5474 *Inorg. Chem.* **1999,** *38,* 5474−5475

Carboxylate-Shift-like Dynamic Equilibrium in Bromomagnesium Diethylcarbamate

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Received June 30, 1999

The coordination chemistry of divalent metal carbamate complexes is relevant as a model for carbamate-containing enzymes. These include (1) the ribulose 1,5-bisphosphate carboxylase/oxygenase (RubisCO) enzyme, which has a magnesium-containing active site coordinated by a carboxyl-modified lysine residue critical to its activation[1]; (2) the class of magnesium-dependent biotin enzymes which catalyze carboxyl transfer via an N-carboxylated biotin intermediate;[2] and (3) urease, which has a dinickel(II) active site bridged by a carbamate ligand also derived from carboxylation of a lysine side chain.[3] RubisCO and urease are crystallographically characterized. The biotin-dependent enzymes containing the metal ion are not structurally characterized, so it is unclear whether the $-NCO_2^-$ unit in N^1-carboxybiotin is a ligand to a functionally required magnesium ion.

In understanding the structure of dinuclear carbamate complexes, it is useful to make an analogy with the carboxylate shift, which has been applied to the structural systematization of numerous complexes bridged by carboxylate ligands[4] and in rationalizing chemical features observed in dinuclear metalloenzyme active sites.[5,6] The carboxylate-shift paradigm should also be applicable to complexes containing carbamate bridging ligands. Calderazzo and others have synthesized diethylcarbamate clusters of Co^{2+}, Mn^{2+}, and Fe^{2+} of general formula $[M(Et_2NCO_2)_2]_6$ which exhibit both $\mu_{1,3}$ and $\mu_{1,1}$ bridging carbamate ligands.[7a−c] However, understanding these compounds in terms of the carboxylate shift is complicated by the high nuclearity of the complexes. Dimeric Cr^{2+} and Cu^{2+} carbamates exhibit a copper acetate structure type with $\mu_{1,3}$ bridging carbamate ligands.[7d,e] To establish if substantial structural and chemical analogy exists between carboxylate and carbamate complexes vis-à-vis the carboxylate shift, we are preparing dinuclear carbamate complexes of the general form $[M(R_2NCO_2)(L)_2Br]_2$ ($R_2NCO_2^- =$ dialkylcarbamate, L = solvent). In this report, the dimagnesium complex $[Mg(Et_2NCO_2)(THF)_2Br]_2$ is prepared and shown to possess an unusual structural equilibrium in the solid state and in solution which can be understood in terms of the carboxylate shift.

Dropwise addition of 30 mmol of methylmagnesium bromide to 30 mmol of diethylamine in tetrahydrofuran (THF) under nitrogen gave a pale pink solution. Exposure of the solution to CO_2 gave an exothermic reaction. Dropwise addition of *n*-hexane to the solution precipitated the partially hydrated material $[Mg(Et_2NCO_2)(THF)(H_2O)Br]\cdot(THF)_{0.25}$.[8] Slow evaporation of an anhydrous THF/*n*-hexane solution gave colorless crystals of the THF solvate used for single-crystal X-ray diffraction.[9]

The crystal structure obtained consists of discrete dimeric units formulated as the THF solvate $[Mg(Et_2NCO_2)(THF)_2Br]_2$. However, this complex is unusual in that it formed crystals containing independent molecules with two different carbamate bridging modes. In structure **1** (Figure 1), the two magnesium ions are bridged by two diethylcarbamate ligands in a syn-syn mode to give a Mg···Mg distance of 3.779 Å. Two carbamate oxygens and a terminal bromide ligand form a trigonal plane capped above and below by axial THF ligands to give a five-coordinate magnesium ion.

In the same crystal, structure **2** cocrystallized. This molecule has two Mg ions bridged by two diethylcarbamate ligands in a $\mu_{1,1}$ bridging mode, resulting in a shorter Mg···Mg distance of 3.354 Å. The equatorial ligands attached to each magnesium ion in **2** consist of three oxygen donors provided by the carbamate ligands and a terminal bromide ligand. The coordination sphere is completed by two axial THF molecules on each metal ion, so the overall geometry of the complex may be considered as two highly distorted edge-shared octahedra.

In the carboxylate-shift paradigm, **2** is most consistent with a class III type bridging mode characterized by a strong interaction between the metal ion and the nonbridging oxygen. It is unusual in having very disparate Mg−O(bridging) bond lengths. The Mg(1a)−O1 distance is nearly 0.4 Å shorter than Mg(1)−O(1). The bond between the nonbridging carboxyl oxygen and the Mg ion, Mg(1)−O(2), is 2.072 Å, considerably shorter than the Mg(1)−O(1) bond at 2.402 Å. In **1** and **2**, the carbamate nitrogen is planar, which is consistent with other metallocarbamate complexes and indicates delocalization of the nitrogen lone pair into the carboxyl

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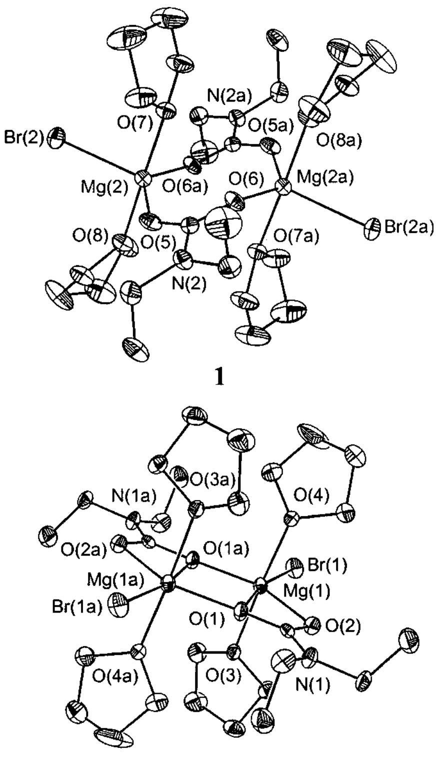
(8) Anal. Found (calcd): C, 36.2 (36.6); H, 7.0 (6.7); N, 4.1 (4.3); Mg, 7.6 (7.3). IR (cm^{-1}): 1580 (asym $-CO_2$), 1325 (sym $-CO_2$), 804 (bend $-CO_2$).

(9) Crystal data (158 K): monoclinic $P2_1/c$; $a = 16.1980(2)$ Å, $b = 12.35040(10)$ Å, $c = 17.8146(2)$ Å; $\alpha = 90°$, $\beta = 91.8330(10)°$, $\gamma = 90°$; $V = 3562.02(7)$ Å^3; $Z = 4$; $\lambda = 0.710\,73$ Å; $m = 2.354$ mm^{-1}; 34 660 reflections collected ($2.29° < \theta < 28.24°$), 8518 independent reflections refined using full-matrix least squares on F^2, final R1 [$I > 2\sigma(I)$] = 0.0953, GOF = 1.160. See Supporting Information for complete crystallographic details.

10.1021/ic990765b CCC: $18.00



1

2

Figure 1. ORTEP drawings of **1** and **2**. Important bond lengths (Å) and bond angles (deg): **1**, Mg···Mg = 3.779, Mg(2)−Br(2) = 2.581(3), Mg(2)−O(6a) = 1.966(6), Mg(2)−O(5) = 1.984(6), C(14)−O(5) = 1.290(9), C(14)−O(6a) = 1.279(9), C(14)−N(2) = 1.381(9), O(6a)−Mg(2)−O(5) = 127.7(3), O(5)−Mg(2)−Br(2) = 117.3(2), O(6a)−Mg(2)−Br(2) = 114.9(2), Mg(2)−O(5)−C(14) = 129.9(5), Mg(2)−O(6a)−C(14a) = 140.2(5), O(5)−C(14)−O(6) = 124.5(7); **2**, Mg···Mg = 3.354, Mg(1)−Br(1) = 2.583(3), Mg(1)−O(1) = 2.402(6), Mg(1)−O(1a) = 2.009(6), Mg(1)−O(2) = 2.072(6), C(1)−O(2) = 1.298(9), C(1)−O(1) = 1.300(9), Mg(1)−O(1)−Mg(1a) = 98.6(2), O(1)−Mg(1)−O(2) = 59.4(2), O(2)−C(1)−O(1) = 118.7(7), C(1)−O(1)−Mg(1a) = 177.6(5).

group. The O−C−O angle in the carbamate group is 118.7°, which is compressed from 124.5° observed in **1** and consistent with bidentate coordination by the carboxyl group in **2**.

A view of the packing diagram is provided in Figure 2.[10] It is a monoclinic system consisting of equal numbers of **1** and **2** in alternating layers. This unique arrangement could arise from rather subtle packing interactions which conspire to make both **1** and **2** stable in the solid state, or it could be reflective of a solution phase in which both **1** and **2** are present in equilibrium. The ^{13}C NMR spectra, Figure 3, clearly demonstrate the existence of two species in solution. At room temperature, the spectrum shows a broad resonance corresponding to the carboxyl carbon. At −50 °C, the carboxyl signal splits into two distinct and sharp signals at 161.4 and 166.0 ppm. These signals arise from two different carboxyl species in rapid exchange and suggest that **1** and **2** are in equilibrium.

Integration of the ^{1}H NMR spectrum at −50 °C[10] indicates a ≈1:1 equilibrium ratio, i.e., $\Delta G \approx 0$ for their interconversion. $[Mg(Et_2NCO_2)(THF)_2Br]_2$ is an unusual example of a complex exhibiting a dynamic carboxylate-shift-like equilibrium without a change in the total number of ligands and, therefore, makes an excellent example of carboxylate-shift dynamics. The structures **1** and **2** can be interchanged by a simple rocking motion of the carbamate ligands. Since the carbamate ligand is symmetrically disposed between the two Mg ions in **1**, it suggests a potential intermediate by which **1** and **2** may be interconverted as shown in Scheme 1. This would be consistent with the very long Mg(1)−O(1) bond length of 2.402 Å, suggesting a weak bonding interaction which may be offset by additional steric repulsion between the ethyl group and the bromide ligand in **2**. Chemical exchange of the ethyl groups might also occur via rotation about the C−N bond, which occurs with $\Delta G^{\ddagger}$ of about 15−20 kcal/mol for typical amides and organic carbamate esters[11] at 25 °C. Rotamer equilibria may contribute to the overall line width in the NMR spectrum and may provide an additional mechanism by which the ethyl groups in **2** are exchanged. Additional complexity in the NMR spectra was observed at intermediate temperatures, which may be explained if both C−N bond rotation and Scheme 1 were operating simultaneously but with different temperature dependencies.

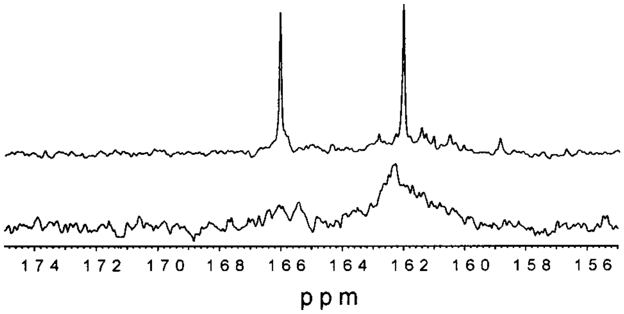
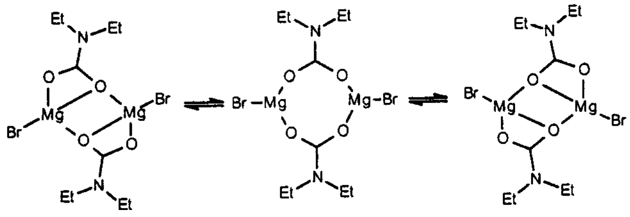


Figure 3. 500 MHz ^{13}C NMR spectra of **1** and **2** in the $-CO_2^-$ region, solvent = $CDCl_3$. Spectra were measured on a sample enriched in ^{13}C. Bottom: 25 °C. Top: −50 °C.

Scheme 1



Examination of **1** and **2** suggests that the structural stability of $[Mg(Et_2NCO_2(THF)_2Br]_2$ may be biased by designing suitable substituents for the carbamate ligand. We are therefore investigating the influence of ligand structure on the dynamic equilibrium between **1** and **2** in order to prepare derivatives of $[Mg(R_2NCO_2(THF)_2Br]_2$ whose carboxylate-shift structure and dynamics are perturbed from that observed in$[Mg(Et_2NCO_2(THF)_2Br]_2$.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Faculty Grant-in-Aid Program, Arizona State University, for support of this research. We also acknowledge Mike Williams for assistance in measuring the low-temperature NMR spectra.

Supporting Information Available: Figure 2, packing diagram; Figure 4, temperature-dependent ^{1}H NMR; Tables 1−5 containing crystallographic data, positional and thermal parameters, complete listing of bond lengths and angles, and ORTEP with full numbering scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Deposited in the Supporting Information.

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