
2-2013

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Wei La

Steven M. Berry

William P. Kaplan

et al.

John C. Poutsma

William & Mary, jcpout@wm.edu*See next page for additional authors*

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Recommended Citation

La, Wei; Berry, Steven M.; Kaplan, William P.; et al.; Poutsma, John C.; Pike, Robert D.; and Bebout, Deborah C., Carbonate-Templated Self-Assembly of an Alkylthiolate-Bridged Cadmium Macrocycle (2013). *Inorganic Chemistry*, 52(5), 2286-2288.
<https://doi.org/10.1021/ic302740j>

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Authors

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Carbonate-Templated Self-Assembly of an Alkylthiolate-Bridged Cadmium Macrocycle

Wei Lai,[†] Steven M. Berry,^{†,‡} William P. Kaplan,[†] Malia S. Hain,[†] John C. Poutsma,[†] Raymond J. Butcher,[§] Robert D. Pike,[†] and Deborah C. Bebout^{*,†}[†]Department of Chemistry, The College of William & Mary, Williamsburg, Virginia 23187, United States[§]Department of Chemistry, Howard University, Washington, D.C. 20059, United States

Supporting Information

ABSTRACT: In the presence of $\text{Cd}(\text{ClO}_4)_2$ and a base, a new mixed N,S-donor alkylthiolate ligand supported both carbonate formation from atmospheric CO_2 and the self-assembly of a novel bicapped puckered $(\text{CdS})_6$ molecular wheel. The remarkable stability of the complex was demonstrated by slow intermolecular ligand exchange on the $^2\text{J}(\text{HH})$ and $\text{J}(^{111/113}\text{Cd}^1\text{H})$ time scales at elevated temperature. Both CO_2 and the base were required to convert amorphous “ CdLClO_4 ” precipitated in the absence of air to the carbonate complex. The complex shares structural features with the ζ -carbonic anhydrase class associating cadmium(II) with the biogeochemical cycling of carbon and is the first structurally characterized carbonate complex of any metal involving an alkylthiolate ligand.

Carbonate is a versatile bridging species found in two-dimensional and mono-, di-, tri-, tetra-, hexa-, and enneanuclear and higher complexes with at least 14 different coordination motifs.¹ Several hundred carbonate complexes involving all of the physiologically essential metals and a wide range of nonessential transition metals are structurally characterized.² In many cases, precursors to these carbonate complexes are able to hydroxylate atmospheric CO_2 , forming an intermediary species that spontaneously effects CO_2 fixation through combinatorial self-assembly and selective crystallization.³ Global environmental problems associated with rising greenhouse gas concentrations justify continued investigation of these intriguing processes.

In biological systems, hydration of carbon dioxide (CO_2) is catalyzed by carbonic anhydrase (CA), a possibly ubiquitous metalloprotein with five zinc(II)-dependent forms across taxonomic kingdoms sharing no significant similarity in their primary sequence or overall structure.⁴ Zinc(II) was viewed as an essential cofactor for this enzyme activity until the seemingly anomalous nutrient-like vertical oceanic profile of cadmium was linked to a highly active cadmium(II) carbonic anhydrase (CdCA) variant from the marine diatom *Thalassiosira weissflogii* grown under zinc(II)-limiting conditions, thus establishing the ζ form of CA.⁵ All six CA forms use invariant histidine residues for metal ligation and related aromatic N donors are quite common in synthetic complexes. Both the β and ζ forms of these enzymes also have two invariant cysteine residues bound to the metal, but

alkylthiolates have not yet been reported as metal ligands in synthetic carbonate complexes.²

Our interest in multidentate ligands providing simple models of amino acid side-chain donors for zinc triad coordination studies led to the preparation of LH.⁶ Herein LH is reported to react with 1 equiv of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and excess Et_3N in air-saturated acetone to form $[(\text{CdL})_6(\mu_3\text{-CO}_3)_2](\text{ClO}_4)_2$ (**1**), the first synthetic carbonate complex with alkylthiolate metal ligation (Figure 1a). The isolated carbonate complex provides a rare

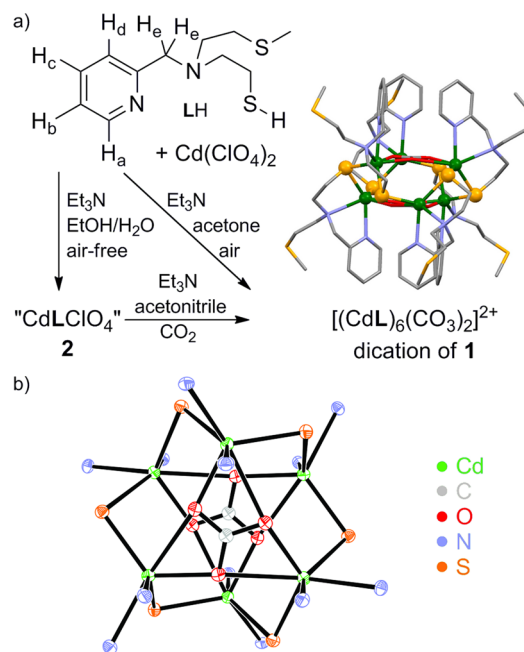


Figure 1. (a) Synthesis of **1** showing a stick structure of its dication. Atoms of the $(\text{CdS})_6$ macrocycle are highlighted as balls. (b) Perspective view of carbonate binding to the $(\text{CdS})_6$ macrocyclic core of **1**.

example of a bicapped molecular wheel (Figure 1b).⁷ Alternatively, a noncrystalline “ CdLClO_4 ” (**2**) precipitate could be isolated from an EtOH/ H_2O solution of these reactants in the absence of air. ^1H NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS) are used to document the stability of **1** in solution and to show that both the base and CO_2 are

Received: December 13, 2012

Published: February 13, 2013



required for its formation from **2**. Furthermore, this is the first study to provide experimental evidence for the fixation of CO₂ by a cadmium(II) complex on a time scale of minutes or less.

Complex **1** has six crystallographically identical CdL units (Figure 2a). Each Cd^{II} atom has a bicapped tetrahedral NN'S₂O₂

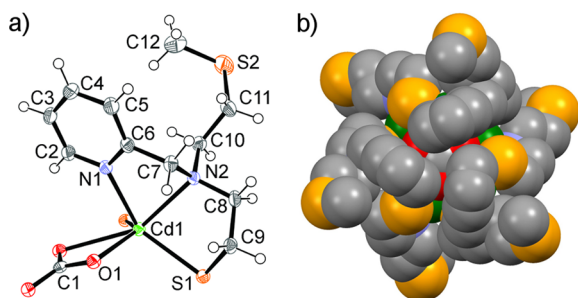


Figure 2. (a) ORTEP diagram of cadmium(II) coordination in **1** with an atomic numbering scheme and thermal ellipsoids at the 50% level. (b) Space-filling diagram of the 1²⁺ cation looking down the C₃ axis.

metal coordination environment (Figure S1 in the Supporting Information, SI). Each ligand uses an NN'S donor set to form a pair of fused five-membered chelate rings to one metal ion and a thiolate bridge to an adjacent Cd^{II} atom. The thioether sulfur of **L** is pendant in **1**, separated from the closest Cd^{II} atom by nearly 6 Å. The O donors are derived from asymmetric η²-carbonate coordination with Cd–O distances of 2.230(2) and 2.690(3) Å, well within the sum of the van der Waals radii for Cd^{II} (1.58 Å) and O (1.52 Å).⁸ The asymmetric unit contains one.

The novel obloid core of **1** is comprised of two trinuclear [(CdL)₃(μ₃-CO₃)] units with 3-fold molecular symmetry (Figure 1b). Two trinuclear units with opposite chirality at N2 (all *R* vs all *S*) and joined to each other by six bridging thiolato S atoms form a puckered bicapped 12-membered (CdS)₆ macrocycle. The distance between the symmetry-equivalent Cd atoms in individual Cd₃(μ₃-CO₃) units is 4.882(4) Å. Sulfur-bridged Cd^{II} atoms are separated by 3.679(3) Å. The asymmetric η²-carbonate O atoms are bound 0.2628(17) Å above the coordinated plane of three alternate macrocycle Cd^{II} atoms (Figure S2a in the SI). The carbonate C separation of 2.906(8) Å, less than the sum of the van der Waals radii (3.40 Å)⁸ (Figure S2b in the SI), suggests assembly stabilization by π–π interaction.

The bicapped (MetalS)₆ macrocycle is unique to **1**. The dodecanuclear complex [(cyclyam)Mn^{IV}(μ-O)₂Mn^{III}(H₂O)(μ-OH)]₆(μ₃-CO₃)₂Cl₈·24H₂O⁹ provides the only precedent for CO₂ fixation in a puckered bicapped (MetalX)₆ macrocycle.² To the best of our knowledge, 1,3,5-triazine is the only other established 3-fold-symmetric templating species for a puckered (MetalX)₆ macrocycle.¹⁰ One hexanuclear dodecacarbonate of cadmium(II) is known,¹¹ but there are no bis(carbonates) of just zinc(II) or cadmium(II).² The five reported cadmium(II) carbonate complexes have varied metal coordination environments, including N₄O₂, N₂O₆, and N₄(SR₂)₂O₂ (Figure S3 in the SI).¹² The published cadmium(II) carbonate complexes and **1** share perchlorate counterions and ligands with multiple N-donor groups. Both μ₂ and μ₃ binding modes are observed for carbonate in these cadmium(II) complexes, with hapticities ranging from nearly symmetrical η² to highly asymmetrical η¹. As observed for **1**, each Cd center in the μ₃-carbonato complexes^{12b–d} has two carbonate O atoms within the sum of the van der Waals radii for Cd^{II} and O.⁸ Although there is considerable ligand diversity among known metal carbonate complexes, the S donors have

been limited to a handful of thiolates bound to sp²-hybridized C atoms (Figure S4 in the SI) and thioethers.²

In the context of extensive metal thiolate coordination studies, the paucity of synthetic carbonate complexes with alkylthiolate ligands is intriguing given their importance to biological CO₂ chemistry. Adventitious crystallization of multinuclear carbonate complexes requires kinetically efficient CO₂ (<0.04% of air by volume) hydroxylation and deprotonation, as well as thermodynamic redistribution of the molecular assembly to exceed the saturation limit. Structural features likely to enhance carbonate-driven dynamic combinatorial self-assembly and prevent intermolecular interactions are evident. The staggered carbonates are close enough for π–π stacking (Figure S2b in the SI) and the sterically demanding pyridyl rings circumscribing the macrocycle faces have approximate edge-to-face orientations, severely limiting carbonate solvent exposure (Figure 1b). Thermodynamic and kinetics aspects of the formation of **1** were further investigated by ¹H NMR and ESI-MS.

¹H NMR comparisons of **1** and **2** in CD₃CN supported the thermodynamic stability of **1** in solution (Figure 3). The ¹H

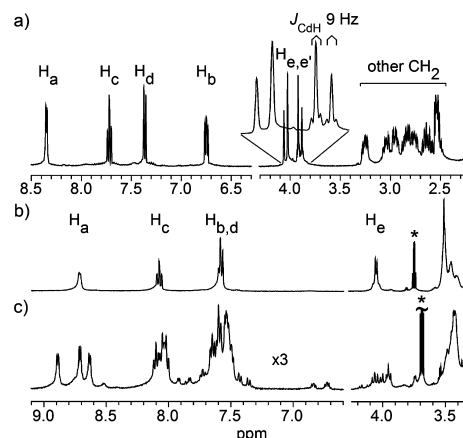


Figure 3. ¹H NMR spectra of (a) **1** at 80 °C and **2** at (b) +80 and (c) –40 °C (CD₃CN; * indicate CH₂ resonances of coprecipitated HNEt₃ClO₄).

NMR spectrum of **1** had a single set of ligand resonances from –40 to +80 °C and was stable to extended periods at elevated temperature. Strong geminal coupling between all of the methylene and ethylene ¹H atoms at elevated temperature is consistent with a well-defined structure. In addition, one of the methylene H_e atoms had 9 Hz *J*(^{111/113}Cd/¹H) satellites, which is to our knowledge the first observation of this interaction in a thiolate-ligated cadmium(II) complex (Figure 3a) and comparable in magnitude to couplings observed for related complexes. In contrast, the ¹H NMR spectrum of **2** had three major ligand environments in a 1:1:1 ratio and two minor ligand environments in a 1:1 ratio at –40 °C, suggesting at least two components (Figure 3c). A single exchange-averaged ligand environment was observed for **2** at 80 °C (Figure 3b) with geminal coupling of the methylene protons but not the ethylene protons. There was no evidence for any of the components of **2** in the ¹H NMR spectra of **1**.

Similarly, acetonitrile solutions of **1** and **2** had distinct ESI-MS speciation. The base peak for **1** was centered on *m/z* 1121 (Figure 4e) and corresponded to a combination of [Cd₃L₃CO₃]⁺ and [Cd₆L₆(CO₃)₂]²⁺ (Figure S5a in the SI). In the high mass spectrum (*m/z* 200–4000), a peak centered on *m/z* 2343 was

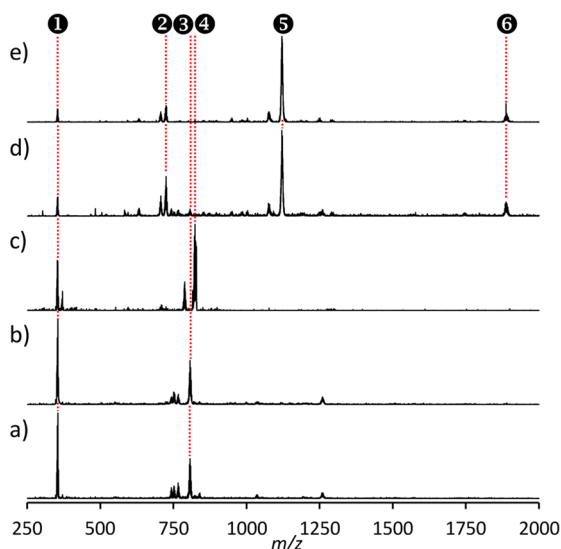


Figure 4. ESI-MS spectra for 0.2 mg/mL CH_3CN solutions of **2** (bottom to top) (a) originally, (b) bubbled with CO_2 for 5 min, (c) with 1 μL of NEt_3 added, (d) with 1 μL of NEt_3 added and then bubbled with CO_2 for 5 min (qualitatively similar to the reverse order of the addition), and (e) **1**. Selected assignments with m/z of the isotope distribution maximum are (1) 355 ($[\text{CdL}]^+$), (2) 725 ($[\text{Cd}_2\text{L}_2\text{OH}]^+$), (3) 807 ($[\text{Cd}_2\text{L}_2(\text{ClO}_4)]^+$), (4) unassigned (atypical isotope distribution), (5) 1121 ($[\text{Cd}_3\text{L}_3(\text{CO}_3)]^+$ and $[\text{Cd}_6\text{L}_6(\text{CO}_3)_2]^{2+}$), and (6) 1887 ($[\text{Cd}_5\text{L}_5(\text{CO}_3)_2]^{3+}$).

observed for $[\text{Cd}_6\text{L}_6(\text{CO}_3)_2\text{ClO}_4]^+$ (Figure S5b in the SI). A modest number of additional ions with low relative abundance were observed. None of the carbonate-containing ions were detected in the ESI-MS spectra for dilute acetonitrile solutions of **2** prepared using stringent air-free conditions (Figure 4a). The base peak for **2** was $[\text{CdL}]^+$ (Figure 4a). The other major component was $[\text{Cd}_2\text{L}_2\text{ClO}_4]^+$ (m/z 807). Interestingly, the ESI-MS speciation of **2** was fairly limited compared to that observed for $\text{Hg}(\text{ClO}_4)_2$ with *N*-(2-pyridylmethyl)-*N*-(2-ethylthiolato)-amine.¹³ The thioether-group-found pendant in **1** may help to limit the oligomeric speciation in the absence of carbonate.

Finally, in situ generation of **1** by the addition of CO_2 and NEt_3 to **2** in acetonitrile was explored. Individually, neither of these additives produced solutions with ESI-MS (Figure 4b,c) or ^1H NMR (Figure S6b,c in the SI) peaks matching those for **1**. The treatment of **2** with both additives resulted in ESI-MS ion patterns (Figure 4d) and ^1H NMR (Figure S6d in the SI) spectra that were qualitatively similar to those of samples prepared directly from **1**. Furthermore, this transformation was complete within minutes, providing the first documentation of rapid CO_2 fixation by a cadmium(II) complex.¹²

In summary, in the presence of $\text{Cd}(\text{ClO}_4)_2$ and a base, the new potentially tetradentate thiol ligand LH was found to limit complex oligomerization, support efficient carbonate formation from atmospheric CO_2 , and effectively sequester carbonate by the assembly of a novel puckered $(\text{CdS})_6$ macrocycle. Parallels between **1** and the metal binding sites of two CA forms, including the recently discovered CdCA, suggest that additional mixed N,S-donor alkylthiolate ligands may provide favorable electronics and sterics for carbonate formation and capture by cadmium(II) as well as possibly by zinc(II). We are actively investigating this possibility.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format for **1** (CDC 902277), syntheses, crystal structure, and ESI-MS and NMR details. This material is available free of charge via the Internet at <http://pubs.acs.org>. The atomic coordinates for **1** have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dcbebo@wm.edu. Tel.: +17572212558.

Present Address

[‡]Department of Chemistry and Biochemistry, University of Minnesota—Duluth, Duluth, Minnesota 55812, United States.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported, in part, by the Camille and Henry Dreyfus Foundation, the NIH, the U.S. NSF, and the College of William & Mary. R.J.B. acknowledges funding from DoD-ONR to upgrade and NIH-MBRS to maintain the diffractometer at Howard University. Rita N. Strauss and Justine V. Arrington assisted with ESI-MS.

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