Carbon Dioxide Fixation

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 CO_2 is an atmospheric pollutant and also because CO_2 could be used as an attractive C_1 feedstock for the preparation of useful carbon-containing compounds by the reaction of CO_2 with metal complexes.[3] So far, a great deal of research has been performed on the coordination chemistry of CO_2 and its hydration products HCO_3^- and CO_3^{2-}.[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 CO_3^{2-}.

Treatment of a mixture of L and $M(ClO_4)_2{\cdot}6H_2O$ ($M = Cu, Zn$) with imidazole at pH 9 in air gave the complexes $[M_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4{\cdot}n\,CH_3CN$ (**1a**: $M = Cu$, $n = 3$; **1b**:

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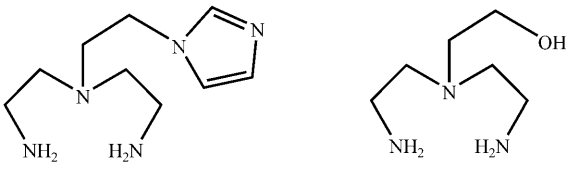
L

L0

Scheme 1. Structures of ligands L and L0.

M = 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 $Zn(ClO_4)_2{\cdot}6H_2O$ at pH 9 without addition of imidazole.

As illustrated in Figure 1a, each metal atom is coordinated by four N atoms from two different ligands L, and, in 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 μ_3-CO_3^{2-} anions through their three O atoms to generate a 2D network structure (Figure 1b). 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.

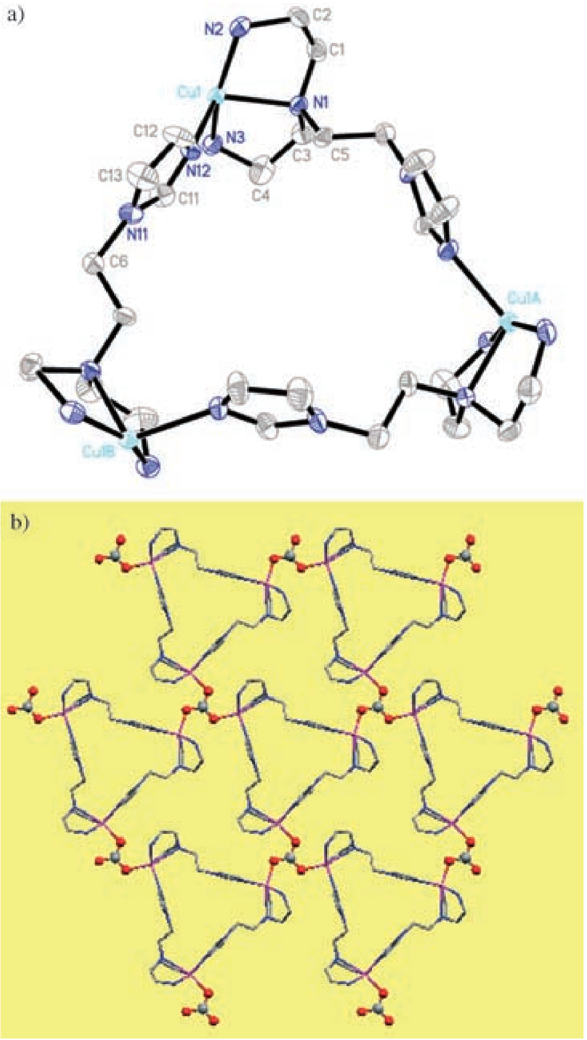

Figure 1. ORTEP drawing of a) the trigonal M_3L_3 structure of **1a**, with thermal ellipsoids at the 50% probability level, and b) the 2D network linked by carbonate anions.

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 $[Zn_2(L)_2(im)](ClO_4)_3{\cdot}2CH_3CN{\cdot}0.5H_2O$ (**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 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 2a) rather than an M_3L_3 ring (see Figure 1a). The imidazolate groups link zinc(II) centers from two 1D chains to form a noninterpenetrating 1D ladder structure (Figure 2a). The Zn···Zn distances in the ladder are 6.02 Å along the rungs and 9.45 Å along the side-rails (Figure 2b). 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.

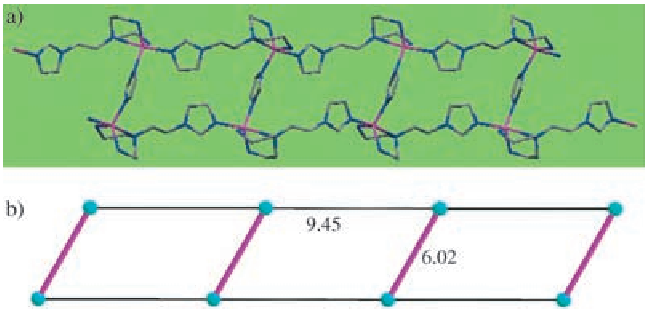

Figure 2. a) 1D ladder structure of **2**. b) The simplified ladder of **2**, where the ligands L and the imidazole units are presented by thin (black) and thick (violet) lines, respectively, and the solid balls denote zinc(II) centers.

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 vibrations 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 $\delta = 167.9$ ppm is observed in the ^{13}C NMR spectrum of **1b**, which can be assigned to the coordinated 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 CD_3CN/D_2O (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]

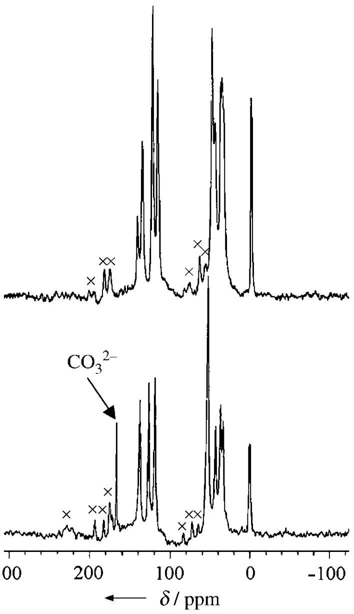

Figure 3. Solid-state ^{13}C NMR spectra of **1b** (bottom) and **2** (top). Peaks labeled with × are spinning sidebands.

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 95–100 °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-phthalimidoethyl)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 $Cu(ClO_4)_2 \cdot 6H_2O$ (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. $C_{34}H_{66}N_{18}O_{19}Cl_4Cu_3$: 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 $Zn(ClO_4)_2 \cdot 6H_2O$ (42.2 mg, 0.11 mmol) instead of $Cu(ClO_4)_2 \cdot 6H_2O$. Yield: ca. 60 %. $C_{30}H_{60}N_{16}O_{19}Cl_4Zn_3$: 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 %. $C_{21}H_{42}N_{12}O_{12.5}Cl_3Zn_2$ (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 $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). 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 $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). 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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[7] Crystal data for **1a**: $C_{34}H_{66}N_{18}O_{19}Cl_4Cu_3$, crystal size: $0.30 \times 0.30 \times 0.25$ mm^3, hexagonal, space group $P6_3$, $a = b = 13.668(9)$, $c = 17.200(15)$ Å, $V = 2782(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.627$ g cm^{-3}, $\mu = 1.413$ mm^{-1}, $T = 200$ K. 4253 Reflections and 257 parameters were used for the full-matrix, least-squares refinement on F^2. $R1 = 0.0324$ ($I > 2\sigma(I)$), $wR2 = 0.0545$ (all data). Crystal data for **1b**: $C_{30}H_{60}N_{16}O_{19}Cl_4Zn_3$, crystal size: $0.20 \times 0.20 \times 0.15$ mm^3, trigonal, $P3c1$, $a = b = 13.664(7)$, $c = 16.696(11)$ Å, $V = 2699.6(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.583$ g cm^{-3}, $\mu = 1.601$ mm^{-1}, $T = 173$ K. The final refinement on F^2 gave $R1 = 0.057$ ($I > 2\sigma(I)$), $wR2 = 0.1650$ (all data) using 3910 observed reflections.

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[9] Crystal data of **2**: $C_{25}H_{48}N_{14}O_{12.5}Cl_3Zn_2$, crystal size: $0.10 \times 0.10 \times 0.08$ mm^3, triclinic, $P\bar{1}$, $a = 10.805(5)$, $b = 11.222(5)$, $c = 18.333(6)$ Å, $\alpha = 75.22(1)$, $\beta = 72.94(1)$, $\gamma = 86.46(2)°$, $V = 2054.5(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.587$ g cm^{-3}, $\mu = 1.436$ mm^{-1}, $T = 123$ K. The final refinement on F^2 gave $R1 = 0.085$ ($I > 2\sigma(I)$), $wR2 = 0.236$ (all data) using 4238 observed reflections.

[10] a) A. Schrodt, A. Neubrand, R. van Eldik, *Inorg. Chem.* **1997**, *36*, 4579–4584; b) M. Kato, T. Ito, *Inorg. Chem.* **1985**, *24*, 504–508.

[11] See the Supporting Information for the IR and ^{1}H NMR spectra.

[12] X-ray structural analysis confirmed that the recrystallization product of **2** from aqueous acetonitrile solution is **1b**.

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[14] For example, when $M(NO_3)_2 \cdot 4H_2O$ (M = Cu, Zn) was treated with ligand L under the same conditions as for the preparation of complexes **1a** and **1b**, the IR spectra of the reaction products showed no carbonate-related vibrations, which means that no carbon dioxide has been absorbed.