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A binuclear cadmium(II) hydroxide complex and its CO_2 reaction product†

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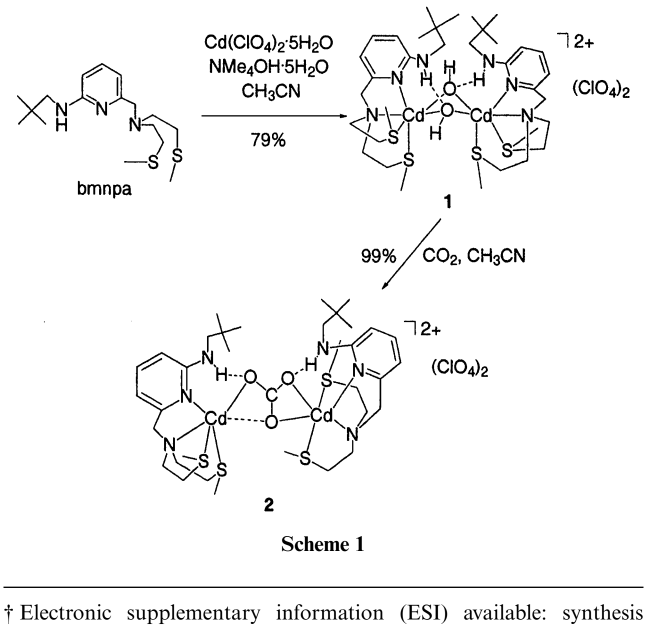
A novel binuclear cadmium hydroxide complex has been isolated, structurally and spectroscopically characterized, and has been shown to undergo reaction with CO_2 to yield a binuclear cadmium carbonate complex.

Currently, very little is known about the reaction chemistry of cadmium hydroxide (Cd–OH) complexes. For example, while five structurally characterized complexes containing at least one bridging Cd–(μ-OH)–M (M = Cd^{2+}, Co^{2+}, or Cr^{3+}) unit have been reported, the reactivity properties of the Cd–(μ-OH)–M moiety in these systems were not explored.[1] Cadmium complexes capable of reacting with CO_2 under basic conditions to produce a cadmium carbonate or bicarbonate complex have been reported.[2] However, potential Cd–OH intermediates involved in these reactions were not investigated. As elucidation of the reactivity properties of Cd–OH complexes may provide insight into the chemistry of cadmium-substituted hydrolytic enzymes, we report herein our initial efforts toward examining the structural and reactivity properties of a novel binuclear Cd–OH complex stabilized by hydrogen bonding and CH/π interactions.

Treatment of a CH_3CN solution of the bmnpa[3] ligand (Scheme 1) with equimolar amounts of $Cd(ClO_4)_2\cdot 5H_2O$ and $Me_4NOH\cdot 5H_2O$ under anaerobic conditions followed by work-up and crystallization from CH_3CN–Et_2O yielded crystalline $[(bmnpaCd)_2(\mu\text{-}OH)_2](ClO_4)_2\cdot CH_3CN$ (**1**) in 79% yield.† The structure of **1** was determined by X-ray diffraction.‡ Only one of two independent but chemically similar molecules in the asymmetric unit is shown. In the binuclear cationic portion of **1** (Fig. 1, top), each cadmium ion exhibits a distorted octahedral geometry. The $Cd_2(\mu\text{-}OH)_2$ core of **1** is nearly symmetric ($Cd–O(H)_{avg}$ 2.22 Å) and exhibits a slight hinge-type distortion, resulting in a Cd ··· Cd distance of 3.32 Å.



Scheme 1

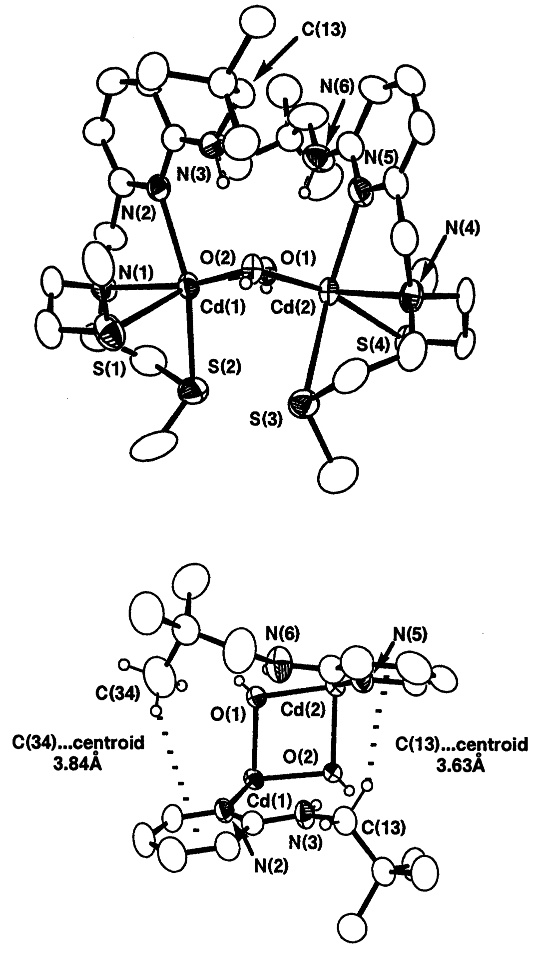


Fig. 1 Drawing of the cationic portion of the X-ray crystal structure of **1** (top) and the secondary interactions surrounding the $Cd_2(\mu\text{-}OH)_2$ core (bottom). All ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (°): **1** (Molecule 1): Cd(1)–O(1) 2.237(5), Cd(1)–O(2) 2.215(4), Cd(2)–O(1) 2.188(4), Cd(2)–O(2) 2.258(5), Cd(1)–N(1) 2.412(5), Cd(2)–N(4) 2.391(5), Cd(1)–N(2) 2.360(5), Cd(2)–N(5) 2.372(5), Cd(1)–S(1) 2.732(2), Cd(1)–S(2) 2.757(2), Cd(2)–S(3) 2.875(3), Cd(2)–S(4) 2.720(3), O(1)–Cd(1)–O(2) 79.37(18), O(1)–Cd(2)–O(2) 79.49(18); hydrogen bonding interactions: N(3) ··· O(2) 2.876(6), N(3)–H(3) ··· O(2) 169.1, N(6) ··· O(1) 2.946(8), N(6)–H(6) ··· O(1) 164.3.

Notably, the neopentylamino portion of both bmnpa ligands of **1** are positioned on one face of the $Cd_2(\mu\text{-}OH)_2$ core (Fig. 1,

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† Electronic supplementary information (ESI) available: synthesis and characterization data. See http://www.rsc.org/suppdata/dt/b1/b109883g/

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bottom). In this orientation, two hydrogen bonding interactions are formed with the oxygen atoms of the bridging hydroxyl groups. Two CH/π interactions are also present in the solid state.[4] In one such interaction, a methylene unit (C(13)) is positioned in front of the pyridine ring of the bmnpa ligand bound to Cd(2) (Fig. 1, bottom). The perpendicular C(13) ··· arene centroid distance is 3.63 Å. A second CH/π interaction is present between C(34) and the pyridyl ring of the bmnpa ligand attached to Cd(1), wherein a C(34) ··· arene centroid distance of 3.84 Å is observed. Significant shifts of the secondary amine (δ 8.81) and neopentyl proton resonances (δ 2.15 (–CH_2–), 0.71 (–CH_3)) in CD_3CN solution spectra of **1** as compared to their position in spectra of the free bmnpa ligand (δ 5.01 (N–H), 3.12 (–CH_2–), 0.93 (–CH_3)) suggest that the binuclear structure and these secondary interactions are maintained in acetonitrile solution. We note that the binuclear formulation of **1** in CH_3CN solution is also supported by conductance measurements wherein the complex behaves as a 1 : 2 electrolyte.

Bubbling of dry CO_2 through a CH_3CN solution of **1** followed by crystallization from CH_3CN–Et_2O under a CO_2 atmosphere yielded $[(\text{bmnpaCd})_2(\mu\text{-}CO_3)](ClO_4)_2\cdot CH_3CN$ (**2**). † The cationic portion of **2** is shown in Fig. 2. ‡ The bridging carbonate binds in an essentially unidentate fashion to Cd(1), with only a very weak interaction with O(1) (Cd(1)–O(1) 2.616(3), Cd(1)–O(2) 2.192(3) Å). At Cd(2), the bridging carbonate is bound in a symmetric bidentate fashion (Cd(2)–O(1) 2.379(4), Cd(2)–O(3) 2.391(4) Å). Notably, the coordination mode of the bound CO_3^{2-} in **2** is distinctly different from that observed in the bridging carbonate derivative $[Cd_2(\text{npda})_4(\mu\text{-}CO_3)(H_2O)](ClO_4)_2\cdot H_2O$ (npda = N'-isopropyl-2-methylpropane-1,2-diamine) wherein three different Cd–O(carbonate) distances (Cd(1)–O(1) 2.172(4), Cd(1)–O(2) 2.768(4), Cd(2)–O(3) 2.238(3) Å) are observed.[2b]

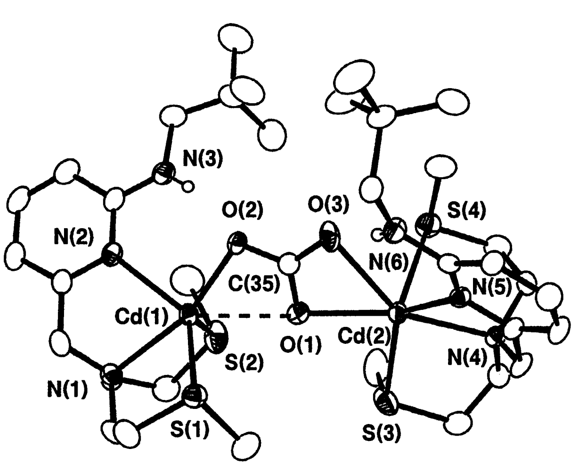

Fig. 2 Drawing of the cationic portion of the X-ray crystal structure of **2**. All ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (°): **2**: Cd(1)–O(1) 2.616(3), Cd(1)–O(2) 2.192(3), Cd(2)–O(1) 2.379(4), Cd(2)–O(3) 2.391(4), Cd(1)–N(1) 2.428(4), Cd(1)–N(2) 2.355(4), Cd(1)–S(1) 2.6400(16), Cd(1)–S(2) 2.6159(16), Cd(2)–N(4) 2.458(4), Cd(2)–N(5) 2.337(4), Cd(2)–S(3) 2.7308(16), C(35)–O(1) 1.271(6), C(35)–O(2) 1.299(6), C(35)–O(3) 1.260(6), O(1)–Cd(1)–O(2) 53.64(12), O(1)–Cd(1)–O(3) 54.68(12), O(1)–C(35)–O(2) 118.0(5), O(2)–C(35)–O(3), 122.1(5), O(1)–C(35)–O(3) 119.9(5); hydrogen bonding interactions: N(3) ··· O(2) 2.842(6), N(3)–H(3) ··· O(2) 163(5), N(6) ··· O(3) 2.816(6), N(6)–H(6) ··· O(3) 174(5).

To our knowledge, ^{113}Cd NMR spectral properties have not been previously reported for any structurally characterized cadmium hydroxide, carbonate, or bicarbonate complex.[1,2] Examination of the ^{113}Cd NMR spectra of **1** and **2** (CD_3CN, 25(1) °C) revealed a single resonance for each complex at 304 and 245 ppm, respectively.[5,6]

In summary, we have structurally and spectrosopically characterized a novel binuclear cadmium hydroxide complex stabilized by secondary hydrogen bonding and CH/π interactions. This complex reacts with CO_2 to yield the binuclear cadmium carbonate derivative **2**, a reaction that provides the first direct chemical precedent for the ability of a Cd–OH moiety to participate in CO_2 fixation.

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Notes and references

‡ Crystal data for **1**: $C_{36}H_{67}Cd_2Cl_2N_7O_{10}S_4$, M = 1181.91, monoclinic, space group $P2_1/c$, a = 11.4211(3), b = 44.9639(13), c = 20.3932(6) Å, β = 101.5637(14)°, V = 10260.1(5) Å^3, Z = 8, T = 200(1) K, μ = 1.151 mm^{-1}. Using Mo-Kα radiation (0.71073 Å), a total of 27431 reflections were collected (4.98 < 2θ < 54.88°), of which 17652 were independent. Refinements converged to $R1$ = 0.0568, $wR2$ = 0.1082 ($I > 2\sigma I$) and $R1$ = 0.1023, $wR2$ = 0.1251 (all data). Hydrogen atoms of the hydroxy groups were located and refined isotropically. All other hydrogen atoms were assigned isotropic displacement coefficients and were allowed to ride on their respective carbons using SHELXL97. There are two independent dimeric cations (and corresponding anions) in the asymmetric unit, with the second cation being denoted by atom numbering possessing a prime (′) notation. There is one molecule of CH_3CN per dimeric cation in the asymmetric unit.

For **2**: $C_{37}H_{65}Cd_2Cl_2N_7O_{11}S_4$, M = 1207.90, triclinic, space group $P\bar{1}$, a = 9.1633(2), b = 15.1298(6), c = 18.9463(8) Å, α = 99.5467(2), β = 93.106(2), γ = 93.443(2)°, V = 2580.15(16) Å^3, Z = 2, T = 200(1) K, μ = 1.148 mm^{-1}. Using Mo-Kα radiation (0.71073 Å), a total of 14352 reflections were collected (6.04 < 2θ < 52.34°), of which 9915 were independent. Refinements converged to $R1$ = 0.0501, $wR2$ = 0.0938 ($I > 2\sigma I$) and $R1$ = 0.0897, $wR2$ = 0.1080 (all data). Hydrogen atoms of the secondary amine groups were located and refined isotropically. All other hydrogen atoms were assigned isotropic displacement coefficients and were allowed to ride on their respective carbons using SHELXL97. CCDC reference numbers 164433 and 164444. See http://www.rsc.org/suppdata/dt/b1/b109883g/ for crystallographic data in CIF or other electronic format.

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5 Referenced to external aqueous 0.5 M $Cd(ClO_4)_2\cdot 5H_2O$ in D_2O at 25(1) °C.

6 The ^{113}Cd resonance at 245 ppm for **2** ($\Delta\nu_{1/2}$ = 84.3 Hz) is notably broader than in **1** ($\Delta\nu_{1/2}$ = 64.8 Hz) due to the differences in the coordination environment of the two cadmium ions in **2**.