  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$ -heptane

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	<(DHA)
N16–H16A···O2	0.90	2.08	2.858(13)	143.9
N16–H16A···O102	0.90	2.36	3.018(14)	130.3
N16–H16B···O22	0.90	1.80	2.671(15)	161.3
N17–H17A···O6	0.90	2.17	2.907(14)	139.0
N17–H17B···O1	0.90	2.01	2.886(14)	163.6
N18–H18A···O152	0.90	1.74	2.631(14)	168.9
N18–H18B···O5	0.90	2.06	2.900(13)	155.3

Mg1, Mg2 and to C1, Mg2, Mg4, respectively, with a marked pyramidal geometry, being 0.691 and 0.577 Å, respectively, out of the coordination planes. These deviations from planarity can be ascribed to the acceptance of strong hydrogen bonds from the ammonium ions containing N17 and N16, respectively.

The architecture of the aggregate with the two  $\mu_6$ -carbonato ligands resembles that of  $[\text{Mg}_9(\mu_5\text{-CO}_3)(\text{O}_2\text{COMe})_8(\mu_3\text{-OMe})_8(\text{MeOH})_{13}] \cdot \text{MeOH} \cdot \text{C}_7\text{H}_8$ , as reported by Mingos et al. [17]. In this case, the presence of the carbonato groups has been explained as due to partial hydrolysis of the precursor  $[\text{Mg}(\text{O}_2\text{COMe})(\text{OMe})(\text{MeOH})_{1.5}]_n$ . In the ennea-nuclear complex, the Mg–O distances within the  $\mu_5\text{-CO}_3$  ligand range between 2.031 and 2.148 Å. Recently the synthesis of a magnesium carbamato–carbonato complex  $\text{Mg}_5(\mu_5\text{-CO}_3)(\text{O}_2\text{CN}^i\text{Pr}_2)_8(\text{HMPA})_2$  has been reported [11], where the magnesium atoms form a five-membered ring through the bridging carbonato group.

The  $\mu_5$  coordination hapticity of a carbonato ligand is unusual. Even more rare is the  $\mu_6$  coordination mode of the carbonato ligand. A literature survey has pointed out the existence of a few cases of this coordination mode for vanadium [18], molybdenum [19,20], nickel [21], and lanthanides [22].

### 3. Experimental section

All preparations were carried out in standard Schlenk tubes. All solvents were freshly distilled over conventional drying agents under dinitrogen and all reactions were carried out under an atmosphere of dinitrogen, or carbon dioxide, as indicated. Dimethylammonium dimethylcarbamate,  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ , was purchased from Fluka or freshly prepared from dimethylamine and carbon dioxide, as specified. Magnesium oxide (99.9%) was obtained by calcining commercial  $\text{MgH}_2$  (Aldrich) and kept in sealed vials under a dry atmosphere. Elemental analysis: found% (calc.% for  $\text{MgO}$ ): Mg 59.4 (60.3). The metal content of commercial magnesium in turnings (Aldrich) was 99.0%. Pure magnesium metal ( $\geq 99.9\%$ ) was obtained as the unreacted residue (used in excess) after treatment of commercial magnesium with  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ .

IR spectra were measured with a Perkin Elmer FT–IR mod. 1725X spectrophotometer. NMR spectra

were recorded using a Varian Gemini 200 MHz instrument, the data being expressed in ppm from TMS for  $^1\text{H}$  and  $^{13}\text{C}$ . GC analyses were carried out on a Dani 3800 gas chromatograph. Elemental analyses (C, H, N) were performed by the ‘Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa’, with a Carlo Erba mod. 1106 elemental analyzer. Magnesium analyses were carried out by complexometry [23] using standard EDTA solutions. Carbon dioxide was determined by gas-volumetric measurements, the samples being attacked with 20% sulphuric acid.

#### 3.1. Reaction of $\text{MgO}$ with $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$

To a toluene (100 ml) solution of  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  (32.0 ml, 0.250 mol) freshly prepared from  $\text{NHMe}_2$  and  $\text{CO}_2$ ,  $\text{MgO}$  (1.32 g, 32.76 mmol) was added under an atmosphere of carbon dioxide. After 1 d stirring at room temperature, the mixture was filtered under carbon dioxide to remove traces of unreacted magnesium oxide. By removing all the volatiles from the filtrate at room temperature under reduced pressure, a colourless residue was obtained. Upon addition of heptane (100 ml), the product was recovered by filtration of the resulting suspension under dinitrogen. The solid was dried in vacuo (5.21 g, 84% yield based on the starting magnesium). Elemental analysis: found% (calc.% for  $[\text{NH}_2\text{Me}_2][\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{13}]$ ,  $\text{C}_{43}\text{H}_{86}\text{N}_{14}\text{Mg}_8\text{O}_{32}$ ): Mg 12.8 (12.9),  $\text{CO}_2$  43.9 (43.8), corresponding to a  $\text{CO}_2/\text{Mg}$  molar ratio of 1.89 (th. 1.87). IR (nujol,  $3000\text{--}600\text{ cm}^{-1}$ ): 1605 (sh), 1567 (s), 1507 (s), 1282 (m). The analytical data were found to depend on the drying procedure: variable compositions,  $[\text{Me}_2\text{NH}_2]_n[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12+n}]$ , with  $n$  ranging from 3 to 0, were obtained. Similar results were obtained by using commercial  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ .

Starting from commercial  $\text{MgO}$  (Aldrich, fused, pieces, 99.96%), the reaction was found to be extremely slow at room temperature.

#### 3.2. Reaction of $\text{Mg}$ with $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$

Freshly prepared ( $T \sim -10\text{ }^\circ\text{C}$ )  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  from dimethylamine (30 ml, 0.65 mol) and carbon dioxide was reacted with commercial magnesium turnings (3.00 g, 0.12 mol) in toluene (100 ml). The suspension was stirred and a slow evolution of

di-hydrogen was confirmed by a gas-chromatographic control. Vacuum/carbon dioxide cycles were repeated at regular intervals of time. After 12 d, the unreacted metal was filtered off, and the solution was evaporated to dryness in vacuo at room temperature. The solid residue was suspended in heptane, filtered under di-nitrogen and dried in vacuo. The colourless product was recovered (1.21 g, 5% yield based on the starting magnesium). Elemental analysis: found% (calc.% for  $[\text{Me}_2\text{NH}_2][\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{13}]$ ,  $\text{C}_{43}\text{H}_{86}\text{N}_{14}\text{Mg}_8\text{O}_{32}$ ): Mg 13.1 (12.9),  $\text{CO}_2$  41.7 (43.8), corresponding to a  $\text{CO}_2/\text{Mg}$  molar ratio of 1.76 (th. 1.87)). IR (nujol, 2000–1250  $\text{cm}^{-1}$ ): 1611 (sh), 1568 (sh), 1515 (s), 1283 (s).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 2,9 (m, 81H); 2,3 (s, 19H) ppm.

The reaction was also carried out starting from commercial  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ . After 13 d, the unreacted metal was filtered off and the solution was evaporated to dryness in vacuo at room temperature. The work-up was as in the previous syntheses, taking care in this case to keep the temperature below 30 °C throughout the whole procedure (39.4% yield with respect to magnesium metal). Elemental analysis: found% (calc.% for  $[\text{Me}_2\text{NH}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$ ,  $\text{C}_{53}\text{H}_{114}\text{Mg}_8\text{N}_{18}\text{O}_{36}$ : Mg 11.4 (11.0),  $\text{CO}_2$  42.6 (42.2), corresponding to a  $\text{CO}_2/\text{Mg}$  molar ratio of 2.06 (2.12)). IR (nujol, 2000–1250  $\text{cm}^{-1}$ ): 1611 (sh), 1582 (sh), 1515 (s), 1283 (s).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): [2.9; 2.8] (81 H); 2.4 (19 H) ppm.  $^{13}\text{C-NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 162.8; 36.2 ppm. This compound was recrystallized from hot heptane under carbon dioxide and single crystals suitable for X-ray diffraction studies were thus obtained.

When high-purity (99.9%) magnesium was treated with freshly prepared  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$ , after 1 month, about 80% of the starting magnesium was recovered by filtration and only a negligible amount of a solid residue was obtained by removing all the volatiles from the filtrate.

### 3.3. Crystallographic study

Crystals of **1** were small and poorly diffracting. A crystal of dimensions  $0.32 \times 0.28 \times 0.18$  mm was selected under a dinitrogen atmosphere saturated with heptane and sealed in a glass capillary. The diffractions were collected at room temperature with a Bruker SMART CCD area detector diffractometer. Crystal data are reported in Table 3.

Table 3  
Crystal data and structure refinement

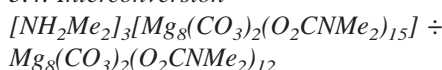
Empirical formula	$\text{C}_{60}\text{H}_{130}\text{Mg}_8\text{N}_{18}\text{O}_{36}$
Formula weight	1874.30
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
$a$ (Å)	14.305(1)
$b$ (Å)	37.079(3)
$c$ (Å)	18.940(2)
$\beta$ (°)	92.215(2)
$U$ (Å <sup>3</sup> )	10038(2)
$Z$	4
$D_{\text{calc}}$ ( $\text{Mg m}^{-3}$ )	1.240
$\mu$ ( $\text{mm}^{-1}$ )	0.144
Data/restr./param.	13990/0/885
$R(F_o)$ [ $I > 2 \sigma(I)$ ] <sup>a</sup>	0.1034
$Rw(F_o^2)$ [ $I > 2 \sigma(I)$ ] <sup>a</sup>	0.2233
Goodness of fit <sup>a</sup> on $F^2$	0.695

Goodness of fit =  $[\sum [w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$ , where  $N$ ,  $P$  are the numbers of observations and of parameters, respectively

<sup>a</sup>  $R(F_o) = \sum | |F_o| - |F_c| | / \sum |F_o|$ ;  $Rw(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (A Q)^2 + B Q]$ , where  $Q = [\text{MAX}(F_o^2, 0) + 2 F_c^2]/3$ ;

Graphite-monochromatized Mo–K $\alpha$  ( $\lambda = 0.71073$  Å) radiation was used with the generator working at 50 kV and 35 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on 315 reflections measured in three different sets of 15 frames each, in the range  $0 \leq \theta \leq 23^\circ$ . The diffraction pattern showed measurable intensities only at low  $\theta$  angle, so we limited the data collection to  $\theta \leq 23^\circ$  in a half sphere (scan method), with the sample–detector distance being fixed at 5 cm. Only 20% of the measured reflections had  $I > 2 \sigma(I)$ . No crystal decay was observed, and absorption correction was not applied owing to the relatively low absorption factor. A total of 27701 reflections were collected (13990 unique,  $R_{\text{int}} = 0.159$ ;  $R_{\text{int}} = [\sum |F_o^2 - F_o^2(\text{mean})| / \sum F_o^2]$ ). The structure was solved by direct methods (SIR-92) [24] and refined with full-matrix-block least-squares (SHELX-97) [25]. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogens were let ride on their carbon or nitrogen atoms.

### 3.4. Interconversion



A toluene (60 ml) solution of  $[\text{NH}_2\text{Me}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$  (2.18 g, 1.23 mmol) was

evaporated to dryness in vacuo at 50 °C. The residue (1.68 g, 84% yield) was sealed in vials. Elemental analysis: found% (calc.% for  $\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12}$ ,  $\text{C}_{38}\text{H}_{72}\text{N}_{12}\text{Mg}_8\text{O}_{30}$ ): Mg 13.7 (14.2),  $\text{CO}_2$  43.2 (44.9), corresponding to a  $\text{CO}_2/\text{Mg}$  molar ratio of 1.74 (th. 1.75)).

The magnesium complex  $\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{12}$  (2.05 g, 1.49 mmol) was dissolved in toluene (50 ml) in the presence of  $[\text{Me}_2\text{NH}_2][\text{O}_2\text{CNMe}_2]$  (5.0 ml, 0.04 mmol). The product was recovered as colourless crystals upon cooling the resulting solution at 4 °C. The product was dried in vacuo at a temperature below 30 °C (2.53 g, 96% yield). Elemental analysis: found% (calc.% for  $[\text{NH}_2\text{Me}_2]_3[\text{Mg}_8(\text{CO}_3)_2(\text{O}_2\text{CNMe}_2)_{15}]$ ,  $\text{C}_{53}\text{H}_{114}\text{N}_{18}\text{Mg}_8\text{O}_{36}$ : Mg 10.7 (11.0)).

### Acknowledgments

This work was supported by the 'Ministero dell'Istruzione, dell'Università e della Ricerca', MIUR, 'Progetti di Rilevante Interesse Nazionale' 2002–2003 and by the 'Consiglio Nazionale delle Ricerche', 'Programma CNR/MIUR Nanotecnologie, Processi litografici per nanofabbricazione'. The authors wish to thank Professor L. Busetto of the University of Bologna for allowing us to collect the X-ray data on their Bruker SMART CCD area detector diffractometer and Dr. E. Di Martino for help during data collection.

### Supplementary material

Details about the structure determination have been deposited in the form of the CIF file with the *Cambridge Crystallographic Data Centre* as deposit number CCDC 225857 for **1**. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Rd, Cambridge CB21EZ UK (fax: +44 –1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### References

- [1] D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, *Chem. Rev.* 103 (2003) 3857 and references therein.
- [2] A. Belforte, D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, L. Labella, *Gazz. Chim. It.* 123 (1993) 119.
- [3] D. Belli Dell'Amico, C. Bradicich, F. Calderazzo, A. Guarini, L. Labella, F. Marchetti, A. Tomei, *Inorg. Chem.* 41 (2002) 2814 and references therein.
- [4] L. Abis, D. Belli Dell'Amico, C. Busetto, F. Calderazzo, R. Caminiti, F. Garbassi, A. Tomei, *J. Mater. Chem.* 8 (1998) 2855 and references therein.
- [5] R. Alessio, D. Belli Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, P. Strasser, *Helv. Chim. Acta* 81 (1998) 219.
- [6] D. R. Lide (Ed.), *Handbook of Chemistry and Physics*, 82nd ed., CRC Press, Boca Raton, FL, USA, 2001–2002.
- [7] D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, *Inorg. Chim. Acta* 350 (2003) 661.
- [8] F. Calderazzo, G. Pampaloni, M. Sperrle, U. Englert, *Z. Naturforsch.* 47b (1992) 389.
- [9] M. Ruben, D. Walther, R. Knake, H. Görls, R. Beckert, *Eur. J. Inorg. Chem.* (2000) 1055.
- [10] M.T. Caudle, J.B. Benedict, C.K. Mobley, N.A. Straessler, T.L.G. Groy, *Inorg. Chem.* 41 (2002) 3183 and references therein.
- [11] K.C. Yang, C.C. Chang, C.S. Yeh, G.H. Lee, S.M. Peng, *Organometallics* 20 (2001) 126.
- [12] (a) W.W. Cleland, T.J. Andrews, S. Gutteridge, F.C. Hartman, G.H. Lorimer, *Chem. Rev.* 98 (1998) 549; (b) D. Walther, M. Ruben, S. Rau, *Coord. Chem. Rev.* 182 (1999) 67.
- [13] D. Belli Dell'Amico, F. Calderazzo, U. Giurlani, G. Pelizzi, *Chem. Ber.* 120 (1987) 955.
- [14] D.A. Palmer, R. van Eldik, *Chem. Rev.* 83 (1983) 651.
- [15] A. Belforte, F. Calderazzo, *J. Chem. Soc., Dalton Trans.* (1989) 1007.
- [16] J. Klunker, M. Biedermann, W. Schäfer, H. Hartung, *Z. anorg. allg. Chem.* 624 (1998) 1503.
- [17] V.C. Arunasalam, I. Baxter, J.A. Darr, S.R. Drake, M.B. Hursthouse, K.M.A. Malik, D.M.P. Mingos, *Polyhedron* 17 (1998) 641.
- [18] T.C.W. Mak, P.-J. Li, C.-M. Zheng, K.-Y. Huang, *Chem. Commun.* (1986) 1597.
- [19] M.-C. Suen, C.-W. Tseng, J.-D. Chen, T.-C. Keng, J.-C. Wang, *Chem. Commun.* (1999) 1185.
- [20] M.J. Manos, A.D. Keramidis, J.D. Woollins, A.M.Z. Slawin, T.A. Kabanos, *J. Chem. Soc., Dalton Trans.* (2001) 3419.
- [21] A. Graham, S. Meier, S. Parsons, R.E. Winpenney, *Chem. Commun.* (2000) 811.
- [22] S. Romero, A. Mosset, J.-C. Trombe, *J. Solid-State Chem.* 127 (1996) 256.
- [23] H.A. Flaschka in: *EDTA Titrations; An Introduction to Theory and Practice*, Pergamon Press, New York, 1959, pp. 75.
- [24] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gagliardi, *J. Appl. Crystallogr.* 26 (1993) 343.
- [25] G.-M. Sheldrick, *Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.