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

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Supporting Information

ABSTRACT: In the presence of Cd(ClO4)2 and a base, a new mixed N,S-donor alkylthiolate ligand supported both carbonate formation from atmospheric CO2 and the self-assembly of a novel bicapped puckered (CdS)6 molecular wheel. The remarkable stability of the complex was demonstrated by slow intermolecular ligand exchange on the 2J(HH) and 1J(111/113Cd1H) time scales at elevated temperature. Both CO2 and the base were required to convert amorphous "CdLClO4" 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 CO2 forming an intermediary species that spontaneously effects CO2 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 (CO2) 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.2 Alternatively, a noncrystalline "CdLClO4" (2) precipitate could be isolated from an EtOH/H2O 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 CO2 are

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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 CdL₃ units (Figure 2a). Each Cd³⁺ atom has a bicapped tetrahedral NN'S₄O₃ coordination environment (Figure S1 in the Supporting Information, SI). Each ligand uses an NN′ set to form a pair of fused five-membered chelate rings to one metal ion and a thiolate bridge to an adjacent Cd³⁺ atom. The thioether sulfur of L is pendant in 1, separated from the closest Cd³⁺ 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 CdII (1.58 Å) and O (1.52 Å). 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 Cd³⁺ 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 macrocyclic Cd³⁺ 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) (Figure S2b in the SI), suggests assembly stabilization by π–π interaction.

The bicapped (MetalS)₆ macrocycle is unique to 1. The dodecanuclear complex ([cyclam]MnIV(μ₃-O)₂MnIII(H₂O)(μ-OH)]₃(μ₃-CO₃)₂Cl₂·2H₂O provides the only precedent for CO₂ fixation in a puckered bicapped (MetalX)₆ macrocycle. 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. One hexanuclear dodecacarboxylate of cadmium(II) is known, but there are no bis(carbonates) of just Zn(II) or cadmium(II). The five reported cadmium(II) carbonate complexes have varied metal coordination environments, including N₄O₂N₄O₂ and N₄(SR₂)₂O₂ (Figure S3 in the SI). The published cadmium(II) carbonate complexes and 1 share perchlorate counterions and ligands with multiple N-donor groups. Both μ₂ and μ₁ binding modes are observed for carbonate in these cadmium(II) complexes, with hapticities ranging from nearly symmetrical η² to highly asymmetrical η³. As observed for 1, each Cd center in the μ-carbonato complexes has two carbonate O atoms within the sum of the van der Waals radii for Cd³⁺ and O. Although there is considerable ligand diversity among known metal carbonato 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.

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 carboxylates 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 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 atoms had 9 Hz J₁₁¹CaCd 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 [Cd₃L₃(CO₃)]²⁻ (Figure S5a in the SI). In the high mass spectrum (m/z 200–4000), a peak centered on m/z 2343 was...
observed for [Cd6L6(CO3)2ClO4]+ (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 CdL2 (m/z 807). The other major component was [CdL]+ (Figure 4a). The isotope distribution maximum for [Cd5L5(CO3)2]+ (m/z 1121) may help to limit the oligomeric speciation in the absence of carbonate.

Finally, in situ generation of carbonate from atmospheric CO2, and efi (a) originally, (b) bubbled with CO2 for 5 min, (c) with 1 μL of NEt3 added, (d) with 1 μL of NEt3 added and then bubbled with CO2 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 ([CdL]+), (2) 725 ([Cd2L2OH]+), (3) 807 ([Cd2L2(ClO4)]+), (4) unassigned (atypical isotope distribution), (5) 1121 ([Cd5L5(CO3)]+ and [Cd6L6(CO3)2]+), and (6) 1887 ([Cd6L6(CO3)2]2+). The treatment of NMR (Figure S6b,c in the SI) peaks matching those for Hg(ClO4)2 with 1μl of NEt3 added, (d) with 1 μL of NEt3 added and then bubbled with CO2 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 ([CdL]+), (2) 725 ([Cd2L2OH]+), (3) 807 ([Cd2L2(ClO4)]+), (4) unassigned (atypical isotope distribution), (5) 1121 ([Cd5L5(CO3)]+ and [Cd6L6(CO3)2]+), and (6) 1887 ([Cd6L6(CO3)2]2+).

Figure 4. ESI-MS spectra for 0.2 mg/mL CH3CN solutions of 2 (bottom to top) (a) originally, (b) bubbled with CO2 for 5 min, (c) with 1 μL of NEt3 added, (d) with 1 μL of NEt3 added and then bubbled with CO2 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 ([CdL]+), (2) 725 ([Cd2L2OH]+), (3) 807 ([Cd2L2(ClO4)]+), (4) unassigned (atypical isotope distribution), (5) 1121 ([Cd5L5(CO3)]+ and [Cd6L6(CO3)2]+), and (6) 1887 ([Cd6L6(CO3)2]2+).

In summary, in the presence of CdCl2 and a base, the new potentially tetradentate thiol ligand LH was found to limit complex oligomerization, support efficient carbonate formation from atmospheric CO2, and effectively sequester carbonate by the assembly of a novel puckerer (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 alkythiolate 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.