Notes

Insertion of Carbon Dioxide into Mg−N Bonds. Structural Characterization of a Previously Unknown η^2 Chelation Mode to Magnesium in Magnesium Carbamates

Yongjun Tang,[†] Lev N. Zakharov,[‡] Arnold L. Rheingold,[‡] and
Richard A. Kemp*,[†,§]

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131,
Department of Chemistry and Biochemistry, University of California,
San Diego, La Jolla, California, and Advanced Materials Laboratory,
Sandia National Laboratories, Albuquerque, New Mexico

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*Summary: Insertion reactions of CO_2 into magnesium amides that yield carbamates are known, and several different bonding modes of the $-O_2CNR_2$ moiety to magnesium have been previously identified. However, conspicuous by its absence is the simplest mode of chelation of the carbamate to a single Mg atom, the η^2 chelating mode. We have now discovered that the insertion of CO_2 into $Mg_2(NCy_2)_4$ (Cy = cyclohexyl) in THF/HMPA (HMPA = hexamethylphosphoramide) forms the unsymmetrical dinuclear compound $[Mg_2(O_2CNCy_2)_4(HMPA)]$ (**1**). X-ray diffraction analysis shows that **1** contains three different bonding modes of the carbamate to the Mg atoms, including the first example of the terminal bidentate η^2 mode.*

Introduction

Carbon dioxide has several potential sites of reactivity—the carbon atom is a Lewis acid and susceptible to nucleophilic attack while the oxygen atoms are weak Lewis bases and prone to attack by electrophiles. The activation of CO_2 by reaction with organometallic compounds has been a topic of study for many years, with the major goal being the conversion of a relatively useless and abundant compound into more valuable organic products.[1,2] One such reaction is the transformation of CO_2 into metal carbamates using metal amides,[3] a subject that has been recently comprehensively reviewed.[4] More specifically, the reactions of CO_2 with main-group amides has also been of recent interest,[5] and in particular, the fixation of CO_2 using various magnesium complexes has been demonstrated in a series of papers from the Chang group.[6] In these papers Chang discusses the various bonding modes possible of carbamates to either mononuclear or dinuclear magnesium complexes (Figure 1). He notes that bonding modes (a), (c), and (d) have been observed and are common in Mg carbamates, while the simple chelating mode (b) has not yet been observed.[6c,d] He discusses the absence of this chelating mode extensively and attributes the deficiency to the fact that in a chelating mode such as (b) the electron density donated by the two oxygen atoms is so great that the highly strained four-membered ring cannot form. Chang indicates that mode

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* To whom correspondence should be addressed at the University of New Mexico. E-mail: rakemp@unm.edu. Phone: (505) 277-0510. Fax: (505) 277-2609.

[†] University of New Mexico.

[‡] University of California, San Diego.

[§] Sandia National Laboratories.

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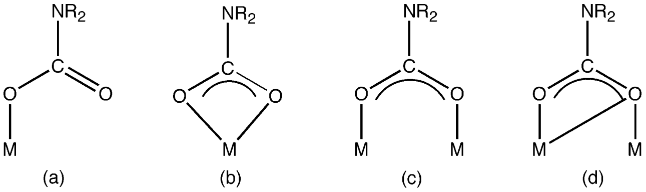

Figure 1. Possible bonding modes for carbamato ligands to either a mononuclear or dinuclear metal atom system:[6c] (a) η^1; (b) η^2; (c) μ_2,η^2; (d) μ_2,η^3.

(b) only occurs in less electron donating systems, such as those seen when the oxygens are replaced by sulfur or $-NR$ species. In $Mg-CO_2$ systems the oxygen atoms will form bridging modes to multiple Mg atoms in order to reduce electron density.

We have now discovered that the formal insertion of CO_2 into $Mg_2(NCy_2)_4$ (Cy = cyclohexyl) in THF/HMPA (HMPA = hexamethylphosphoramide) forms the unsymmetrical dinuclear compound $[Mg_2(O_2CNCy_2)_4(HMPA)]$ (**1**). X-ray diffraction analysis of **1** indicates the bonding modes of the four carbamates formed after CO_2 insertion are of three different types: the previously described modes (c) and (d) as well as the heretofore unknown chelating mode (b).

Results and Discussion

Compound **1** was formed via bubbling an excess of gaseous CO_2 into a mixed THF/HMPA solution of $Mg_2(NCy_2)_4$[7] for 30 min. The insertion reaction of CO_2 was mildly exothermic. After removal of the more volatile THF cosolvent, hexane was added to the remaining solution. Recrystallization of the solid at −20 °C afforded colorless single crystals of **1** suitable for X-ray analysis.

The X-ray crystal structure of **1** reveals a dinuclear structure of the product in which the two magnesium centers are connected by four bridging carbamato ligands (Figure 2). Quite interestingly, the four carbamato ligands bind to the two Mg atoms by using three of the four different bonding modes discussed above: two of the carbamato groups bind in the μ_2,η^2 fashion (c), one in the μ_2,η^3 fashion (d), and one in the previously unknown mode η^2 (b). The Mg(1)−Mg(2) distance of 3.3802 Å in **1** is found to be significantly longer than the Mg−Mg bond distance (3.150 Å) seen in a similar molecule, $[Mg_2(O_2CNPh_2)_4(HMPA)_2]$, but slightly shorter than that seen in the Mg trimers $[Mg_3(O_2C^iPr)_6(HMPA)_2]$ (3.496 Å) and $[Mg_3(O_2CNMe_2)_6(HMPA)_2]$ (3.459 Å).[6c] The Mg atoms in **1** are found to be dissimilar in the structure, due to the presence of an HMPA solvent molecule coordinated to only one of the Mg atoms. This solvated magnesium atom Mg(1) is surrounded by two shorter Mg−O bonds (1.951 and 1.96 Å) from the O-donor atoms of the two symmetrical bridging carbamato ligands (mode c),[6c] as well as two longer Mg−O interactions (2.027 and 2.274 Å) from the unsymmetrical chelating carbamato group (mode d). The HMPA solvent also coordinates to Mg(1) through the oxygen donor atom O(1). Using the Mg(1)−O(1) bond as the point of the pyramid, it can be seen that the Mg(1) atom adopts a very distorted square pyramidal structure using the four oxygen atoms of the carbamato groups, with the one longer Mg(1)−O(2) bond from the unsymmetrical binding mode adding further to the distortion around Mg.

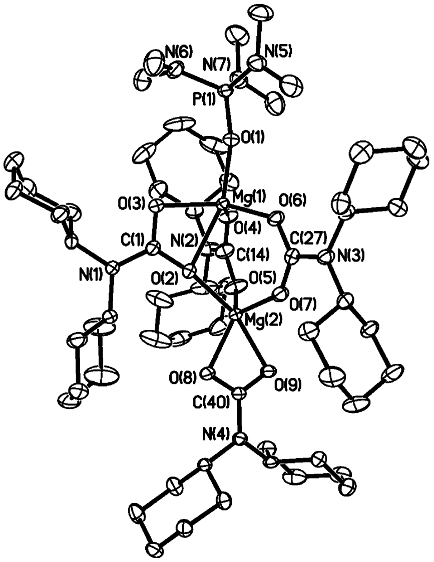

Figure 2. X-ray crystal structure of **1** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Mg(1)−O(1) = 1.9408(15), Mg(1)−O(6) = 1.9514(15), Mg(1)−O(4) = 1.9600(16), Mg(1)−O(3) = 2.0275(15), Mg(1)−O(2) = 2.2739(15), Mg(1)−Mg(2) = 3.3802(9), Mg(2)−O(7) = 1.9440(15), Mg(2)−O(5) = 1.9592(16), Mg(2)−O(2) = 2.0133(15), Mg(2)−O(8) = 2.0409(15), Mg(2)−O(9) = 2.1080(14); O(8)−Mg(2)−O(9) = 64.18(5), C(40)−O(8)−Mg(2) = 89.47(11), C(40)−O(9)−Mg(2) = 86.71(10), O(9)−C(40)−O(8) = 119.63(16).

The other Mg atom, Mg(2), is surrounded by five O-donor atoms of the various carbamato ligands. It is important to note that in the geometry around Mg(2) is seen the first example of a terminal bidentate carbamato ligand bound to a Mg atom in an η^2 mode (vide infra).[6c] The two symmetrically bridging carbamato linkages bind to Mg(2) exactly as is seen with Mg(1), with identical bond Mg−O lengths resulting in both cases. The unsymmetrically bridging carbamato group is bound to Mg(2) via O(2), and, as was seen with Mg(1), the Mg(2)−O(2) bond length from this unsymmetrically bound ligand is lengthened relative to the Mg−O bonds of the symmetrically bound carbamato ligands (2.013 versus 1.959 and 1.944 Å).

As we noted, Mg(2) has additionally a terminal bidentate (η^2) carbamato ligand bound through O(8) and O(9). To our knowledge, this is the initial example of this structural feature found in Mg−O chemistry. In this ligand, the Mg(2)−O(8) and Mg(2)−O(9) bond lengths of 2.041 and 2.108 Å, respectively, are longer than the Mg−O bonds seen in the μ_2,η^2 bonding mode for Mg(1)−O(5) and Mg(1)−O(7) (1.959 and 1.944 Å). The O(8)−Mg(2)−O(9) bond angle of 64.18° is quite similar to the N−Mg−N bond angles of 62.3−65.6° seen in related terminal bidentate Mg carbodiimides, and it is slightly less than that seen in the sulfur analogues which use carbon disulfide as ligands (Scheme 1).[6c]

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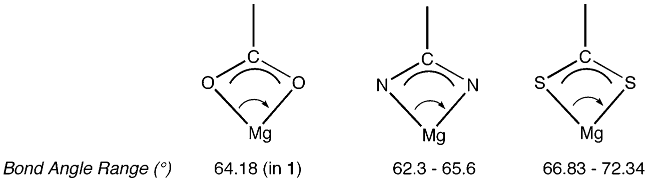
(7) Olmstead, M. M.; Grigsby, W. J.; Chacon, D. R.; Hascall, T.; Power, P. P. *Inorg. Chim. Acta* **1996**, *251*, 273.

Scheme 1. Bond Angle Ranges in Magnesium Chelates



It is interesting to speculate on why the previously unknown terminal bidentate mode (b) exists in **1**. While we do not know for certain, we surmise that the lack of coordinating solvent to Mg(2) versus Mg(1) in the solid state must play a role. As mentioned, Chang[6c] hypothesizes the electron density on the highly electron rich oxygen atoms must be reduced in order to form the highly strained terminal four-membered ring; otherwise, the ligands will form bridges to multiple Mg atoms in order to reduce electron density. It appears to us that the *absence* of any coordinating (electron donating) solvent ligand on Mg(2) in the solid state allows the Mg(2) atom to be more receptive to the higher electron density donated by the oxygens in the terminal η^2 bonding mode. In previous related examples, electron populations at the magnesium atoms were increased due to coordination to solvent molecules or carbonate groups or the magnesium atoms had become more coordinatively saturated by bonding with alkoxy groups.[6] Thus, the key in our system that appears to allow this unknown bonding mode to now exist is the lack of solvent (HMPA) coordination to Mg(2).

The solution structure at 25 °C as shown by NMR does not appear to mimic the static solid-state structure. Rather than observing one set of $N(Cy)_2$ resonances for the carbamato groups bonding via mode (c), one set of $N(Cy)_2$ resonances for mode (d) at half the intensity, and one set of $N(Cy)_2$ resonances for the terminal mode (b), also at half intensity, we observed what appears to be dynamic averaging of all of these bonding modes. The ^{1}H NMR spectrum of **1** in C_6D_6 shows a complex pattern of overlapping multiplets in the region of δ 1.21−2.06 ppm due to the $-CH_2-$ protons on the 2-C, 3-C, and 4-C carbons of the cyclohexyl rings, as well as a broad multiplet downfield at δ 3.62 ppm due to the proton on the carbon attached to the N (1-C). The HMPA methyl groups, as expected, appear as a sharp doublet at δ 2.42 ppm with a $^3J_{P-H}$ value of 9.5 Hz. The ^{13}C NMR spectrum of **1** is more informative and straightforward. Four sharp resonances are observed for the cyclohexyl carbon atoms at 26.25 (4-C), 27.05 (3-C), 31.79 (2-C), and 55.01 (1-C) ppm. A doublet at 36.71 ppm ($^2J_{P-C}$ = 3.7 Hz) is seen for the coordinated $[(CH_3)_2N]_3P{=}O$, and the quaternary carbon of the carbamato group is found at 163.85 ppm. The ranges of values seen here are consistent with the related compounds $[Mg_5(\mu_5,\eta^6\text{-}CO_3)(O_2CN^iPr_2)_8(HMPA)_2]$ and $[Mg_6(\mu_4\text{-}O)(O_2CN^iPr_2)_8]$ prepared earlier.[6c]

In summary, we have prepared and structurally characterized for the first time a magnesium carbamate that contains the heretofore unknown $Mg-CO_2$ terminal bidentate bonding mode (b). Compound **1** now completes the structural motifs believed possible for CO_2 bonding to mono- and dinuclear Mg carbamato complexes.

Table 1. Crystallographic Data for Compound 1

empirical formula	$C_{64}H_{120}Mg_2N_7O_9P$
fw	1211.26
temp, K	100(2)
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	16.906(3)
b, Å	19.819(3)
c, Å	21.176(3)
$\alpha = \beta = \gamma$, deg	90
V, Å^3	7095.0(18)
Z	4
calcd density, g/cm^3	1.134
abs coeff, mm^{-1}	0.112
F(000)	2656
cryst size, mm^3	0.30 × 0.10 × 0.08
θ range, deg	1.41−27.55
no. of rflns collected	45 332
no. of indep rflns	16 193 (R(int) = 0.0299)
max and min transmissn	1.000 and 0.829
GOF on F^2	1.030
final R indices ($I > 2\sigma(I)$)	R1 = 0.0491, wR2 = 0.1249
R indices (all data)	R1 = 0.0546, wR2 = 0.1293
largest diff peak and hole, e/Å^3	0.547 and −0.284

Experimental Section

General Data. All experiments were carried out in an Ar-flushed drybox or a vacuum line using standard Schlenk techniques.[8] Dibutylmagnesium in heptane, dicyclohexylamine, and carbon dioxide were purchased from Aldrich and used as received. All high-purity anhydrous solvents were purchased from Aldrich, dried with 4 Å molecular sieves, and degassed prior to use. ^{1}H and ^{13}C spectra were obtained on a Bruker AMX 250 spectrometer using C_6D_6 as a solvent. All ^{1}H chemical shifts reported are relative to residual proton resonances in the deuterated solvent, while all ^{13}C resonances are reported relative to the deuterated solvent. Elemental analyses for carbon, hydrogen, and nitrogen content were measured in sealed volatile sample pans using a Perkin-Elmer Series II CHNS/O 2400 analyzer. $Mg_2(NCy_2)_4$ was prepared according to the literature.[7]

$[Mg_2(O_2CNCy_2)_4(HMPA)]$ (1). An excess of carbon dioxide was bubbled into a solution of $Mg_2(NCy_2)_4$ (2.16 g, 2.81 mmol) in a mixed solvent system of THF and HMPA (80 mL, 5:1 v/v) for 30 min. A slightly exothermic reaction ensued. After removal of the more volatile THF solvent, hexane (20 mL) was added to the solution, and **1** was obtained as colorless crystals upon prolonged cooling at −20 °C. Yield: 2.21 g (65.0%). Anal. Calcd for **1** ($C_{64}H_{120}Mg_2N_7O_9P$): C, 63.46; H, 9.99; N, 8.09. Found: C, 63.17; H, 9.89; N, 8.18. ^{1}H NMR (benzene-d_6): δ 1.26 (m, 32H, $-CH_2-$), 1.75 (m, 32H, $-CH_2-$), 2.06 (m, 16H, $-CH_2-$), 2.42 (d, 18H, $(Me_2N)_3PO$), 3.62 (m, 8H, $-NCH-$). ^{13}C NMR (benzene-d_6): δ 26.25 (4-C), 27.05 (3-C), 31.79 (2-C), 36.71 ($(Me_2N)_3PO$, $^2J_{P-C}$ = 3.7 Hz), 55.01 (1-C), 163.85 (CO_2).

X-ray Crystallography. Crystallographic data for **1** are given in Table 1. Data were collected at 100 K on a Bruker Smart Apex CCD diffractometer using λ(Mo Kα) = 0.710 73 Å. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. The main molecule cocrystallized with hexane solvent molecules. The Flack parameter is 0.03(8). All

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(8) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1986.

software and sources of scattering factors are contained in the SHELXTL (5.10) program package.[9]

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Supporting Information Available: Crystallographic data as a CIF file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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