

Copper(II) and Zinc(II) Complexes Can Fix Atmospheric Carbon Dioxide**

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In the past few decades various zinc(II) complexes with polyamine ligands have been synthesized as models of zinc(II)-containing enzymes, in particular carbonic anhydrase.^[1] From these studies, zinc(II) and zinc(II)-bound hydroxides have been demonstrated to play important roles in the hydrolysis of the substrates. However, zinc(II)-polyamine complexes that can fix carbon dioxide have not been reported until recently.^[2]

The chemical fixation and activation of carbon dioxide has drawn long-standing interest as excess CO₂ is an atmospheric pollutant and also because CO₂ could be used as an attractive C₁ feedstock for the preparation of useful carbon-containing compounds by the reaction of CO₂ with metal complexes.^[3] So far, a great deal of research has been performed on the coordination chemistry of CO₂ and its hydration products HCO₃⁻ and CO₃²⁻.^[4]

The focus of our attention is the reaction of imidazole-containing ligands with a variety of metal salts.^[5] Previous studies have shown that the nature of the organic ligand is crucial for determining the structure and properties of metal complexes.^[6] Following this approach, we prepared a new ligand L (Scheme 1) by incorporation of an imidazole group into a polyamine ligand and report herein its copper(II) and zinc(II) complexes, which contain a network formed with the aid of CO₃²⁻.

Treatment of a mixture of L and M(ClO₄)₂·6H₂O (M = Cu, Zn) with imidazole at pH 9 in air gave the complexes [M₃(L)₃(μ₃-CO₃)](ClO₄)₄·nCH₃CN (**1a**: M = Cu, n = 3; **1b**:

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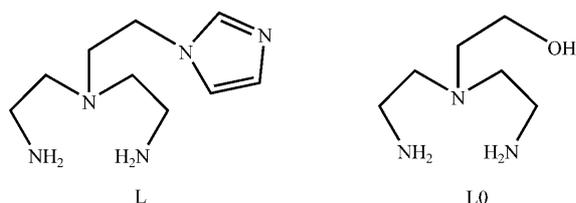
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Scheme 1. Structures of ligands L and L0.

$M = \text{Zn}$, $n = 1$) by slow evaporation. Subsequent crystallographic studies confirmed that **1a** and **1b** have the same framework structure, although they crystallize in a hexagonal unit cell with space group $P6_3$ and a trigonal unit cell with space group $P3c1$, respectively.^[7] No imidazole or imidazolate group is found in the complex; instead, a carbonate anion is present. Complex **1b** can also be obtained by treatment of L with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ at pH 9 without addition of imidazole.

As illustrated in Figure 1 a, each metal atom is coordinated by four N atoms from two different ligands L, and, in

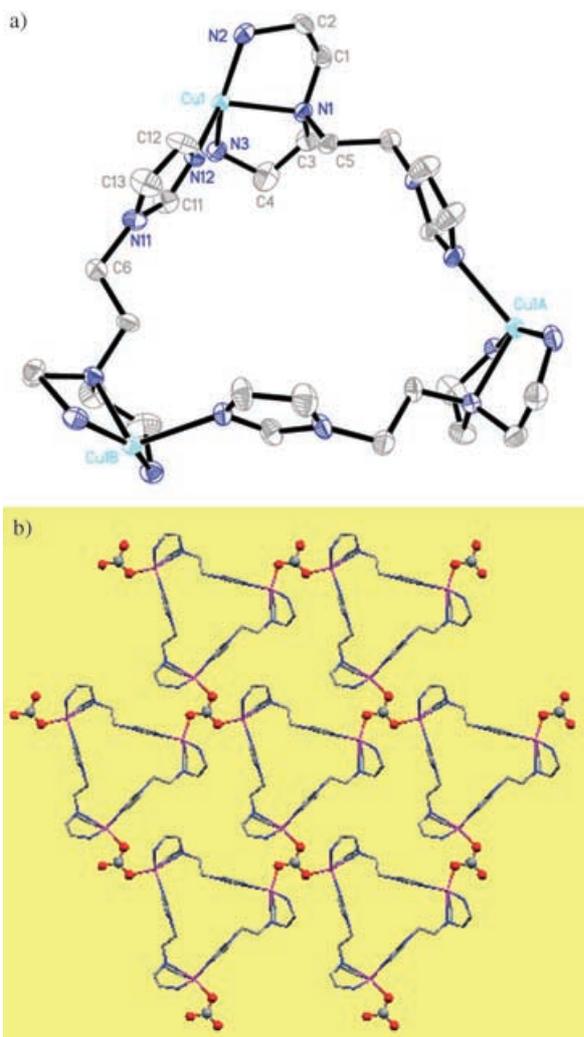


Figure 1. ORTEP drawing of a) the trigonal M_3L_3 structure of **1a**, with thermal ellipsoids at the 50% probability level, and b) the 2D network linked by carbonate anions.

turn, each ligand L links two metal centers through its N donor atoms. It is noteworthy that three metal atoms and three ligands L form a trigonal M_3L_3 21-membered ring with a metal–metal separation of 9.24 Å in **1a** and 9.15 Å in **1b**. These trigonal rings are further linked by the $\mu_3\text{-CO}_3^{2-}$ anions through their three O atoms to generate a 2D network structure (Figure 1 b). Thus, each metal center is pentacoordinated with a distorted trigonal-bipyramidal geometry. To the best of our knowledge, this is the first example of a polymeric carbonate complex with supramolecular use of a polyamine ligand containing an imidazole group, although di-, tri-, and tetranuclear zinc(II) carbonate complexes are known.^[8] The cationic layers of **1a** and **1b** are packed in an ABAB fashion along the c axis to form trigonal channels filled with acetonitrile molecules. The perchlorate anions are located between the cationic layers.

To determine the origin of the carbonate ligands in **1a** and **1b**, the same reactions of L and imidazole with metal perchlorate salts were carried out under an inert atmosphere (Ar or N_2); the zinc(II) complex $[\text{Zn}_2(\text{L})_2(\text{im})](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ (**2**; im = imidazolate anion) was successfully isolated and characterized. A single-crystal X-ray analysis^[9] revealed that complex **2** features an infinite 1D ladder structure in which the imidazolate units act as the rungs (Figure 2). Each zinc(II) center has a slightly distorted

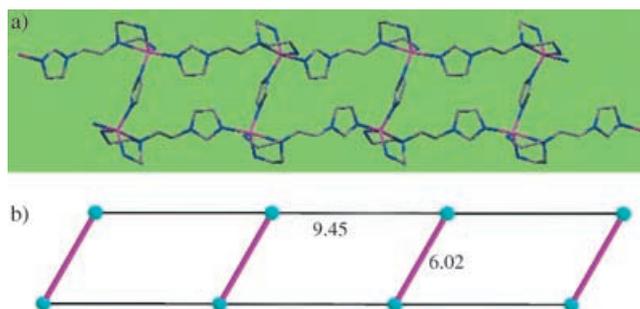


Figure 2. a) 1D ladder structure of **2**. b) The simplified ladder of **2**, where the ligands L and the imidazole units are presented by thin (black) and thick (violet) lines, respectively, and the solid balls denote zinc(II) centers.

trigonal-bipyramidal geometry which is the same as that in **1b**, except that the N atoms of the imidazolate ligands in **2** replace the O atoms of the carbonate ligands in **1b**. Similar to **1b**, each ligand L bridges two zinc(II) centers and each metal atom links two ligands L, although in this case to give an infinite 1D chain structure (Figure 2 a) rather than an M_3L_3 ring (see Figure 1 a). The imidazolate groups link zinc(II) centers from two 1D chains to form a noninterpenetrating 1D ladder structure (Figure 2 a). The Zn...Zn distances in the ladder are 6.02 Å along the rungs and 9.45 Å along the side-rails (Figure 2 b). The 1D ladders are linked together by hydrogen bonds with the perchlorate anions, and the voids between the ladders are filled with CH_3CN molecules.

The existence of the carbonate ligands in **1a** and **1b**, and the reaction of **2** with CO_2 , were further investigated by IR and NMR spectroscopy. The IR spectra of **1a**, **1b**, and **2** were measured in the solid state. Strong carbonate-related vibra-

tions are observed at 1440 cm^{-1} in **1a** and at 1457 cm^{-1} in **1b**.^[10,11] The presence of carbonate ligands in **1b** was further confirmed by the solid-state ^{13}C NMR spectrum. As shown in Figure 3, a peak at $\delta = 167.9\text{ ppm}$ is observed in the ^{13}C NMR spectrum of **1b**, which can be assigned to the coordinated

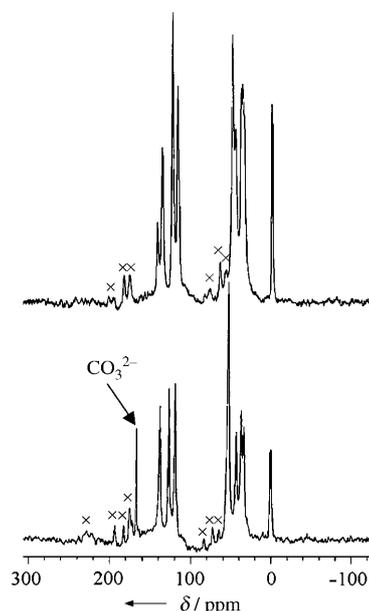


Figure 3. Solid-state ^{13}C NMR spectra of **1b** (bottom) and **2** (top). Peaks labeled with \times are spinning sidebands.

carbonate ligand. Complex **2** was found to be stable in the solid state since no IR spectral changes were observed after three weeks of exposure of powdered **2** to the air.^[11] However, in solution, the ^1H NMR spectra in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (2:1) show that **2** reacts with CO_2 quickly.^[11] The reaction product of **2** with CO_2 in solution is **1b**, as confirmed by recrystallization of **2** from an aqueous acetonitrile solution in air by slow evaporation.^[12]

These results clearly show that the carbonate anion in **1a** and **1b** comes from the hydration of atmospheric carbon dioxide, therefore the copper(II) and zinc(II) complexes of L can fix carbon dioxide. It should be noted that the introduction of the imidazole group into the ligand L plays a crucial role in fixing the CO_2 , since the polyamine ligand L0 (see Scheme 1), which contains a hydroxy group, reacts with zinc(II) perchlorate hexahydrate in air to give mono- and dinuclear zinc(II) complexes without absorption of carbon dioxide.^[13] In addition, the anion was found to strongly influence the formation of the infinite framework.^[14]

Experimental Section

Synthesis of L: The amino groups of L0 were protected by reaction of L0 with phthalic anhydride. The amine-protected L0 (35 g, 0.086 mol) was brominated by slow addition of freshly distilled PBr_3 (7.5 mL) under N_2 in the temperature range $95\text{--}100^\circ\text{C}$. The pure brominated product (10 g, 0.021 mol), well-ground K_2CO_3 (7.1 g, 0.051 mol), and imidazole (2.9 g, 0.042 mol) in dry dimethylformamide (50 mL) were

stirred for 8 h at 100°C . After cooling to room temperature, the solution was poured into saturated brine (100 mL) and extracted with ethyl acetate to give *N*-(2-imidazolylethyl)-*N*-bis(2-phthalimidomethyl)amine. Deprotection of the amino groups was carried out by treatment with hydrazine to give ligand L-4 HCl. Total yield from L0: ca. 20%, m.p. 192°C .

Synthesis of 1a: The reaction was carried out in an open vessel equipped with a magnetic stirrer at room temperature. A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (42.0 mg, 0.11 mmol) in water (2 mL) was added to an aqueous solution (2 mL) of L-4 HCl (38.9 mg, 0.11 mmol) at pH 8 (adjusted by addition of 0.5 M NaOH), and the pH value of the solution was then adjusted to 9 by further addition of 0.5 M NaOH. An aqueous solution (1.5 mL) of imidazole (7.7 mg, 0.11 mmol) was then added and the mixture stirred. The resulting colorless precipitate was dissolved by addition of acetonitrile (ca. 5 mL) to the mixture. Colorless crystals of **1a** were obtained, in about 50% yield, by slow evaporation of the filtrate over two or three days. $\text{C}_{34}\text{H}_{66}\text{N}_{18}\text{O}_{19}\text{Cl}_4\text{Cu}_3$; calcd. C 29.95, H 4.88, N 18.49; found C 29.72, H 4.84, N 18.43.

Synthesis of 1b: This compound was obtained by the same procedure as described for **1a** but with $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (42.2 mg, 0.11 mmol) instead of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Yield: ca. 60%. $\text{C}_{30}\text{H}_{60}\text{N}_{16}\text{O}_{19}\text{Cl}_4\text{Zn}_3$; calcd. C 28.00, H 4.70, N 17.42; found C 28.10, H 4.80, N 17.48.

Synthesis of 2: This complex was synthesized following the same procedure as that for **1b** except that the reaction was carried out under an argon atmosphere at room temperature. The yield was ca. 50%. $\text{C}_{21}\text{H}_{42}\text{N}_{12}\text{O}_{12.5}\text{Cl}_3\text{Zn}_2$ (noncoordinated CH_3CN was lost upon drying) calcd. C 28.03, H 4.70, N 18.68; found C 27.77, H 4.63, N 18.65.

Crystallographic analyses: Crystallographic data for complex **1a** were collected with a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.7107\text{ \AA}$). The structure was solved by direct methods with SIR92 and expanded using Fourier techniques. The collection of crystallographic data for complexes **1b** and **2** was carried out on a Rigaku Mercury or a Saturn CCD area detector at 173 and 123 K, respectively, using graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation ($\lambda = 0.7107\text{ \AA}$). The structure of **1b** was solved by Patterson methods with DIRDIF99 PATTY and that of **2** was solved by direct methods with SIR97 and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms, except those of the water molecules, were generated geometrically. CCDC-263621 (**1a**), -263622 (**1b**), and -263623 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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