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Structural characterization of ({[tren]Zn(HOMe)} · ClO_4 · BPh_4) (tren = tris(2-aminoethyl)amine) and CO_2 fixation into monomethyl carbonato zinc(II) complex

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Abstract

The reaction of both tris(2-aminoethyl)amine and tris(2-dimethylaminoethyl)amine with $Zn(ClO_4)_2$ in the presence of equimolar amount of $NaBPh_4$ in methanol afforded two different zinc(II) complexes, namely ({[tren]Zn(HOMe)} · ClO_4 · BPh_4) **1** and ({[trenMe$_6$]Zn} · ClO_4 · BPh_4) **2**. Zinc(II) Complex **1**, which has been structurally characterized by X-ray crystallography, takes up CO_2 in methanol in the presence of base to fix it into monomethyl carbonato complex ({[tren]Zn(OCO_2Me)} · BPh_4 · 2MeOH) **3**.

Keywords: Zinc(II) complexes; X-ray crystal structure; CO_2 fixation

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1. Introduction

The reaction chemistry of CO_2 with transition metal complexes is particularly interesting since CO_2 is a combustion product and environmental pollutant, yet it is also a potentially useful carbon source [1]. Thus, the development of an effective chemical method for the fixation and activation of CO_2 for its conversion to various carbonate, formic acid, and other stock chemicals has been receiving a long-standing interest [2].

Besides direct coordination of CO_2 to transition metals with its intact form [3], many insertion reactions of CO_2 into an M–O bond have been reported for metal alkoxide complexes [4]. Chisholm et al. [5] proposed an alcohol catalyzed chain mechanism for apparent CO_2 insertion into a Mo–O bond of $Mo_2(OR)_6$ in solution Eq. (1). These reactions are in principle simple solvolysis and hydrolysis processes and involve no redox chemistry

$$\begin{aligned} &\mathrm{ROH} + \mathrm{CO_2} \rightarrow \mathrm{ROCOOH} \\ &\mathrm{M{-}OR} + \mathrm{ROCOOH} \rightarrow \mathrm{M{-}O_2COR} + \mathrm{ROH} \end{aligned} \tag{1}$$

As one of the approaches, various types of successful zinc model complexes have been used to fix CO_2 in alcoholic medium as monoalkyl carbonate [6].

Tris(2-aminoethyl)amine, tren and tris(2-dimethylaminoethyl)amine, trenMe$_6$ are well known and widely studied tripodal amines containing four coordination sites [7]. They bind Zn(II) ion in aqueous and methanolic solutions. The species present in solution for both systems tren/Zn(II) and trenMe$_6$/Zn(II) and the corresponding stability constants were previously reported [8]. In both systems, monohydroxo species are present at alkaline pH.

Recently [9], we have reported the simulation and hydration of CO_2 as hydrogen carbonate using zinc enzyme model complexes. Here we report structural characterization of ({[tren]Zn(HOMe)} · ClO_4 · BPh_4) and CO_2 fixation into monomethyl carbonato zinc(II) complex using zinc(II) complexes derived from the tripodal ligands tren and trenMe$_6$.

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2. Experimental

2.1. Materials

All reagents and solvent used were of analytical grade. tren was taken from Tokyo Kasei Organic Chemical Company. TrenMe$_6 \cdot 3HClO_4$, has been synthesized by a modification of Ciampolint, synthesis [7]. ^{1}H and ^{13}C NMR spectra were measured by a JEOL EX-400 spectrometer. IR measurements were measured using JASCO FT-IR 300E spectrophotometer.

2.2. Syntheses

2.2.1. Synthesis of ({[*tren*]*Zn*(*HOMe*)} · $ClO_4 \cdot BPh_4$) **1**

Zinc(II) complex **1** was synthesized by the reaction of tren (0.37 ml, 2.48 mmol) with equimolar amounts of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.93 gm, 2.5 mmol) and $NaBPh_4$ (0.85 gm, 2.5 mmol) in methanol. The mixed solution was stirred for 3 h and white precipitate was obtained by adding diethyl ether. Single crystals suitable for X-ray crystallography were obtained by the slow evaporation of diethy lether into acetonitrile solution of the complex. Yield: 1.36 g (82.9%). Found: C, 55.84%; H, 6.41%; N, 8.51%; Cl, 5.23%. Anal. Calc. for $C_{31}H_{42}N_4O_5BClZn$ ({[tren]Zn(HOMe)} · $ClO_4 \cdot BPh_4$): C, 56.21%; H, 6.39%; N, 8.46%; Cl, 5.35%. ^{1}H NMR (DMSO-d$_6$): 7.15–6.77 (m, 20H, –C_6H_5), 3.61 (s, 6H, –NH_2), 2.79 (t, 6H, –$C^{\alpha}H_2$), 2.76 (t, 6H, –$C^{\alpha}H_2$–), and 1.99 ppm (s, 3H, –CH_3). IR (KBr, cm^{-1}): (ClO_4^-), 1060 and 628 cm^{-1}.

2.2.2. Synthesis of ({[*trenMe*$_6$]*Zn*} · $ClO_4 \cdot BPh_4$) **2**

Zinc(II) complex **2** was synthesized in a fashion similar to complex **1**. Yield: 1.49 g (80.3%). Found: C, 60.61%; H, 6.94%; N, 7.95%; Cl, 4.85%. Anal. calcd. For $C_{36}H_{50}N_4O_4BClZn$ ({[trenMe$_6$]Zn} · $ClO_4 \cdot$ BPh$_4$): C, 59.15%; H, 6.89%; N, 7.67%; Cl, 4.85%. ^{1}H NMR (DMSO-d$_6$): 7.26–6.93 (m, 20H, –C_6H_5), 2.89 (t, 6H, $C^{\alpha}H_2$–), 2.73 (t, 6H, $C^{\beta}H_2$–), and 2.84 ppm (s, 18H, –CH_3). IR (KBr, cm^{-1}): (ClO_4^-), 1100 and 626 cm^{-1}.

2.2.3. Synthesis of ({[*tren*]*Zn*(*OCO*$_2$*Me*)} · $BPh_4 \cdot$ 2*MeOH*) **3**

Bubbling of CO_2 into a methanolic solution (10 ml) of zinc(II) complex **1** (0.166 gm, 25 mM) in the presence of equimolar amount of MeONa (57 μl (25 mM), 25 wt%) for 4 h at room temperature. The resultant solution was evaporated to dryness under vacuum, and the white solid thus obtained was characterized as monomethyl carbonato complex. Yield: 0.169 g (94.9%). Found: C, 64.86%; H, 6.67%; N, 7.54%. Anal. Calc. for $C_{40}H_{49}N_4O_3BZn$ ({[tren]Zn(OCO$_2$Me)} · BPh$_4 \cdot$ 2MeOH): C, 64.74%; H, 6.65%; N, 7.55%. ^{1}H NMR (DMSO-d$_6$): 7.19–6.75 (m, 20H, –C_6H_5), 3.65 (s, 6H, –NH_2), 2.84 (t, 6H, –$C^{\alpha}H_2$), 2.76 (t, 6H, –$C^{\beta}H_2$–), and 2.00 ppm (s, 3H, –CH_3). ^{13}C NMR (DMSO-d$_6$): 164.52 (–OCO_2–), 136.02–121.67 (phenyl C), 52.11–48.93 (–CH_2–CH_2–), and 37.04 ppm (–CH_3). IR (KBr, cm^{-1}): (–OCO_2), 1620 and 1307 cm^{-1}.

2.3. X-ray crystallography

The structure of zinc(II) complex **1** was studied by X-ray crystallography. The diffraction data were collected using a Rigaku RAXIS-IV Imaging Plate Diffractometer using graphite monochromated Mo-K$_{\alpha}$ radiation ($\lambda = 0.7107$ Å). Crystal data: $C_{31}H_{42}N_4O_5BClZn$, $M_r =$ 662.34, monoclinic, space group Pn(#7), $a = 10.013(1)$ Å, $b = 10.304(1)$ Å, $c = 15.394(2)$ Å, $\beta = 90.36(1)°$, $V = 1588.3(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.385$ g cm^{-3}, $F_{000} =$ 696, $\mu = 9.03$ cm^{-1}. The structure was solved by direct methods [10] and expanded using Fourier techniques [11]. The non-hydrogen atoms were refined anisotropically. Hydrogens were included but not refined. The final cycle of full-matrix least-squares refinements [12] was based on 3146 observed reflections ($I > 0.00\sigma(I)$) and 389 variable parameters gave $R = \sum \| F_o | - | F_c \| / \sum | F_o | 0.043$ and $R_w = [\sum \omega(|F_o| - |F_o|)^2 / \sum \omega(F_o^2)^2]^{1/2} =$ 0.059, and GOD on $F = 1.22$. the maximum and minimum peaks on the final difference Fourier map corresponded to 0.96 and −0.59 e$^-$/Å^3, respectively.

2.4. Reactions of both **1** and **2** with CO_2

0.166 gm of **1** and 0.178 gm of **2** were placed in two test tubes under N_2 and dissolved in 10 ml of methanol in the presence of equimolar amount of MeONa (57 μl (25 mM), 25 wt%). The atmosphere was replaced with CO_2 and the solutions were set at room temperature for 4 h. After that the resultant solutions were evaporated to dryness under vacuum, and the white solids thus obtained were characterized by IR and NMR spectroscopies. Zinc(II) complex **1** showed almost quantitative formation of the monomethyl carbonato complex **3** whereas zinc(II) complex **2** showed no change and gave only the starting material. In view of this facile interconversion, attempts to isolate complex **3** as single crystals for X-ray measurements were unsuccessful. The reversibility of this reaction has been confirmed and removal of CO_2 atmosphere by warming the solution to 40 °C results in rapid generation of the methanol zinc(II) complex **1**. In another technique: dissolving both **1** and **2** (50 mM) in DMSO-d$_6$ in the presence of eqimolar amount of MeONa (114 μl (50 mM), 25 wt%). CO_2 was bubbled for 4 h in to these solutions. Reaction of **1** with CO_2 was monitored from the product of the monomethyl carbonato zinc(II) complex using ^{13}C NMR spectroscopy.

3. Results and discussion

3.1. Description of the molecular structure of ({[tren]-Zn(HOMe)} · ClO_4 · BPh_4) **1**

Treatment of tren ligand with equimolar amounts of $Zn(ClO_4)_2 \cdot 6H_2O$ and $NaBPh_4$ in methanol followed by crystallization via diethyl ether into acetonitrile solution at an ambient temperature yielded ({[tren]Zn(HOMe)} · ClO_4 · BPh_4) **1** as colorless crystalline blocks [13].

Fig. 1 shows an ORTEP drawing of the molecular structure of **1**. The essential part of **1** consists of zinc(II) ion, four nitrogen atoms from the coordinated tren, and one methanol molecule, which is hydrogen-bonded to the oxygen atoms of the perchlorate anion. A view of the structure down the Zn(1)–O(1) bond reveals the nearly threefold symmetry of the coordinated tren molecule neatly coiled around the zinc atom. The zinc atom adopts the slightly distorted trigonal-bipyramidal coordination geometry with N(1), N(2), and N(3) on the basal plane where N(4) and the oxygen atom of coordinated methanol are at the apex.

The axial Zn(1)–N(4) interactions with bond distance of 2.16(1) Å is significantly longer than the equatorial Zn–N distances, which are in the range of 2.05(1)–2.07(3) Å. Similar values have been found in ({[tren] Zn(NCS)} · NCS) [14] and ({[tren]Zn(H_2O)} · $(ClO_4)_2$) [15]: 2.058(5) and 2.051(5), respectively, for the equatorial Zn–N distances and 2.292(4) and 2.193(4), respectively, for the apical Zn–N distances. The equatorial N–Zn–N bond angles are all with an average of 118.5(3)°. The interchelate N–Zn–N(4) bond angles, all three of which are equal to the value of 83.03(6)°, are similar to the value of 83.07(2)° [14] and differ from the value of 80.9° [15].

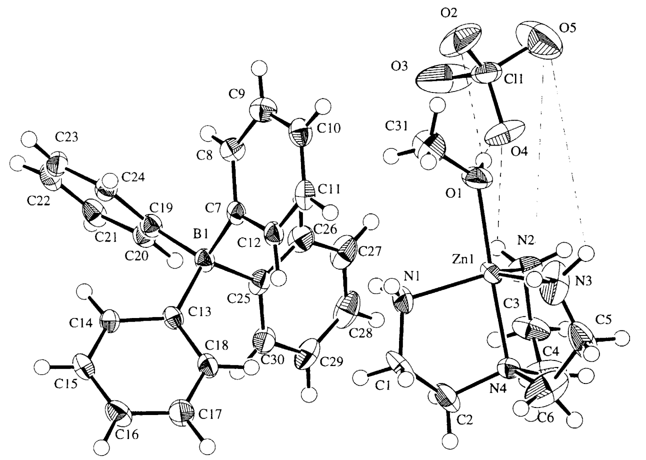


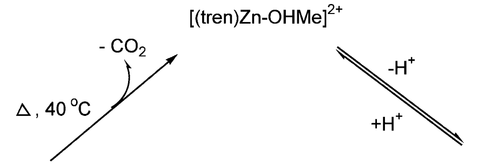
Fig. 1. ORTEP drawing of molecular structure of ({[tren]-Zn(HOMe)} · $ClO_4 \cdot BPh_4$) **1**. Ellipsoids are depicted at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Zn(1)–O(1) 2.11(1), Zn(1)–N(1) 2.05(2), Zn(1)–N(2) 2.07(1), Zn(1)–N(3) 2.05(1), Zn(1)–N(4) 2.16(1); O(1)–Zn(1)–N(1) 98.0(7), O(1)–Zn(1)–N(2) 92.4(6), O(1)–Zn(1)–N(3) 100.5(4), O(1)–Zn(1)–N(4) 175.0(7), N(1)–Zn(1)–N(2) 122.1(4), N(1)–Zn(1)–N(3) 115.9(7), N(1)–Zn(1)–N(4) 84.7(6), N(2)–Zn(1)–N(3) 117.6(7), N(2)–Zn(1)–N(4) 82.6(5), N(3)–Zn(1)–N(4) 81.8(6).

The methanol molecule acts as a monodentate ligand occupying the fifth site of the coordination sphere around the zinc atom in *trans*-position with respect to the four bridgehead nitrogen atoms. Due to the pentacoordinate nature of the zinc atom, the Zn(1)–O(1) distance in this complex (2.22(1) Å) is longer than that found in a recently reported S_3-ligated tetrahedral zinc(II) complex possessing a single methanol ligand ({$[Tm^{MeS}]$Zn(HOMe)} · ClO_4 · MeOH): 1.993(3) Å [16] and close to that found in the pentacoordinated trigonal-bipyramidal ({[bmapa]Zn(HOMe)} · $(ClO_4)_2$ · MeO H):2.077(1) Å [17].

Zinc(II) complex **1** exhibits comparable hydrogen-bonding interactions in the solid state between the hydroxyl proton of the coordinated methanol, the primary amine protons, and the oxygen atoms of the perchlorate anion: O(1)···O(2) 3.56(2), O(1)···O(4) 2.74(2), O(4)···N(2) 3.05(2), and O(5)···N(3) 3.36(2) Å. This short hydrogen-bonding interactions involving the zinc(II)-bound methanol were also found with other related zinc(II) complexes [16,17].

3.2. Fixation of CO_2 by using zinc(II) complexes **1** and **2**

Zinc(II) complex **1** takes up CO_2 in methanol at room temperature to fix it into monomethyl carbonato complex: ({[tren]Zn(OCO_2Me)} · BPh_4 · 2MeOH) **3**. Reaction routes are given in Scheme 1. Zinc(II) complex **3** is obtained by bubbling CO_2 through methanolic solution containing equimolar amounts of Zinc(II) complex **1** in the presence of an equimolar amount of MeONa as a base. When CO_2 is bubbled in the absence of base, the reaction gives only the methanol complex **1**. The resulting zinc(II) complex **1** also reacts with CO_2 in DMSO-d_6 to give the desired zinc(II) complex **3**, which has been revealed by NMR spectroscopies. ^1H and ^{13}C NMR spectra (Fig. 2) indicated the evidence of CO_2 fixation. The signal at 164.5 ppm has been attributed to the formation of methyl carbonato complex. It also showed two IR strong bands (ν_{CO}) that appeared around 1620 and 1307 cm^{-1}, which are characteristic of



Scheme 1.

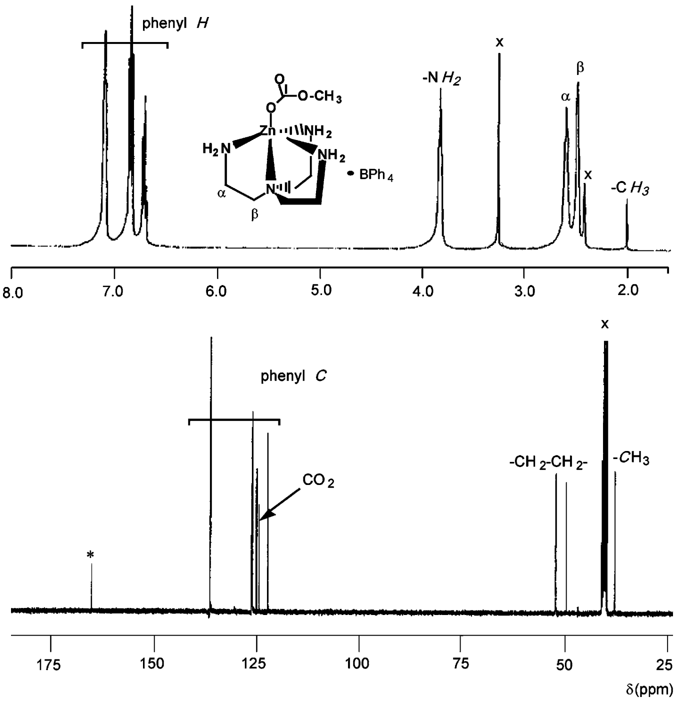


Fig. 2. ^{1}H and ^{13}C NMR spectra of zinc(II) complex **1** after bubbling CO_2 for 4 h. The peak with * was assigned to zinc(II)-bound methyl carbonate and X points out the solvent peaks.

–OCO_2– group, as was found in monomethyl carbonato complexes of zinc and other metals [4,6].

As shown in Scheme 1, the reaction of **1** with CO_2 is reversible. When methanolic solution of the resulting methyl carbonato complex is warmed to ca. 40 °C, the starting methanol complex **1** was recovered, which has been characterized by X-ray crystallography.

Efficiency of CO_2 uptake depends strongly on the type of ligand used. When CO_2 is bubbled for 3 h into a similar solution containing zinc(II) complex **2** in the presence and absence of base, the starting material is recovered. The inactivity of that complex towards the fixation of CO_2 was in accordance with Canary hypothesis [8b]: zinc ions require the ability to accommodate expanded coordination numbers in hydrolytic catalytic cycle. Since zinc(II) complexes of tren can form six coordinate complexes but those of trenMe$_6$ cannot. In five coordinate complexes, both ligands adopt a C_3-symmetric conformation [18] (see Fig. 1). However, in six coordinate complexes, tren adopts a C_δ conformation [8b] that is sterically inaccessible to trenMe$_6$ due to the steric hindrance caused by the bulky Me_2N substituents.

The formation of zinc(II)-bound methoxy species in solution seems to play a fundamental role in the process of fixation of CO_2. Most likely, the metal-bound methoxy ion combines with CO_2 to produce the carbonate complex. Previously, Ito et al. [6b,6c] have found that the hydroxo complex of macrocyclic ligands combines reversibly with CO_2 in methanolic solution giving a methyl carbonato adduct.

Supplementary materials

Atomic parameters and complete lists of bond lengths and angles will be deposited at the Cambridge Crystallographic Data Centre, CCDC. Please contact the corresponding author for further details.

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