

Chemistry of a Binuclear Cadmium(II) Hydroxide Complex: Formation from Water, CO₂ Reactivity, and Comparison to a Zinc AnalogRussell A. Allred,[†] Lenore H. McAlexander,[‡] Atta M. Arif,[§] and Lisa M. Berreau^{*†}

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Treatment of the bmnpa (*N,N*-bis-2-(methylthio)ethyl-*N*-((6-neopentylamino-2-pyridyl)methyl)amine) ligand with equimolar amounts of Cd(ClO₄)₂·5H₂O and Me₄NOH·5H₂O in CH₃CN yielded the binuclear cadmium hydroxide complex [((bmnpa)Cd)₂(μ-OH)₂](ClO₄)₂·CH₃CN (**1**). Complex **1** may also be prepared (a) by treatment of a CH₃CN solution of (bmnpa)Cd(ClO₄)₂ (**2**) with 1 equiv of *n*-BuLi, followed by treatment with water or (b) from **2** in the presence of 1 equiv each of water and NEt₃. The hydroxide derivative **1** is not produced from **2** and water in the absence of an added base. Complex **1** possesses a binuclear structure in the solid state with hydrogen-bonding and CH/π interactions involving the bmnpa ligand. The overall structural features of **1** differ from the halide derivative [((bmnpa)Cd)₂(μ-Cl)₂](ClO₄)₂ (**3**), particularly in that the Cd₂(μ-OH)₂ core of **1** is symmetric whereas the Cd₂(μ-Cl)₂ core of **3** is asymmetric. In acetonitrile solution, **1** behaves as a 1:2 electrolyte and retains a binuclear structure and secondary hydrogen-bonding and CH/π interactions, whereas **3** is a 1:1 electrolyte, indicating formation of a mononuclear [(bmnpa)CdCl]ClO₄ species in solution. Treatment of **1** with CO₂ in anhydrous CH₃CN yields the bridging carbonate complex [((bmnpa)Cd)₂(μ-CO₃)](ClO₄)₂·CH₃CN (**4**). Treatment of a chemically similar zinc hydroxide complex, [((benpa)Zn)₂(μ-OH)₂](ClO₄)₂ (benpa = *N,N*-bis-2-(ethylthio)ethyl-*N*-((6-neopentylamino-2-pyridyl)methyl)amine, with CO₂ also results in the formation of a carbonate derivative, [((benpa)Zn)₂(μ-CO₃)](ClO₄)₂ (**5**), albeit the coordination mode of the bridging carbonate moiety is different. Treatment of **4** with added water results in no reaction, whereas **5** under identical conditions will undergo reaction to yield the zinc hydroxide complex [((benpa)Zn)₂(μ-OH)₂](ClO₄)₂.

Introduction

The coordination chemistry of cadmium hydroxide (Cd–OH) species has received little attention in the literature. To our knowledge, this area is limited to six reports of multinuclear complexes that contain one or more Cd–(μ-OH)–M units (M = Cd²⁺, Co²⁺, or Cr³⁺), reactivity studies of which were not reported.¹ Cadmium hydroxide species

may be involved in two reported reactions of synthetic cadmium complexes with CO₂ under basic aqueous conditions, albeit they were not isolated or spectroscopically characterized.² Our interest in the structural and reactivity properties of complexes possessing a Cd–OH unit stems in part from the proposed formation of a Cd–OH moiety in several cadmium-substituted binuclear zinc hydrolytic enzymes and from the recent identification of a naturally occurring cadmium-containing carbonic anhydrase (CCA1).^{3–5}

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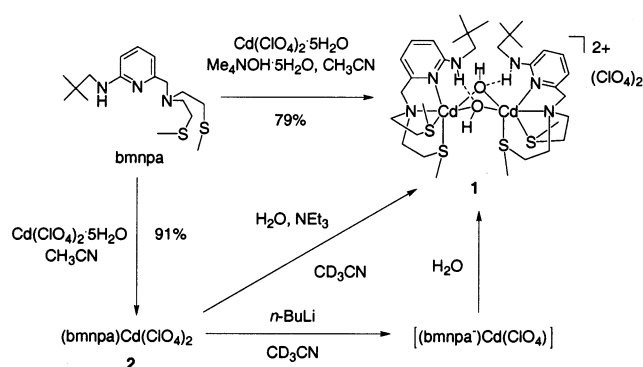
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Scheme 1



Notably, the complete amino acid sequence of CCA1 reveals the presence of a number of cysteine residues, which may be involved in cadmium binding to the enzyme.⁵

Due to the dearth of structural and spectroscopic data and reactivity studies of cadmium hydroxide species, we became interested in examining whether mixed nitrogen/sulfur ligand systems capable of secondary interactions (e.g., hydrogen bonding) would enable the isolation of reactive cadmium hydroxide complexes. Previous studies by Borovik and Masuda, using tripodal ligand systems that incorporate multiple secondary hydrogen bond donors, have demonstrated that secondary interactions may be utilized to stabilize a variety of oxo and hydroxo moieties.^{6,7} In our own laboratory, we have prepared several mixed nitrogen/sulfur ligands possessing a single internal hydrogen bond donor and have shown that one such ligand (**bmnpa**, Scheme 1) enables the isolation of a binuclear nitrogen/sulfur-ligated zinc hydroxide species.⁸ We note that our goal in using only one hydrogen bond donor group in these systems is to stabilize the moiety of interest (e.g., $\text{Cd}-\text{OH}$) without inhibiting further reactivity studies with suitable substrates.

In the work described herein, we are not seeking to model a particular metalloenzyme but instead to examine the formation and reactivity of a cadmium hydroxide species wherein direct comparison could be made to relevant cadmium and zinc analogue complexes. To our knowledge, this type of study has not previously appeared in the inorganic literature but is directly relevant toward developing an understanding of the differences in coordination chemistry between cadmium hydroxide and halide derivatives and, more importantly, between cadmium and zinc hydroxide species. The studies outlined herein encompass (1) develop-

ment of synthetic routes to a binuclear $\text{Cd}-\text{OH}$ complex, including its formation from water, (2) reactivity studies of the $\text{Cd}-\text{OH}$ complex with CO_2 , and (3) extensive structural, spectroscopic, and reactivity comparisons with cadmium and zinc analogues. Of particular importance, the results of this work demonstrate that, in a specific ligand environment, zinc and cadmium hydroxide complexes differ notably in their structural features and reactivity properties with CO_2 . A preliminary account of this work has previously been reported.⁹

Experimental Section

General Methods. All reagents and solvents were obtained from commercial sources and were used as received unless otherwise noted. Solvents were dried according to published procedures¹⁰ and were distilled under N_2 prior to use. Air-sensitive reactions were performed in a MBraun Unilab glovebox under an atmosphere of purified N_2 .

Physical Methods. FTIR spectra were recorded on a Shimadzu FTIR-8400 spectrometer as KBr pellets. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 20(1) °C on a JEOL GSX-270 spectrometer. Chemical shifts (in ppm) are referenced to the residual solvent peak(s) (^1H , 1.94 ppm (quintet); $^{13}\text{C}\{^1\text{H}\}$, 1.39 (heptet) ppm). Details regarding the acquisition of ^{113}Cd NMR spectra are given in the Supporting Information. Fast atom bombardment (FAB) mass spectra were obtained at the University of California, Riverside, CA, using a VG ZAB2SE high-resolution mass spectrometer in a matrix of *m*-nitrobenzyl alcohol (MNBA). Elemental analyses were performed by Atlantic Microlabs of Norcross, GA.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.¹¹

Synthesis of Ligands and Complexes. The **bmnpa** and **benpa** ligands and the zinc complexes $[(\text{bmnpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ and $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ were prepared as previously reported.^{8,12}

$[(\text{bmnpa})\text{Cd}_2(\mu\text{-OH})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (1**).** The entire previously reported synthetic procedure for this complex was performed under an atmosphere of purified N_2 .⁹ ^{113}Cd NMR (CD_3CN , 88.8 MHz): δ 304 ppm.

$(\text{bmnpa})\text{Cd}(\text{ClO}_4)_2$ (2**).** A CH_3CN solution (3 mL) of **bmnpa** (0.13 g, 0.37 mmol) was added to solid $\text{Cd}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.15 g, 0.37 mmol) in a glass vial. Following 30 min of rapid stirring, an excess of diethyl ether (~30 mL) was added and the resulting cloudy mixture was cooled to ~-10 °C for 14 h. A white solid that had deposited was dried under vacuum. Diffusion of Et_2O into a CH_3CN solution at ambient temperature yielded the product as a crystalline solid (0.24 g, 91%). ^1H NMR (dry CD_3CN , 270 MHz): δ 7.70 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 6.71 (d, J = 7.4 Hz, 1H), 5.40 (t, J = 5.9 Hz, 1H, *N-H*), 3.91 (s, 2H), 3.09 (d, J = 5.9 Hz, 2H), 3.04–2.74 (m, 8H), 2.19 (s, 6H), 1.00 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 67.9 MHz): δ 160.1, 152.2, 142.7, 114.9, 108.6, 59.7, 55.1, 50.4, 33.1, 32.3, 27.5, 15.1 (12 signals expected and observed). ^{113}Cd NMR (dry CD_3CN , 88.8 MHz): δ 280 ppm.

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FTIR (KBr, cm^{-1}): 3405 ($\nu_{\text{N-H}}$), 1120 ($\nu_{\text{O}^*-\text{ClO}_3}$, ClO^* asym bend), 1021 ($\nu_{\text{O}^*-\text{ClO}_3}$, ClO_3 sym stretch), 914 ($\nu_{\text{O}^*-\text{ClO}_3}$, ClO stretch), 629 ($\nu_{\text{O}^*-\text{ClO}_3}$, ClO_3 sym bend), 624/619 ($\nu_{\text{O}^*-\text{ClO}_3}$, ClO_3 asym bend).¹⁴ Anal. Calcd for $\text{C}_{17}\text{H}_{31}\text{N}_3\text{S}_2\text{Cl}_2\text{O}_8\text{Cd}$: C, 31.24; H, 4.78; N, 6.43. Found: C, 31.54; H, 4.82; N, 6.52.

Deprotonation of Secondary Amine of 2 Followed by Addition of H_2O : NMR Tube Reaction. A NMR tube containing **2** (84 mg, 0.13 mmol) in dry CD_3CN was prepared. The ^1H NMR spectrum was identical to that reported above for complex **2** in dry CD_3CN . Following the addition of 1 equiv of *n*-BuLi (81 μL , 1.6 M hexane solution (Aldrich)), the tube was vigorously shaken and a second ^1H NMR spectrum was obtained wherein some peak broadening had occurred and the signal for the $\text{N}(3)\text{-H}$ proton had disappeared. To this solution was added 1 equiv of water (2.4 μL), the tube was shaken vigorously for ~ 30 s, and a third ^1H NMR spectrum was obtained. This spectrum indicated the clean formation of **1**.

Treatment of 2 with H_2O in the Presence of NEt_3 : NMR Tube Reaction. A NMR tube containing **2** (26 mg, 0.040 mmol) in CD_3CN was prepared containing ~ 1 equiv of water. To this tube was added NEt_3 (1 equiv), and the tube was shaken vigorously. A ^1H NMR spectrum of this solution indicated the quantitative formation of **1**.

Treatment of 2 with H_2O : NMR Tube Reaction. A NMR tube containing **2** (38 mg, 0.058 mmol) in dry CD_3CN was prepared. ^1H NMR (dry CD_3CN , 270 MHz): δ 7.71 (t, $J = 8.0$ Hz, 1H), 6.82 (d, $J = 8.6$ Hz, 1H), 6.71 (d, $J = 7.4$ Hz, 1H), 5.36 (br, 1H, N-H), 3.91 (s, 2H), 3.11 (d, $J = 5.9$ Hz, 2H), 3.04–2.74 (m, 8H), 2.20 (s, 6H), 1.02 (s, 9H). This spectrum is highly similar to that reported above for complex **2** in dry CD_3CN , albeit the $\text{N}(3)\text{-H}$ proton is shifted ~ 0.04 ppm upfield and slightly broadened, which may indicate some degree of ion pairing. Following the addition of 1.0 equiv of water (1.0 μL), the tube was vigorously shaken and a second ^1H NMR spectrum was obtained. ^1H NMR (dry CD_3CN , 270 MHz): δ 7.71 (t, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 8.6$ Hz, 1H), 6.71 (d, $J = 7.4$ Hz, 1H), 5.43 (br, 1H, N-H), 3.90 (s, 2H), 3.10 (d, $J = 5.9$ Hz, 2H), 3.04–2.74 (m, 10H), 2.20 (s, 6H), 1.01 (s, 9H). A new feature at 2.81 ppm was assigned as H_2O , as it increased with subsequent additions and underwent an upfield shift of only 0.01 ppm or less with each additional 1 equiv of water. Following the addition of 2 and 3 equiv of water, respectively, the $\text{N}(3)\text{-H}$ proton shifted downfield to 5.50 and 5.57 ppm. The ^1H NMR spectrum remained unchanged after several days at room temperature.

$[(\text{bmnpa})\text{Cd}_2(\mu\text{-Cl})_2](\text{ClO}_4)_2$ (3**).** A solution of *bmnpa* (0.10 g, 0.30 mmol) in CH_3CN (3 mL) was added to a vial containing solid $\text{Cd}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.12 g, 0.30 mmol). The resulting clear, colorless solution was stirred for 5 min and then transferred to a vial containing NMe_4Cl (0.033 g, 0.30 mmol). The resulting mixture was stirred for 4 h at ambient temperature at which time the solvent was removed under reduced pressure. The remaining white solid was redissolved in CH_2Cl_2 (10 mL), the mixture was filtered through glass wool/Celite to remove Me_4NClO_4 , and the CH_2Cl_2 filtrate was pumped to dryness. The product was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ to yield crystals suitable for X-ray diffraction analysis (0.11 g, 60%). ^1H NMR (CD_3CN , 270 MHz): δ 7.64 (t, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 5.8$ Hz, 1H, N-H), 6.71 (d, $J = 8.6$ Hz, 1H), 6.61 (d, $J = 6.9$ Hz, 1H), 3.87 (s, 2H), 3.03 (d, $J = 5.9$ Hz, 2H), 3.00–2.72 (m, 8H), 2.16 (s, 6H), 1.02 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR

(CD_3CN , 67.9 MHz): δ 161.0, 152.4, 142.1, 113.9, 108.0, 60.2, 55.4, 50.9, 33.3, 32.1, 27.9, 15.3 (12 signals expected and observed). ^{113}Cd NMR (CD_3CN , 88.8 MHz): δ 361 ppm. FTIR (KBr, cm^{-1}): 3357 ($\nu_{\text{N-H}}$), 3336 ($\nu_{\text{N-H}}$), 1083 (ν_{ClO_4} , asym stretch), 623 (ν_{ClO_4} , asym bend).¹⁴ LRFAB-MS ($\text{CH}_3\text{CN-NBA}$) [m/z (relative intensity)]: 490 ($[(\text{bmnpa})\text{Cd} - \text{Cl}]^+$, 100%). Anal. Calcd for $\text{C}_{34}\text{H}_{62}\text{N}_6\text{S}_4\text{Cl}_4\text{O}_8\text{Cd}_2$: C, 34.67; H, 5.31; N, 7.14. Found: C, 34.73; H, 5.32; N, 7.07.

$[(\text{bmnpa})\text{Cd}_2(\mu\text{-CO}_3)](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (4**), **4**** was prepared as previously reported.⁹ ^{113}Cd NMR (CD_3CN , 88.8 MHz): δ 245 ppm.

Treatment of 2 with $\text{H}_2\text{O}/\text{CO}_2$. A CD_3CN solution (~ 0.5 mL) of **2** was prepared containing ~ 5 equiv of water. This NMR tube was cooled to -78 $^\circ\text{C}$, opened to vacuum to remove headspace gases, and was then returned to ambient temperature under vacuum. CO_2 was then purged into the tube (~ 1 atm). The tube was then sealed via stopcock and vigorously shaken. A ^1H NMR spectrum of this solution obtained at 20(1) $^\circ\text{C}$ exhibited spectral properties consistent only with the presence of **2** and water, indicating that no reaction involving CO_2 had occurred.

Treatment of $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ with CO_2 . Characterization of $[(\text{benpa})\text{Zn}_2(\mu\text{-CO}_3)](\text{ClO}_4)_2$ (5**).** CO_2 (~ 1 atm) was condensed into a dry CD_3CN (1 mL) solution of $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ (0.017 g, 0.015 mmol). A ^1H NMR spectrum of this solution indicated complete conversion to a new complex **5**. ^1H NMR (CD_3CN , 270 MHz, CO_2 atmosphere): δ 7.66 (t, $J = 7.8$ Hz, 1H), 7.59 (br, 1H, N-H), 6.68 (d, $J = 8.6$ Hz, 1H), 6.60 (d, $J = 6.6$ Hz, 1H), 3.90 (s, 2H), 3.01–2.71 (m, 12H), 2.66–2.40 (m, 4H), 1.17 (t, $J = 7.2$ Hz, 6H), 1.01 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 67.9 MHz, CO_2 atmosphere): δ 170.0 ($\mu\text{-CO}_3$), 160.4, 152.0, 142.6, 112.4, 108.0, 59.2, 55.3, 52.3, 32.9, 29.3, 27.9, 27.0, 14.4 (14 signals expected and 14 observed; carbonate carbon found using $^{13}\text{CO}_2$) ppm. Diffusion of Et_2O into this solution at room temperature, under a CO_2 atmosphere, yielded a few clear crystals and a powdered precipitate (total mass: 0.015 g). The ratio of **5** to $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ in this bulk sample, as determined by ^1H NMR in dry CD_3CN , was $\sim 3.5:1$. Despite repeated attempts at recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ solution under a CO_2 atmosphere, conditions under which a ^1H NMR experiment indicated $>95\%$ formation of **5**, the carbonate complex **5** could not be isolated as an analytically pure material. Even when single crystals were harvested, a ^1H NMR spectrum (in dry CD_3CN solution) indicated the presence of $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$.

Note: Treatment of the structurally related $[(\text{bmnpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ with excess CO_2 in CH_3CN resulted in the formation of a new complex **6**. On the basis of ^1H and ^{13}C NMR experiments conducted under a CO_2 atmosphere, we suggest that **6** is the analogous bridging carbonate derivative $[(\text{bmnpa})\text{Zn}_2(\mu\text{-CO}_3)](\text{ClO}_4)_2$. ^1H NMR (CD_3CN , 270 MHz, CO_2 atmosphere): δ 7.66 (t, $J = 7.8$ Hz, 1H), 7.59 (br, 1H, N-H), 6.68 (d, $J = 8.6$ Hz, 1H), 6.60 (d, $J = 6.6$ Hz, 1H), 3.90 (s, 2H), 3.05–2.68 (m, 10H), 2.05 (s, 6H), 1.01 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 67.9 MHz, CO_2 atmosphere): δ 170.1 ($\mu\text{-CO}_3$), 160.6, 152.0, 142.7, 112.5, 108.1, 58.8, 55.4, 51.6, 32.9, 31.9, 27.9, 15.6 (13 signals expected and 13 observed; carbonate carbon found using $^{13}\text{CO}_2$) ppm. As with **5**, all attempts to isolate analytically pure **6** resulted in the isolation of mixtures with the precursor hydroxide complex.

Treatment of 4 with H_2O : NMR Tube Reaction. Approximately 36 mg of dried crystalline **4** was dissolved in ~ 1 mL of dry CD_3CN . A ^1H NMR spectrum was obtained, which was identical to that reported for **4** (see above). To this solution was added 1.5 equiv of H_2O (1.6 μL). The resulting solution was mixed for about 1 min, and a ^1H NMR spectrum was obtained. The spectrum was unchanged except for a slight upfield shift (~ 0.1

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ppm) of the N(3)–H proton and the appearance of the H₂O peak at 2.39 ppm. An additional 5.0 equiv of H₂O (5.3 μL) was added, and the solution was mixed again for about 1 min. A ¹H NMR spectrum of this solution indicated only a further upfield shift (~0.3 ppm) of the N(3)–H proton. After 4 days at 48 °C, another ¹H NMR spectrum was obtained and no changes were observed.

Treatment of 5 with H₂O: NMR Tube Reaction. Approximately 11 mg of bulk compound isolated from attempts to crystallize **5** was dissolved in ~1 mL of dry CD₃CN. A ¹H NMR spectrum (20(1) °C) of this solution showed a ratio of **5** to [(benpa)-Zn)₂(μ-OH)₂](ClO₄)₂ of ~2.7:1 (from integration of *t*-Bu resonances of each complex). To this solution was added 1 equiv of H₂O (0.2 μL). Following mixing for about 1 min, a ¹H NMR spectrum was obtained (20(1) °C), which indicated that the ratio **5** to [(benpa)-Zn)₂(μ-OH)₂](ClO₄)₂ had decreased to ~1.5:1. Addition of a second equiv of water (0.2 μL), followed by mixing for about 1 min, yielded a solution that when analyzed by ¹H NMR indicated a further reduction of the ratio between **5** and [(benpa)Zn)₂(μ-OH)₂](ClO₄)₂ to ~1.3:1. With addition of subsequent equivalents of H₂O, the ratio continued to decrease but in a less dramatic fashion. In addition, a precipitate began to form, consistent with the formation of [(benpa)Zn)₂(μ-OH)₂](ClO₄)₂, which exhibits relatively low solubility in CD₃CN. Using the residual CHD₂CN signal as an internal standard, it was observed that the overall amount of [(benpa)Zn)₂(μ-OH)₂](ClO₄)₂ in the solution remained constant throughout the water additions, whereas the amount of **5** decreased. As **5** is highly soluble in CD₃CN, this behavior is indicative of reaction of **5** with water to produce [(benpa)Zn)₂(μ-OH)₂](ClO₄)₂, which then partially precipitates from solution.

X-ray Crystallography. A crystal of each compound **1–5** was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å) for data collection at 200(1) K. For each compound, an initial set of cell constants was obtained from 10 frames of data that were collected with an oscillation range of 1 deg/frame and an exposure time of 20 s/frame. Indexing and unit cell refinement based on observed reflections from those 10 frames indicated monoclinic *P* lattices for **1**, **2**, and **5**, a monoclinic *C* lattice for **3**, and a triclinic *P* lattice for **4**. Final cell constants for each complex were determined from a set of strong reflections from the actual data collection. For each data set, these reflections were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using DENZO-SMN and SCALEPAC.¹³ The structures were solved by a combination of direct methods and heavy atom using SIR 97. All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Unless otherwise stated, hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{\text{methyl}})$, and their coordinates were allowed to ride on their respective carbons using SHELXL97.

Structure Solution and Refinement. The cadmium hydroxide complex [(bmnpa)Cd)₂(μ-OH)₂](ClO₄)₂·CH₃CN (**1**) crystallized in the space group *P2*₁/*c*. Hydrogen atoms of the hydroxy groups were located and refined independently. There are two independent binuclear 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 CH₃CN/binuclear cation in the asymmetric unit. For one cation, the positions of two carbons and the thioether sulfur atom of each thioether arm bonded to Cd(2) are disordered. These carbon and sulfur atoms of each thioether arm (C(18)/C(19)/S(4) and C(21)/C(22)/S(3)) were split into two fragments (second fragment denoted by "a") and were refined. The refinement led to a 0.68:0.32 ratio in occupancy over two positions for each thioether sulfur atom and a 0.70:0.30 ratio

in occupancy over two positions for each carbon. Two perchlorate anions in the asymmetric unit also exhibit disorder. The O(9') and O(10') oxygen atoms, bonded to Cl(2'), were split into two fragments (O(9')/O(9b), O(10')/O(10b)) and were refined. This refinement led to a 0.61:0.39 ratio in occupancy over two positions for each oxygen atom. The O(9) and O(10) oxygen atoms, bonded to Cl(2), were split into two fragments (O(9)/O(9a) and O(10)/O(10a) and were refined. This refinement led to a 0.75:0.25 ratio in occupancy over two positions for each oxygen atom.

The cadmium perchlorate complex (bmnpa)Cd(ClO₄)₂ (**2**) crystallized in the space group *P2*₁/*a*. A portion of the hydrogen atoms (those on the thioether arms and the benzylic position) were located and refined independently while the remaining atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{\text{methyl}})$, and their coordinates were allowed to ride on their respective carbons using SHELXL97. N(3) as well as carbon atoms of the pyridyl ring exhibit vibrational motion, and three of the carbon atoms of neopentyl group of the bmnpa ligand exhibit disorder. These carbon atoms (C(13)/C(15)/C(16)) were each split into two fragments (second fragment denoted by a prime) and were refined. This refinement led to a 0.64:0.36 ratio in occupancy over two positions for each carbon atom.

The cadmium chloride complex [(bmnpa)Cd)₂(μ-Cl)₂](ClO₄)₂·2CH₃CN (**3**·2CH₃CN) crystallized in the space group *P2*₁/*c*. There is one binuclear cation (and corresponding anions) in the asymmetric unit. Carbon atoms of the neopentyl unit of the bmnpa ligand bonded to Cd(2) exhibit disorder. These carbon atoms (C(31)/C(32)/C(33)) were each split into two fragments (second fragment denoted by "a") and were refined. This refinement led to a 0.51:0.49 ratio in occupancy over two positions for each carbon atom. Of the two perchlorate anions present in the asymmetric unit, one exhibits disorder over two positions. There are two molecules of acetonitrile solvate present in the asymmetric unit, one of which exhibits disorder.

The cadmium carbonate complex [(bmnpa)Cd)₂(μ-CO₃)](ClO₄)₂·CH₃CN (**4**) crystallized in the space group *P* $\bar{1}$. One molecule of acetonitrile is found in the asymmetric unit. Hydrogen atoms on N(3) and N(6) were located and refined independently, while the rest were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{\text{methyl}})$ and their coordinates were allowed to ride on their respective carbons using SHELXL97. Oxygen atoms of both perchlorate anions exhibit disorder. For the first perchlorate anion, two oxygen atoms (O(4) and O(5)) were each split into two fragments (second fragment denoted by a prime) and were refined. This refinement led to a 0.62:0.38 ratio in occupancy over two positions. For the other perchlorate anion, three oxygen atoms (O(10)/O(11)/O(12)) were each split into two fragments (second fragment denoted by a prime) and were refined. This refinement led to a 0.75:0.25 ratio in occupancy over two positions for each oxygen atom.

The zinc carbonate complex [(benpa)Zn)₂(μ-CO₃)](ClO₄)₂ (**5**) crystallized in the space group *P2*₁/*c*. Hydrogen atoms on N(3) and N(6) were located and refined independently. Oxygen atoms of one perchlorate anion exhibit disorder. These oxygen atoms (O(8)/O(9)/O(10)/O(11)) were each split into two fragments (second fragment denoted by prime) and were refined. This refinement led to a 0.61:0.39 ratio in occupancy over two positions for each oxygen atom.

Conductance. Conductance measurements were made at 22(1) °C using a YSI model 31A conductivity bridge with a cell having a cell constant of 1.0 cm⁻¹ using Me₄NClO₄ as a standard.¹⁴ Acetonitrile was used as the solvent and was dried over CaH₂, distilled, and then collected by vacuum distillation prior to use. Each complex was recrystallized and dried in vacuo to obtain clean,

crystalline material. Using a measured amount of material, typically 45–55 mg, solutions ranging from approximately 3–0.05 mg/mL were prepared by serial dilution. While most solutions were prepared open to the air, those of the $[(\text{bmnpa})\text{Cd}_2(\mu\text{-OH})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (**1**) complex were prepared under an inert atmosphere to minimize the reaction with atmospheric CO_2 . To reduce electrolyte contamination, all glassware was rigorously cleaned, rinsed with distilled water, and subsequently oven-dried.

Conductance Data Analysis. The data derived from conductance measurements of all solutions were used to calculate respective equivalent conductances which were plotted as a function of the square root of the equivalent concentration for each complex.^{15,16} The data of the linear portion (found between anomalous behavior at either end of the concentration range) were extrapolated to give a hypothetical equivalent conductance at infinite dilution as the y -intercept. Onsager plots were constructed by plotting the difference between the y -intercept and the equivalent conductance (y) versus the square root of the equivalent concentration (x). For complexes wherein the solution behavior could conceivably be either a 1:1 or 1:2 electrolyte, the Onsager slopes were calculated for both cases. The electrolyte type was then determined by eliminating the slope inconsistent with either possibility.

Results

What Synthetic Routes Will Yield Cd–OH Species?

We have evaluated various synthetic approaches toward generating a cadmium hydroxide complex. Using conditions under which an external base is added, attempts to prepare **1** in MeOH solution using KOH, conditions similar to those utilized for the preparation of a zinc hydroxide complex of the bmnpa ligand,⁸ failed to give clean crystalline product following recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. However, using CH_3CN as the solvent, treatment of the bmnpa ligand (Scheme 1) with equimolar amounts of $\text{Cd}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $\text{Me}_4\text{NOH} \cdot 5\text{H}_2\text{O}$ under anaerobic conditions followed by workup and crystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ yielded the hydroxide derivative $[(\text{bmnpa})\text{Cd}_2(\mu\text{-OH})_2](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (**1**) as a crystalline solid in 79% yield. The chemical makeup of this hydroxide derivative was determined by ^1H , ^{13}C , and ^{113}Cd NMR, FTIR, elemental analysis, and X-ray crystallography. Details of the solid-state and solution properties of **1** will be presented following discussion of other synthetic routes to this complex.

To investigate whether **1** could be prepared using water as the source of hydroxide anion, two independent pathways were examined, both starting from a cadmium perchlorate derivative $(\text{bmnpa})\text{Cd}(\text{ClO}_4)_2$ (**2**) that was independently synthesized. Complex **2** was prepared by mixing equimolar amounts of $\text{Cd}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ and bmnpa in CH_3CN solution followed by recrystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$. Complex **2** has been characterized by several methods including ^1H and ^{13}C NMR, ^{113}Cd NMR, FTIR, elemental analysis, conductance (in dry CH_3CN), and single-crystal X-ray crystallography. In the solid state (Figure 1), the cadmium center is six-coordinate, exhibiting a distorted trigonal prismatic geometry with both perchlorate anions coordinated to the Cd(II) ion. In dry CH_3CN solution, both perchlorate

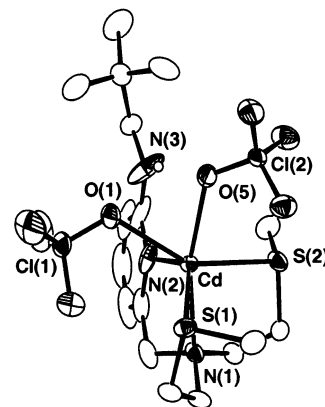


Figure 1. ORTEP representation of **2**. All ellipsoids are drawn at the 35% probability level. Details of the X-ray data collection and refinement may be found in Table 1. Selected bond distances and angles are given in Table 2. Hydrogen atoms (except the secondary amine hydrogen) are not shown for clarity.

anions are released, as determined by conductance measurements (Figure S1). This is consistent with formation of a N/S-ligated Cd(II) ion in CH_3CN solution, perhaps possessing one or more coordinated nitrile ligands.¹⁷

Treatment of a dry CD_3CN solution of **2** with 1 equiv of $n\text{-BuLi}$ yielded ^1H NMR spectroscopic changes suggesting deprotonation of the bmnpa ligand. For example, the $\text{N}(3)\text{-H}$ resonance at 5.40 ppm disappeared. In addition, peak broadening in the ligand proton resonances was observed. However, because notable changes in the chemical shifts of ligand resonances were not observed, the results suggest that the bmnpa ligand undergoes deprotonation under these conditions without drastic structural rearrangement of the complex. Notably, addition of 1 equiv of water to this solution gave **1** in quantitative yield (as determined by ^1H NMR).

A second synthetic route to **1** involving water and **2** is depicted in Scheme 1. Treatment of a CD_3CN solution of **2** with equimolar amounts of water and NEt_3 yielded **1** quantitatively as determined by ^1H NMR spectroscopy.

Finally, we have examined whether the cadmium hydroxide complex **1** could be generated from **2** and water in the absence of an external base. Treatment of a CD_3CN solution of **2** with 1 equiv of water at 20(1) °C results in a slight downfield shift of the N-H resonance of the bmnpa ligand (Figure S2) from 5.36 to 5.43 ppm. A resonance for water is observed at 2.81 ppm, which increases in intensity with

(17) A search of the Cambridge Crystallographic Database (CSD version 5.23, April 2002) revealed 9 examples of Cd(II) complexes possessing one or more coordinated CH_3CN ligands: (a) Adams, H.; Bastida, R.; Fenton, D. E.; Macias, A.; Spey, S. E.; Valencia, L. *Inorg. Chem. Commun.* **1999**, *2*, 513–515. (b) Adams, H.; Bastida, R.; Fenton, D. E.; Macias, A.; Spey, S. E.; Valencia, L. *J. Chem. Soc., Dalton Trans.* **1999**, 4131–4137. (c) Li, S.-L.; Zhang, Z.-Z.; Mak, T. C. W. *Inorg. Chim. Acta* **1998**, *268*, 177–187. (d) Adams, H.; Bailey, N. A.; Fenton, D. E.; Ford, I. G.; Kitchen, S. J.; Williams, M. G.; Tasker, P. A.; Leong, A. J.; Lindoy, L. F. *J. Chem. Soc., Dalton Trans.* **1991**, 1665–1674. (e) Bebout, D. C.; Stokes, S. W.; Butcher, R. J. *Inorg. Chem.* **1999**, *38*, 1126–1133. (f) Brooker, S.; Bertel, N.; Stalke, D.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edlmann, F. T. *Organometallics* **1992**, *11*, 192–195. (g) Barnett, S. A.; Blake, P. A.; Champness, N. R.; Nicolson, J. E. B.; Wilson, C. J. *J. Chem. Soc., Dalton Trans.* **2001**, 567–573. (h) Kitazawa, T.; Kikuyama, T.; Ugajin, H.; Takahashi, M.; Takeda, M. *J. Coord. Chem.* **1996**, *37*, 17–22.

(15) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(16) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587–4591.

the addition of subsequent equivalents of water. The N–H proton resonance of **2** shifts downfield to 5.57 ppm following the addition of a total of 3 equiv of water. The downfield shift of the N–H resonance could arise from formation of a hydrogen-bonding interaction with water, which may be competing with solvent for the open coordination site(s) of the Cd(II) ion.¹⁸ No further change in the ¹H NMR spectrum was observed after several days at room temperature, indicating that the presence of water, in the absence of an external base, does not enable the formation of the cadmium hydroxide complex **1**.

X-ray Crystallographic Characterization. The structure of **1** was determined by X-ray diffraction. An ORTEP representation of the cationic portion of **1** is shown in Figure 2 (top). For structural comparison to the hydroxide derivative, we have prepared a cadmium chloride complex (**3**) as outlined in Scheme 2. An ORTEP representation of the cationic portion of **3** is shown in Figure 2 (bottom). At first glance, the structural features of the cationic portions of **1** and **3** appear similar, with both possessing a binuclear structure, each cadmium ion exhibiting a distorted octahedral geometry, and similar Cd–N_{py} (average 2.36 Å) and Cd–N_{am} (average 2.40 Å) distances. In addition, the neopentyl-amino portions of the bmnpa ligands in both cases are positioned on one side of the Cd₂(μ-X)₂ (X = OH or Cl) core. In this orientation, two hydrogen-bonding interactions are formed with the bridging anions. For the hydroxide derivative **1**, these interactions are classified as moderate hydrogen bonds, having N(3)⋯O(2)/N(6)⋯O(1) heteroatom distances of ~2.9 Å.¹⁹ In **3**, heteroatom distances (N(3)⋯Cl(2) 3.26 Å; N(6)⋯Cl(1) 3.32 Å) indicate hydrogen bonds between the ligand secondary amino groups and the bridging chloride anions.²⁰ Examination of the metrical parameters of the Cd–S interactions, the Cd₂(μ-X)₂ cores, and secondary interactions within the cationic portions of **1** and **3** reveals notable differences between the complexes. For example, the Cd–S distances in **3** (average 2.69 Å) are slightly shorter than the average Cd–S distance in **1** (average 2.76 Å). In addition, whereas the Cd₂(μ-OH)₂ core of **1** is nearly symmetric (Cd–O(H)_{avg} 2.22 Å; Cd⋯Cd 3.32 Å), the Cd₂(μ-Cl)₂ core of **3** is notably asymmetric, with each cadmium ion involved in two distinct Cd–Cl interactions (Cd(1)–Cl(1) 2.7664(11), Cd(1)–Cl(2) 2.5362(5), Cd(2)–Cl(1) 2.5305(12), Cd(2)–Cl(2) 2.7509(6) Å; Cd⋯Cd 3.76 Å). In regard

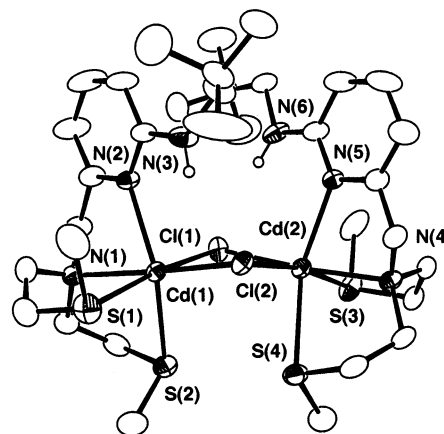
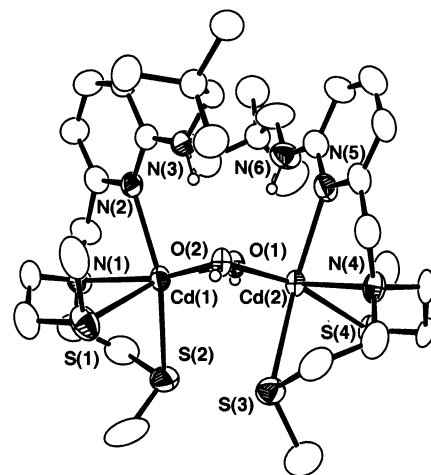
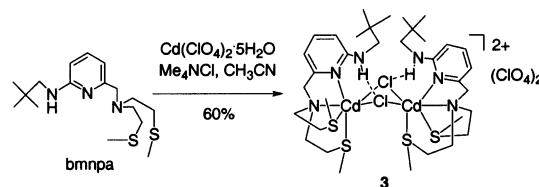


Figure 2. ORTEP representations of the cationic portions of **1** (top) and **3** (bottom). All ellipsoids are drawn at the 35% probability level. Only one of two independent but chemically similar cations in the asymmetric unit of **1** is shown. Hydrogen atoms (except the secondary amine hydrogens and the hydroxyl hydrogens of **1**) are not shown for clarity.

Scheme 2



to secondary interactions within the binuclear cation of **1**, as shown in Figure 3 (top), two similar CH/π interactions²¹ (perpendicular C(alkyl)⋯arene distances of 3.84 and 3.63 Å, respectively) are found between a C–H unit (–CH₃ or –CH₂–) of the neopentyl group of one ligand and the pyridyl group of the second bmnpa ligand. This contrasts with the structural features of **3** (Figure 3 (bottom)), wherein only a single very short CH/π interaction (C(32)⋯arene centroid distance 3.18 Å) is present.

Spectroscopic Properties of [((bmnpa)Cd)₂(μ-OH)₂](ClO₄)₂·CH₃CN (1**).** The solid-state FTIR spectrum of **1** (collected as a KBr pellet) exhibits a ν_{O–H} vibration at 3587 cm^{–1} and ClO₄[–] vibrations. While perchlorate vibrations are also found in the solid-state FTIR spectra of **2** and **3**, the

- (18) A search of the Cambridge Crystallographic Database (CSD version 5.23, April 2002) revealed 7 examples wherein a cadmium coordination environment contained both a water ligand and nitrogen and sulfur donors: (a) Burshtein, I. F.; Volodina, G. F.; Gerbelev, N. V.; Bologna, O. A.; Filippova, I. G.; Malinovskii, T. I. *Koord. Khim.* **1985**, *11*, 692–695. (b) Rodesiler, P. F.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Acta Crystallogr., Sect. C* **1987**, *43*, 1058–1061. (c) Pickardt, J.; Gong, G.-T. *Z. Naturforsch., B* **1993**, *48*, 23–26. (d) Griffith, E. A. H.; Amma, E. L. *Chem. Commun.* **1979**, 1013–1014. (e) Baggio, S.; Baggio, R.; Garland, M. T. *Acta Crystallogr., Sect. C* **1998**, *54*, 1099–1102. (f) Yang, G.; Zhu, H.-G.; Liang, B.-H.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 580–585. (g) Casas, J. S.; Castellano, E. E.; Garcia-Tasende, M. S.; Sanchez, A.; Sordo, J.; Zukerman-Schpector, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 825–831.
- (19) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
- (20) (a) Allerhand, A.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1963**, *85*, 1233–1237. (b) Steiner, T. *Acta Crystallogr., Sect. B* **1998**, *54*, 456–463.

- (21) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665–8701.

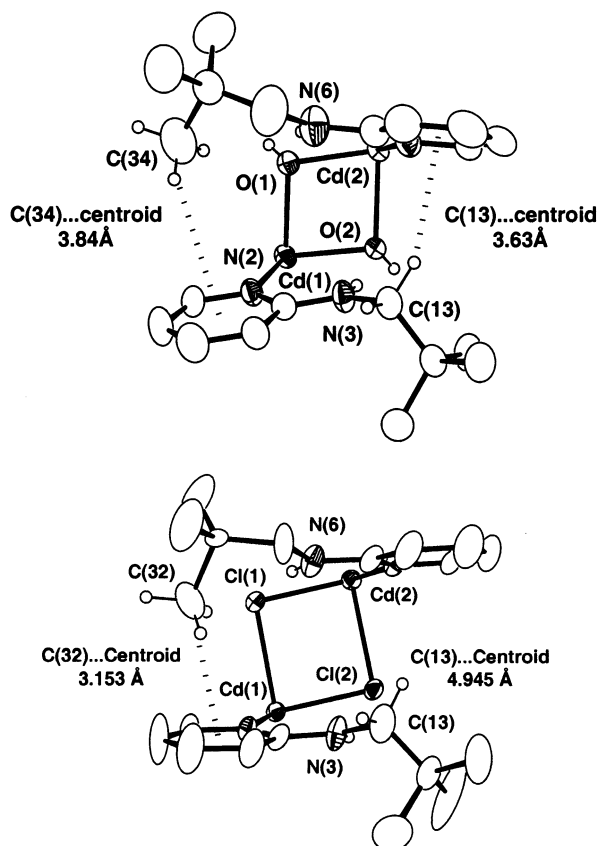


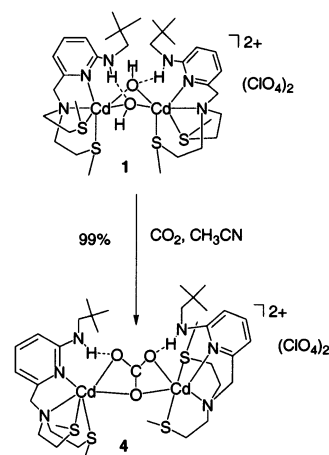
Figure 3. Views of the secondary interactions surrounding the $\text{Cd}_2(\mu\text{-X})_2$ cores in **1** (top) and **3** (bottom).

region $>3500\text{ cm}^{-1}$ in these complexes lacks the feature assigned as $\nu_{\text{O-H}}$ in **1**.

Because reactivity studies of **1** with CO_2 were undertaken in CH_3CN solution, we have further examined the solution properties of **1** by conductance measurements and by ^1H , ^{13}C , and ^{113}Cd NMR. In CH_3CN solution, complex **1** behaves as a 1:2 electrolyte (Figure S1), consistent with the presence of a binuclear cation in solution. Evidence for retention of the secondary hydrogen-bonding and CH/π interactions in CD_3CN is derived from ^1H NMR spectral properties of the complex. Specifically, the observation of a single secondary amine proton resonance shifted notably downfield (δ 8.81 ppm) from its position in the free ligand under identical conditions (δ \sim 5.0 ppm) is consistent with the presence of chemically equivalent hydrogen-bonding interactions between each secondary amine unit of the *bmnpa* ligand and a bridging hydroxyl group. Significant upfield shifts of the neopentyl group proton resonances (δ 2.15 ($-\text{CH}_2-$), 0.71 ($-\text{CH}_3$)) suggest that the CH/π interactions identified in the solid-state structure of **1** are maintained in CD_3CN solution.

The solution behavior of **1** contrasts notably with that of the chloride derivative **3**. In CH_3CN solution, **3** behaves as a 1:1 electrolyte (Figure S1), indicating that the asymmetric Cd_2Cl_2 core undergoes cleavage in CH_3CN to yield mononuclear $[(\text{bmnpa})\text{Cd}-\text{Cl}]^+$ cations in solution. Consistent with cleavage of the binuclear structure and loss of the ligand CH/π interactions, the $-\text{CH}_2-$ and $-\text{C}(\text{CH}_3)_3$ proton resonances of the *bmnpa* neopentyl moiety are found at

Scheme 3



chemical shifts (δ 3.03 and 1.02 ppm, respectively) similar to those found for the mononuclear cadmium complex **2** (δ 3.09 and 1.00 ppm, respectively) under identical conditions.

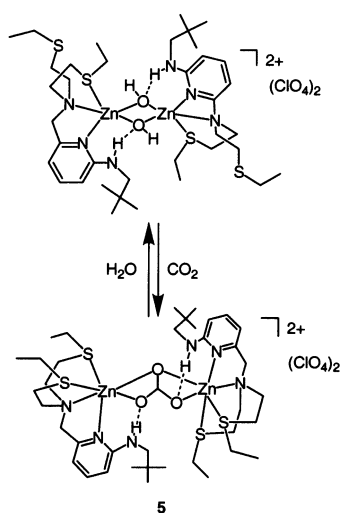
Cadmium Hydroxide vs Zinc Hydroxide Reactivity: CO_2 Hydration. Because a naturally occurring cadmium-containing carbonic anhydrase has been recently identified,⁴ we have focused our initial efforts on examining the CO_2 reactivity properties of **1** versus $[(\text{bmnpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$, a binuclear zinc hydroxide complex of the *bmnpa* ligand that we have previously reported.¹³ As shown in Scheme 3, treatment of a dry CH_3CN solution of **1** with CO_2 , followed by crystallization from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$, yielded the binuclear cadmium carbonate complex $[(\text{bmnpa})\text{Cd}_2(\mu\text{-CO}_3)](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (**4**) in quantitative yield. This carbonate derivative has been characterized by ^1H , ^{13}C , and ^{113}Cd NMR, FTIR, elemental analysis, and X-ray crystallography.

Evidence for the key involvement of the $\text{Cd}-\text{OH}$ moiety of **1** in the observed CO_2 reactivity was derived through examination of the reactivity of $(\text{bmnpa})\text{Cd}(\text{ClO}_4)_2$ (**2**) with CO_2 under varying conditions. Treatment of a CD_3CN solution of **2** containing H_2O (\sim 5 equiv), followed by addition of CO_2 , resulted in no reaction. However, addition of NEt_3 to a CD_3CN solution of **2** containing water (\sim 1 equiv) yielded a ^1H NMR spectrum consistent with the quantitative formation of **1**. Addition of CO_2 to this solution resulted in quantitative formation of the carbonate derivative **4**.

Bubbling of CO_2 through a dry CD_3CN solution of $[(\text{bmnpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ results in the formation of a single new complex **5** as indicated by ^1H NMR. Attempts to isolate this complex on a bulk scale via crystallization under a CO_2 atmosphere have yielded mixtures of **5** and the starting hydroxide complex. As discussed more fully herein, this is consistent with reactivity of the carbonate-bridged complex **5** with water to give the starting hydroxide complex (Scheme 4). Independent experiments (*vide infra*) have confirmed this reactivity pathway, which has previously been identified by Parkin to occur for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{-Zn}-\text{OH}$ in the presence of CO_2 .²²

(22) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690–4697.

Scheme 4



X-ray Crystallographic Characterization of Cadmium and Zinc Carbonate Complexes.

Crystals of **4** suitable for a single-crystal X-ray crystallographic experiment were grown from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ at ambient temperature. The cationic portion of **4** is shown in Figure 4 (top). Details regarding the data collection and refinement are given in Table 1. Selected bond distances and angles are given in Table 2. The bridging carbonate group binds in a bidentate mode to Cd(2) and in an anisobidentate fashion to Cd(1) ($\Delta d = 0.424 \text{ \AA}$, $\Delta\theta = 17.8^\circ$).²³ The bridging motif of the carbonate moiety in **4** is slightly different from that observed for the only other known binuclear cadmium carbonate complex $[\text{Cd}_2(\text{npda})_4(\mu\text{-CO}_3)(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (npda = *N'*-isopropyl-2-methylpropane-1,2-diamine), wherein three distinct Cd–O(carbonate) distances (Cd(1)–O(1) 2.172(4) Å, Cd(1)–O(2) 2.768(4) Å, and Cd(2)–O(3) 2.238(3) Å) are observed and carbonate binding is anisobidentate to Cd(1) and monodentate to Cd(2).^{2b} The Cd(1)⋯Cd(2) distance in **4** (4.99 Å) is notably shorter than the 6.05 Å Cd⋯Cd distance in $[\text{Cd}_2(\text{npda})_4(\mu\text{-CO}_3)(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

The geometric features of the Cd(2) center in **4** differ notably from those found in **1**. Specifically, Cd(2) in **4** (Figure 5b) exhibits a distorted pentagonal bipyramidal geometry²⁴ involving weak coordination of a perchlorate anion, while Cd(1) exhibits a distorted octahedral geometry. In **1** (Figure 5a), both cadmium ions possess a six-coordinate distorted octahedral geometry. The observed Cd–S distances for the pentagonal bipyramidal cadmium ion in **4** (Cd(2)–S(3) 2.7308(16) Å, Cd(2)–S(4) 2.7519(14) Å) are elongated as compared to those involving the distorted octahedral cadmium center in the same complex (Cd(1)–S(1) 2.6400(16) Å, Cd(1)–S(2) 2.6159(16) Å) but compare well with the average of those found for the two cadmium ions in the binuclear core of **1** (Cd–S_{avg} 2.76 Å; Cd(1)–S(1) 2.732(2) Å, Cd(1)–S(2) 2.7572(19) Å, Cd(2)–S(3) 2.875(3) Å, Cd–

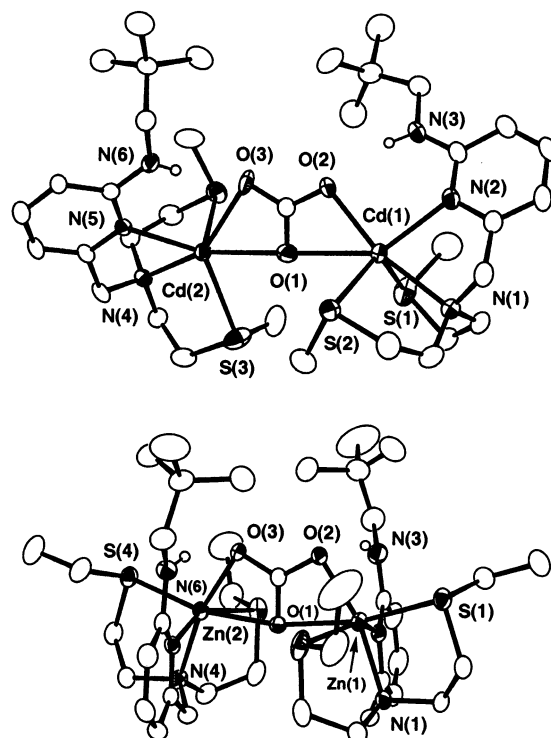


Figure 4. ORTEP representations of the cationic portions of **4** (top) and **5** (bottom). All ellipsoids are drawn at the 35% probability level. Hydrogen atoms (except the secondary amine hydrogens) are not shown for clarity. A perchlorate anion weakly coordinated to Cd(2) in **4** is not shown for clarity.

(2)–S(4) 2.720(3) Å).²⁵ Similar N_{py} ($\sim 2.44 \text{ \AA}$) and N_{am} ($\sim 2.35 \text{ \AA}$) distances are observed for each of the cadmium centers in **1** and **4**. Thus, comparison of the hydroxide and carbonate derivatives reveals that the Cd–sulfur distances are sensitive to the nature of the coordinated anion, whereas the Cd–N distances exhibit little change.

In **4**, heteroatom distances and angles indicate that two oxygen atoms (O(2) and O(3)) of the bridging CO_3^{2-} unit are involved in hydrogen-bonding interactions (N(3)⋯O(2) 2.842(6) Å, N(3)–H(3)⋯O(2) $163(5)^\circ$; N(6)⋯O(3) 2.816(6) Å, N(6)–H(6)⋯O(3) $174(5)^\circ$) with the secondary amine units (N(3)–H and N(6)–H) of the supporting bmnpa ligands. Unlike the binuclear hydroxide and chloride derivatives **1** and **3**, CH/π interactions between components of the two supporting chelate bmnpa ligands are not observed for **4**.

Despite difficulties in isolating clean bulk samples of **5**, we were successful in generating a few single crystals of this complex suitable for X-ray crystallography. As is shown in Figure 4 (bottom) and Figure 5c, the binuclear cation $[(\text{bmnpa})\text{Zn}_2(\mu\text{-CO}_3)]^{2+}$ exhibits bidentate binding of the bridging CO_3^{2-} moiety to both of the zinc centers (Zn(1)–

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(24) A seven-coordinate pentagonal bipyramidal geometry has been observed in other cadmium complexes: Turner, R. W.; Charles, N. G.; Amma, E. L. *Cryst. Struct. Commun.* **1982**, *11*, 241–245.

(25) The two thioether sulfur atoms bound to Cd(2) in the X-ray crystal structure of **1** exhibit disorder. Each was split into two fragments and refined. This refinement led to a 0.68:0.32 ratio in occupancy over two positions for each thioether sulfur atom. The Cd(2)–S(3/4) distances given in the text are for the position each sulfur atom occupies 68% of the time in the X-ray structure. The Cd(2)–S(3/4) distances for the minor occupancy S(3a)/S(4a) positions are Cd(2)–S(3a) 2.649(6) Å and Cd(2)–S(4a) 2.718(10) Å. There are also two independent binuclear cations in the asymmetric unit of **1**. The average Cd–S distances for the two cations are similar (see Table 2).

Table 1. Summary of X-ray Crystallographic Data^a

	1	2	3	4	5
empirical formula	C ₃₆ H ₆₇ Cd ₂ Cl ₂ N ₇ O ₁₀ S ₄	C ₁₇ H ₃₁ CdCl ₂ N ₃ O ₈ S ₂	C ₃₈ H ₆₈ Cd ₂ Cl ₄ N ₈ O ₈ S ₄	C ₃₇ H ₆₅ Cd ₂ Cl ₂ N ₇ O ₁₁ S ₄	C ₃₉ H ₇₀ Cl ₂ N ₆ O ₁₁ S ₄ Zn ₂
fw	1181.91	652.87	1259.84	1207.90	1128.89
cryst system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.4211(3)	15.1058(2)	24.6181(3)	9.1633(2)	11.7254(2)
<i>b</i> (Å)	44.9639(13)	9.9859(3)	24.2867(4)	15.1298(6)	34.9029(7)
<i>c</i> (Å)	20.3932(6)	18.2415(5)	19.3653(3)	18.9463(8)	13.6584(2)
α (deg)	90	90	90	99.5467(2)	90
β (deg)	101.5637(14)	109.7241(16)	102.1589(10)	93.106(2)	109.4825(11)
γ (deg)	90	90	90	93.443(2)	90
<i>V</i> (Å ³)	10260.1(5)	2590.20(11)	11318.6(3)	2580.15(16)	5269.66(16)
Z	8	4	8	2	4
<i>d</i> (calcd) (g cm ⁻³)	1.530	1.674	1.479	1.555	1.423
temp (K)	200(1)	200(1)	200(1)	200(1)	200(1)
cryst size (mm ³)	0.28 × 0.20 × 0.15	0.28 × 0.25 × 0.08	0.28 × 0.18 × 0.16	0.21 × 0.16 × 0.02	0.38 × 0.33 × 0.23
diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
abs coeff (mm ⁻¹)	1.151	1.256	1.138	1.148	1.228
2 θ max (deg)	54.88	64.96	55.70	52.34	55.04
reflcs collcd	27 431	13 195	23 200	14 352	19 387
indep reflcs	17 652	7980	13 383	9915	11 247
variable params	1192	389	602	619	632
R1/wR2 ^b	0.0568/0.1082	0.0408/0.0906	0.0536/0.1185	0.0501/0.0938	0.0502/0.0964
goodness-of-fit (<i>F</i> ²)	1.019	1.026	1.029	1.013	1.060
largest diff features (e Å ⁻³)	0.936/−0.891	1.135/−0.973	1.036/−0.795	0.780/−0.725	0.371/−0.344

^a Radiation used: Mo K α ($\lambda = 0.710 73$ Å). ^bR1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

O(1) 2.3044(19) Å, Zn(1)–O(2) 2.029(2) Å; Zn(2)–O(1) 2.2594(19) Å, Zn(2)–O(3) 2.028(2) Å). This coordination mode for the CO₃²⁻ unit has been observed only once previously in a binuclear zinc carbonate complex (((pmap)-Zn)₂(μ -CO₃)](ClO₄)₂·7H₂O (pmap = bis[2-(2-pyridyl)ethyl]-(2-pyridyl)methyl)amine)).²⁶ The metrical parameters of the Zn₂(μ -CO₃) core in **5** (Zn–O distances, Zn···Zn 4.54 Å) match well with those observed for [((pmap)Zn)₂(μ -CO₃)]-(ClO₄)₂·7H₂O (Zn–O distances: 2.079(3), 2.366(4), 2.067(4), 2.357(4) Å; Zn···Zn 4.70 Å).

Comparison of the solid-state structural features of the cadmium (**4**) and zinc (**5**) carbonate complexes of the bmnpa ligand reveals differences in the coordination geometry of the divalent metal centers, the carbonate binding mode, and the nature of hydrogen-bonding interactions involving the bridging carbonate unit. Specifically, whereas **4** exhibits an essentially anisobidentate/bidentate coordination mode of the carbonate ligand and a seven-coordinate distorted pentagonal bipyramidal geometry for one cadmium center, the zinc analogue exhibits bidentate binding of the carbonate ligand involving both of the octahedral zinc centers. The secondary amine units of the bmnpa ligands in both complexes form hydrogen-bonding interactions with the bridging carbonate ligands. In **4**, these interactions are characterized by N···O heteroatom distances and angles that are slightly shorter and more obtuse, respectively, than those present in the zinc derivative **5** (N(3)···O(2) 2.929(4) Å, N(3)–H(3)···O(2) 155(4)°; N(6)···O(3) 2.949(4) Å, N(6)–H(6)···O(3) 158(4)°). Hence, the hydrogen-bonding interactions involving the bridging carbonate moiety in **4** are slightly stronger than those present in **5**.

Solid-State and Acetonitrile Solution Properties of Binuclear Carbonate Complexes.

Examination of the solid-

state FTIR spectrum of **4** failed to reveal distinguishable C–O vibrations associated with the carbonate group.²⁷ These vibrations would be expected in the region of 1200–1650 cm⁻¹. In **4**, this region does exhibit some subtle differences as compared to the hydroxide derivative **1** but is dominated by vibrations associated with the supporting ligand. As bulk samples of **5** always contain some [((benpa)Zn)₂(μ -OH)₂](ClO₄)₂, solid-state FTIR features of the carbonate moiety in **5** also could not be conclusively assigned.

Conductance measurements (Figure S1) indicate that **4** is a 1:2 electrolyte in CH₃CN solution, suggesting retention of a binuclear cation possessing a bridging carbonate moiety and release of the perchlorate anion from Cd(2). Due to the reactivity of **5** with water, and subsequent difficulties in isolating pure bulk compound, conductance measurements on this complex were not feasible. ¹H NMR spectra of **4** and **5**, collected at ambient temperature, suggest that the supporting ligand environments for the individual metal centers in these binuclear complexes are generally similar, as only one set of sharp ligand resonances is observed for each complex. Significant deshielding of the N–H proton resonance in ¹H NMR spectra (dry CD₃CN) of **4** and **5** (>2 ppm), as compared to its position in a spectrum of the free ligand under identical conditions (dry CD₃CN, 20(1) °C), indicates retention of the secondary hydrogen-bonding interactions involving the bridging carbonate in CH₃CN solutions of both complexes. ¹³C NMR spectra of **4** and **5** in CD₃CN exhibit a resonance at ~170 ppm, consistent with the presence of a carbonate moiety.²⁸

¹¹³Cd NMR Spectral Characterization of **1**–**4**. We have also utilized ¹¹³Cd NMR to characterize the hydroxide

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(28) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496–5508 and also references therein.

Table 2. Selected Bond Distances (Å) and Angles (deg)

[(bmnpa)Cd ₂ (μ-OH) ₂](ClO ₄) ₂ ·CH ₃ CN (1) ^a							
Molecule No. 1							
Cd(1)–O(1)	2.237(5)	Cd(1)–N(2)	2.360(5)	Cd(2)–O(1)	2.188(4)	Cd(2)–N(5)	2.372(5)
Cd(1)–O(2)	2.215(4)	Cd(1)–S(1)	2.732(2)	Cd(2)–O(2)	2.258(5)	Cd(2)–S(3)	2.875(3)
Cd(1)–N(1)	2.412(5)	Cd(1)–S(2)	2.757(2)	Cd(2)–N(4)	2.391(5)	Cd(2)–S(4)	2.720(3)
O(1)–Cd(1)–O(2)	79.37(18)	N(2)–Cd(1)–S(2)	142.53(12)	O(1)–Cd(2)–O(2)	79.49(18)	N(5)–Cd(2)–S(3)	143.14(16)
O(2)–Cd(1)–N(1)	161.24(19)	S(1)–Cd(1)–O(1)	161.90(12)	O(1)–Cd(2)–S(4)	99.27(14)	S(4)–Cd(2)–O(2)	167.17(13)
N(1)–Cd(1)–S(1)	77.85(17)	N(1)–Cd(1)–O(2)	161.24(19)	S(4)–Cd(2)–N(4)	79.78(14)	N(4)–Cd(2)–O(1)	168.59(19)
S(1)–Cd(1)–O(2)	89.60(15)			N(4)–Cd(2)–O(2)	103.95(18)		
Molecule No. 2							
Cd(1')–O(1')	2.205(4)	Cd(1')–N(2')	2.347(4)	Cd(2')–O(1')	2.231(5)	Cd(2')–N(5')	2.361(5)
Cd(1')–O(2')	2.251(5)	Cd(1')–S(1')	2.802(2)	Cd(2')–O(2')	2.180(4)	Cd(2')–S(3')	2.709(2)
Cd(1')–N(1')	2.416(5)	Cd(1')–S(2')	2.720(2)	Cd(2')–N(4')	2.397(5)	Cd(2')–S(4')	2.802(2)
O(1')–Cd(1')–O(2')	78.31(17)	N(2')–Cd(1')–S(2')	151.81(13)	O(1')–Cd(2')–O(2')	79.26(17)	N(5')–Cd(2')–S(3')	99.45(15)
O(1')–Cd(1')–N(1')	166.15(18)	S(1')–Cd(1')–O(1')	90.72(13)	O(1')–Cd(2')–S(4')	82.67(12)	S(4')–Cd(2')–O(2')	114.97(12)
N(1')–Cd(1')–S(1')	76.94(14)	N(1')–Cd(1')–O(2')	114.01(17)	S(4')–Cd(2')–N(4')	78.50(15)	N(4')–Cd(2')–O(1')	107.78(19)
S(1')–Cd(1')–O(2')	169.02(11)			N(4')–Cd(2')–O(2')	165.90(19)		
(bmnpa)Cd(ClO ₄) ₂ (2)							
Cd(1)–O(1)	2.497(2)	Cd(1)–N(2)	2.283(3)	Cd(1)–N(1)	2.424(2)	Cd(1)–S(2)	2.6532(8)
Cd(1)–O(5)	2.358(2)	Cd(1)–S(1)	2.5791(7)				
O(1)–Cd(1)–O(5)	68.11(8)	N(1)–Cd(1)–S(2)	79.15(6)	N(1)–Cd(1)–N(2)	74.25(11)	N(2)–Cd(1)–S(2)	97.73(8)
N(1)–Cd(1)–O(1)	126.87(8)	O(5)–Cd(1)–S(1)	99.58(8)	S(1)–Cd(1)–S(2)	111.81(3)		
N(1)–Cd(1)–O(5)	164.85(8)	N(2)–Cd(1)–S(1)	136.39(9)				
[(bmnpa)Cd ₂ (μ-Cl) ₂](ClO ₄) ₂ ·2CH ₃ CN (3 ·2CH ₃ CN)							
Cd(1)–Cl(1)	2.7664(11)	Cd(1)–N(2)	2.336(4)	Cd(2)–Cl(1)	2.5305(12)	Cd(2)–N(5)	2.358(4)
Cd(1)–Cl(2)	2.5362(5)	Cd(1)–S(1)	2.6688(13)	Cd(2)–Cl(2)	2.7509(6)	Cd(2)–S(3)	2.6825(13)
Cd(1)–N(1)	2.392(4)	Cd(1)–S(2)	2.6909(15)	Cd(2)–N(4)	2.373(4)	Cd(2)–S(4)	2.7035(14)
Cl(1)–Cd(1)–Cl(2)	87.44(3)	N(2)–Cd(1)–S(2)	143.68(9)	Cl(2)–Cd(2)–N(4)	101.30(9)	Cl(1)–Cd(2)–N(4)	169.98(9)
Cl(1)–Cd(1)–N(1)	98.63(10)	Cl(1)–Cd(1)–S(1)	172.99(5)	N(4)–Cd(2)–S(3)	79.15(9)	Cl(2)–Cd(2)–S(3)	171.51(4)
N(1)–Cd(1)–S(1)	78.90(10)	Cl(2)–Cd(1)–N(1)	172.92(10)	S(3)–Cd(2)–Cl(1)	92.35(4)		
S(1)–Cd(1)–Cl(2)	95.49(3)	N(5)–Cd(2)–S(4)	143.73(9)				
[(bmnpa)Cd ₂ (μ-CO ₃)](ClO ₄) ₂ ·CH ₃ CN (4)							
Cd(1)–O(1)	2.616(3)	Cd(1)–N(2)	2.355(4)	Cd(2)–O(3)	2.391(4)	Cd(2)–S(3)	2.7308(16)
Cd(1)–O(2)	2.192(3)	Cd(1)–S(1)	2.6400(16)	Cd(2)–N(4)	2.458(4)	Cd(2)–S(4)	2.7519(14)
Cd(1)–N(1)	2.428(4)	Cd(1)–S(2)	2.6159(16)	C(35)–O(1)	1.271(6)	C(35)–O(2)	1.299(6)
Cd(2)–O(1)	2.379(4)	Cd(2)–N(5)	2.337(4)	C(35)–O(3)	1.260(6)		
O(1)–Cd(1)–O(2)	53.64(12)	O(1)–Cd(1)–N(1)	144.16(14)	O(1)–Cd(2)–S(3)	76.54(10)	O(1)–Cd(2)–N(5)	137.41(13)
O(1)–Cd(1)–S(1)	86.42(9)	O(1)–Cd(1)–N(2)	142.09(14)	O(1)–Cd(2)–S(4)	98.27(10)	O(3)–Cd(2)–N(4)	146.50(13)
O(1)–Cd(1)–S(2)	79.52(9)	O(2)–Cd(1)–N(1)	160.27(14)	O(3)–Cd(2)–S(3)	130.40(9)	O(3)–Cd(2)–N(5)	94.04(12)
O(2)–Cd(1)–S(1)	115.28(10)	O(2)–Cd(1)–N(2)	91.00(14)	O(3)–Cd(2)–S(4)	77.34(10)	S(3)–Cd(1)–S(4)	103.97(5)
O(2)–Cd(1)–S(2)	100.91(10)	S(1)–Cd(1)–S(2)	121.26(6)	O(1)–C(35)–O(2)	118.0(5)	O(1)–C(35)–O(3)	119.9(5)
O(1)–Cd(2)–O(3)	54.68(12)	O(1)–Cd(2)–N(4)	149.38(13)	O(2)–C(35)–O(3)	122.1(5)		
[(benpa)Zn ₂ (μ-CO ₃)](ClO ₄) ₂ (5)							
Zn(1)–O(1)	2.304(2)	Zn(1)–N(2)	2.115(2)	Zn(2)–O(3)	2.028(2)	Zn(2)–S(3)	2.594(1)
Zn(1)–O(2)	2.029(2)	Zn(1)–S(1)	2.462(1)	Zn(2)–N(4)	2.132(3)	Zn(2)–S(4)	2.463(1)
Zn(1)–N(1)	2.138(3)	Zn(1)–S(2)	2.561(1)	C(39)–O(1)	1.282(4)	C(39)–O(2)	1.289(3)
Zn(2)–O(1)	2.259(2)	Zn(2)–N(5)	2.127(2)	C(39)–O(3)	1.291(3)		
O(1)–Zn(1)–O(2)	61.20(8)	S(2)–Zn(1)–N(2)	149.84(8)	O(1)–Zn(2)–O(3)	61.97(8)	S(3)–Zn(2)–N(5)	151.22(8)
O(1)–Zn(1)–N(1)	105.16(8)	O(1)–Zn(1)–S(1)	166.29(6)	O(1)–Zn(2)–N(4)	104.51(9)	O(1)–Zn(2)–S(4)	166.13(6)
N(1)–Zn(1)–S(1)	86.76(7)	O(2)–Zn(1)–N(1)	166.18(9)	N(4)–Zn(2)–S(4)	87.19(7)	O(3)–Zn(2)–N(4)	166.31(9)
S(1)–Zn(1)–O(2)	106.52(6)	S(1)–Zn(1)–S(2)	99.74(3)	S(3)–Zn(2)–O(3)	90.28(6)	S(3)–Zn(2)–S(4)	98.47(3)

^a There are two independent binuclear cations (with corresponding ClO₄[−] anions) in the asymmetric unit of **1**. Metric parameters for both are reported.

derivative **1** and complexes **2–4** in CD₃CN solution. A single ¹¹³Cd resonance was found for **1** at 304 ppm. This resonance is upfield of that of the chloride complex **3** (361 ppm) but downfield of the resonances observed for the perchlorate (**2**: 280 ppm) and carbonate (**4**: 245 ppm) derivatives under similar experimental conditions. In general, the ¹¹³Cd NMR chemical shift range observed for this family of compounds is similar to that of nitrogen-ligated systems.²⁹ Notably, the peak width at half-height of the resonance for **1** (56 Hz) is

narrower than that observed for the other cadmium complexes (**2**, 130 Hz; **3**, 240 Hz; **4**, 160 Hz). This indicates that the cadmium centers in **2–4** may not exist in a strictly homogeneous environment in CD₃CN solution. This behavior can be rationalized on the basis of the previously described structural features and solution properties of **2–4**. For example, in CD₃CN solution, the cadmium ion in **2** may possess one or more coordinated solvent molecules and/or may form weak interactions with the perchlorate anions. For the chloride derivative **3**, which is binuclear in the solid state, but behaves as a 1:1 electrolyte in CH₃CN solution, a small degree of binuclear complex formation in solution could be

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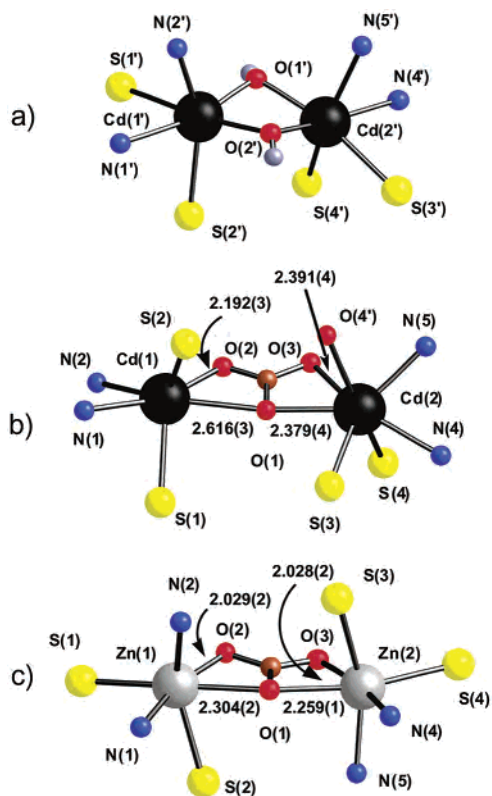


Figure 5. Coordination environments of divalent metal ions in **1** (a), **4** (b), and **5** (c).

responsible for broadening of the ^{113}Cd resonance. Finally, for the cadmium carbonate complex **4**, the anisobidentate/bidentate coordination mode of the bridging carbonate ligand yields cadmium centers that, while generally similar in supporting coordination environment in solution (as indicated by ^1H NMR), may differ in regard to CH_3CN solvation. The subtle broadening that is observed for the ^{113}Cd NMR resonance for **4** supports this hypothesis. We note that measurement of the ^{113}Cd NMR spectrum of **4** at $-35(1)^\circ\text{C}$ produced a slight upfield shift (240 ppm) and broadening ($W_{1/2} = 186$ Hz) of the observed resonance. Thus, perhaps two cadmium resonances might be observable for **4** if low enough temperatures could be utilized for ^{113}Cd NMR data collection. However, the moderate to low solubility of **4** in polar organic solvents with lower freezing points, such as CH_2Cl_2 and MeOH , makes this experiment unfeasible at this point.

Reactivity of Carbonate Complexes with Water. The reactivity properties of **4** and **5** with water were probed in a series of NMR tube experiments to gauge the hydrolytic reactivity of these complexes relative to one another and versus other known divalent metal carbonate complexes.^{23,28} Treatment of a dry CD_3CN solution of **4** with water results in no reaction after several days. However, under the same conditions, the zinc carbonate complex **5** undergoes reaction to yield $[(\text{benpa})\text{Zn}]_2(\mu\text{-OH})_2(\text{ClO}_4)_2$.

Discussion

Preparation of Cd–OH Species. Complex **1** is the first structurally characterized example of a binuclear cadmium

hydroxide complex, regardless of supporting coordination environment. The synthetic routes that may be employed for the preparation of **1** include pathways involving the introduction of hydroxide anion, as well as routes involving water. Addition of water to the mononuclear cadmium perchlorate complex **2**, in the absence of an external base, does not result in formation of **1**. This is consistent with the weak Lewis acidity of the $\text{Cd}(\text{II})$ ion which,³⁰ even upon formation of a water adduct, will not lower the $\text{p}K_a$ of water sufficiently to induce deprotonation and metal hydroxide formation. However, introduction of an internal base through deprotonation of the secondary amine moiety of the *bmnpa* ligand of **2**, followed by addition of water, results in the quantitative formation of **1**. This reactivity is reminiscent of the role a basic amino acid residue may play in deprotonating a substrate in the active site of a metalloenzyme. From a synthetic perspective, generation of a basic site within a supporting ligand has recently been elegantly employed by Borovik and co-workers for the preparation of novel mononuclear hydroxo and oxo complexes of various first-row transition metals.^{6d,e}

Cadmium Hydroxide vs Cadmium Halide Species. While examples of structurally characterized binuclear cadmium hydroxide species were unknown prior to this work, numerous binuclear cadmium chloride complexes, possessing two bridging chloride anions, have been reported.³¹ Comparison of **1** and **3** revealed differences in core structure, secondary CH/π interactions, and solution nuclearity. In regard to differences in solid-state structure, most notable is the symmetric core of **1** versus the asymmetric core found in **3**. The $\text{Cd}-\text{Cl}$ distances in **3** ($\text{Cd}(1)-\text{Cl}(1)$ 2.7664(11), $\text{Cd}(1)-\text{Cl}(2)$ 2.5362(5), $\text{Cd}(2)-\text{Cl}(1)$ 2.5305(12), $\text{Cd}(2)-\text{Cl}(2)$ 2.7509(6) Å) reveal a strong bonding interaction with only one bridging anion/cadmium. Notably, differences also exist in secondary CH/π interactions between **1** and **3**. Specifically, while the two ligand-based CH/π interactions in **1** have an average $\text{C}(\text{alkyl})\cdots\text{centroid}(\text{arene})$ distance of ~ 3.7 Å, the single CH/π interaction in **3** is shorter, with a $\text{C}(\text{alkyl})\cdots\text{centroid}(\text{arene})$ distance of ~ 3.2 Å. However, as these are weak intramolecular interactions, providing < 2 kcal/mol stabilization energy,²¹ subtle differences in secondary interactions are insufficient to explain the acetonitrile solution behavior. Hence, formation of a monomeric $[(\text{bmnpa})\text{Cd}-\text{Cl}]\text{ClO}_4$ species in acetonitrile solutions of **3** is likely a consequence of one weak $\text{Cd}-\text{Cl}$ interaction and solvation effects.

Cd–OH vs Zn–OH: CO_2 Reactivity and Carbonate Hydrolysis. The cadmium hydroxide complex **1** is reactive toward CO_2 , yielding the bridging cadmium carbonate species **4**. The anisobidentate/bidentate coordination mode of the carbonate anion in **4** is different from that observed for the zinc analogue **5**, wherein a symmetric bidentate $\text{Zn}_2(\mu\text{-CO}_3)$ core is observed. Prior studies by Kitajima²⁸ and Parkin²² have suggested that bidentate coordination of a

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(31) Holloway, C. E.; Melnik, M. *Main Group Met. Chem.* **1995**, *18*, 451–585.

carbonate moiety to a metal center results in reduced reactivity of that carbonate moiety toward hydrolysis. Therefore, the symmetric bidentate binding mode to both zinc centers in **5** suggests that this complex should be stable with respect to hydrolysis. Complex **4** might then be expected to exhibit some reactivity with water. However, as outlined herein, we have found that, for this family of complexes, exactly the opposite is true. Specifically, the cadmium carbonate derivative **4** is unreactive with water, whereas the zinc carbonate complex **5** reacts with water to produce the hydroxide complex $[(\text{benpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$. Thus, while, for the tris(pyrazolyl)borate-ligated divalent metal complexes (Zn, Co, Fe, Mn, Ni, Cu) studied by Kitajima and Parkin,^{22,28} the most important determinant for hydrolysis activity was unidentate coordination of the carbonate moiety, in the nitrogen/sulfur-ligated systems presented herein this is not the case. Differences in reactivity between **4** and **5** with water likely involve alternative issues, including the influence of thioether ligation that is typically weak for zinc centers.³² If thioether dissociation can occur in **5**, which seems feasible on the basis of the presence of a long Zn–S interaction (Zn(1)–S(2) 2.561(1) Å, Zn(2)–S(3) 2.594(1) Å) for each zinc center, perhaps coordination of a water molecule to the Lewis acidic zinc center in a site opened by thioether dissociation facilitates hydrolysis of the bridging carbonate moiety and release of CO₂. It is also possible that subtle differences in the hydrogen-bonding interactions

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involving the bridging carbonate groups in **4** and **5** may influence the reactivity of these complexes with water. To address these issues, future studies directed at examining the hydrolytic reactivity of zinc and cadmium carbonate species as a function of the primary and secondary coordination environment are underway.

Conclusions

Synthetic routes to a novel binuclear cadmium(II) hydroxide complex have been evaluated, including reaction pathways involving water. Structural comparison of binuclear cadmium hydroxide and chloride complexes revealed differences in core structure, secondary CH/ π interactions, and solution nuclearity. Comparison of the CO₂ reactivity of the binuclear cadmium(II) hydroxide complex with that of a zinc analogue revealed that while both complexes undergo reaction to yield binuclear carbonate species, only the zinc carbonate derivative is water sensitive.

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Supporting Information Available: Onsager plots of conductance data for **1–4** and $[(\text{bmnpa})\text{Zn}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$, a ¹H NMR figure for **2** in the presence of varying amounts of water, details of ¹¹³Cd NMR spectral acquisition, and X-ray crystallographic files for **1–5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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