

## Research paper

## 2,6-Diaminopurine-zinc complex for primordial carbon dioxide fixation

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## ARTICLE INFO

Dedicated to Prof R N Mukherjee on the occasion of his 65th birthday.

## ABSTRACT

Primordial carbon dioxide fixation to yield value-added anionic products necessitates transition metal catalysis, supported on mineral surfaces. In this context, purines and their metabolites have been implicated as crucial ligands for metal ion coordination and catalysis for primitive chemical reactions. Herein, we report the ability of 2,6-diaminopurine for primordial activation of atmospheric carbon dioxide as confirmed by crystallographic analysis of three model ligands and their complexes. Interestingly, the carbonate-containing complex undergoes autonomous self-organization to afford hollow spherical enclosures, without any external modifier.

## 1. Introduction

The use of carbon dioxide and carbon monoxide as carbon sources for organic biomass synthesis is essential for life and biological evolution [1]. It is believed these gases were present as a part of earth's first atmosphere and their concentration fluctuated over > ~4.5 billion year history of this planet. Interestingly, a chemoautotrophic origin of life hypothesis entails the use of carbon dioxide and carbon monoxide as carbon and energy sources, which are available through hydrothermal vents and volcanic exhalations [2–4]. For example, photoautotroph organisms synthesized their food directly from CO<sub>2</sub> and water using photosynthetic reactions. Thus, bioinspired CO<sub>2</sub>-fixation alternatives could offer novel pathways for converting feedstock of atmospheric CO<sub>2</sub> to address future food and energy requirements [5] (Scheme 1).

In some of the living systems, the transformation of CO<sub>2</sub> to carbonic acid or bicarbonate is catalyzed by carbonic anhydrase or carbonate dehydratase. This transformation would be extremely slow in the absence of this enzyme and it would be difficult to carry out normal life processes [6]. Enzyme active site contains (His)<sub>3</sub>Zn-OH<sub>2</sub>, where three histidine imidazole rings bind zinc metal ions [7,8]. Zinc-containing carbonic anhydrase stimulates carbon dioxide fixation and its further conversion to carbonate regulates biological pH, CO<sub>2</sub> transport in tissues and storage of biosynthetic carbon [9,10]. Consequently, numerous model compounds with Zn(II) ions have been investigated to mimic enzyme active site, where favorable activity could be ascribed to zinc coordination, its Lewis acidity and the lack of redox chemistry [11–17].

Interestingly, side chain imidazole in histidine is also present as a part of purine substructure and is responsible of metal ion coordination (N7 nitrogen) and connection to sugar residues. We have designed three purine ligands adenine acetic acid L1 [18], 2,6-diaminopurine acetic acid L2 [19] and 6-thiol-2-aminopurine acetic acid L3. Out of these three ligands, L2 is able to fix atmospheric CO<sub>2</sub> to carbonate in presence of zinc ions and gave carbonate zinc complex. Recent studies have outlined possible conversions involved in prebiotic synthesis of purine-like precursors from simple building blocks, such as HCN [20–22].

In addition, theories of nucleic acid templates pre-dating protein world are also proposed and many carefully designed experiments lend credence to these theories [23,24]. An intriguing proposition of “Zn world” projects possible/bio-geochemical conditions, where porous ZnS formations, arising from hydrothermal origin, were shown to catalyze photosynthesis on primordial earth [25]. It is proposed that evanescent storage and use of sunlight for the synthesis of useful biomass, catalyzed by ZnS, would have taken place as long as atmospheric CO<sub>2</sub> pressure remained above ~ 10 bar. In fact, photoreduction of carbon dioxide on colloidal ZnS, in the presence of tetramethylammonium chloride, to yield tartaric acid, oxalic acid, formaldehyde and glyoxylic acid has been described [26].

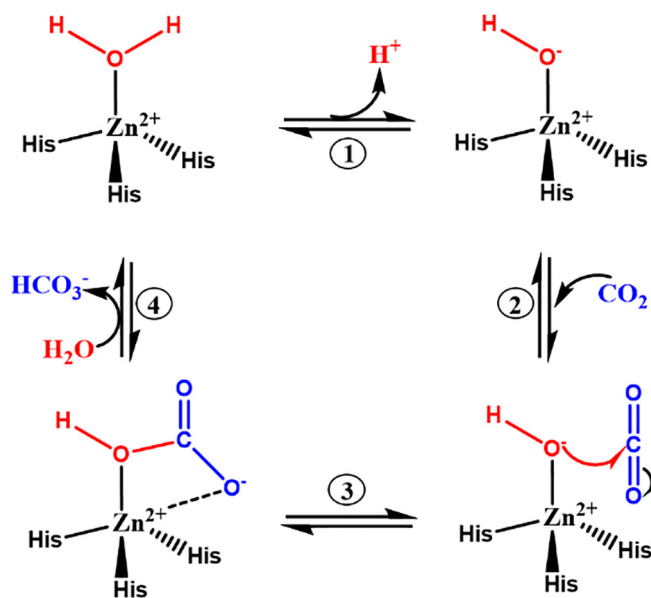
## 2. Experimental section

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained either on JEOL-DELTA2 500 model spectrometer operating at 500 MHz or JEOL JNM-ECS 400 operating at 400 MHz. The spectra were recorded in DMSO-*d*<sub>6</sub> solution, and the chemical shifts were referenced with respect to

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**Scheme 1.** Proposed reaction mechanism of  $\text{CO}_2$  hydration by carbonic anhydrase.

tetramethylsilane. High resolution (ESI<sup>+</sup> mode) mass spectra were obtained on Waters, Q-ToF Premier Micro mass HAB 213 mass spectrometer, Department of Chemistry, IIT Kanpur, India. All the solvents were purified by adopting standard procedures. Methyl bromoacetate, 6-chloroguanine, adenine, thiourea were purchased from (S. R. L). **L1**, **L2** and **L3** were synthesized. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating from 400 to

4000  $\text{cm}^{-1}$ . Elemental analysis is carried out using a thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. Atomic force microscopy (AFM) was carried out in air and ambient temperature using an Agilent Technologies AFM (5500 AFM/SPM) operating in non-contact mode. Field emission scanning electron microscopy (FESEM) images for all complexes were acquired on a FEI QUANTA 200 microscope, equipped with a tungsten filament gun operating at WD 10 mm and 20 kV. Energy dispersive X-ray (EDX) analysis was carried out with INCA-7426 Oxford instruments, operating at 20 kV and 50 sec acquisition time was used for the determination of zinc ion present in the spherical assembly.

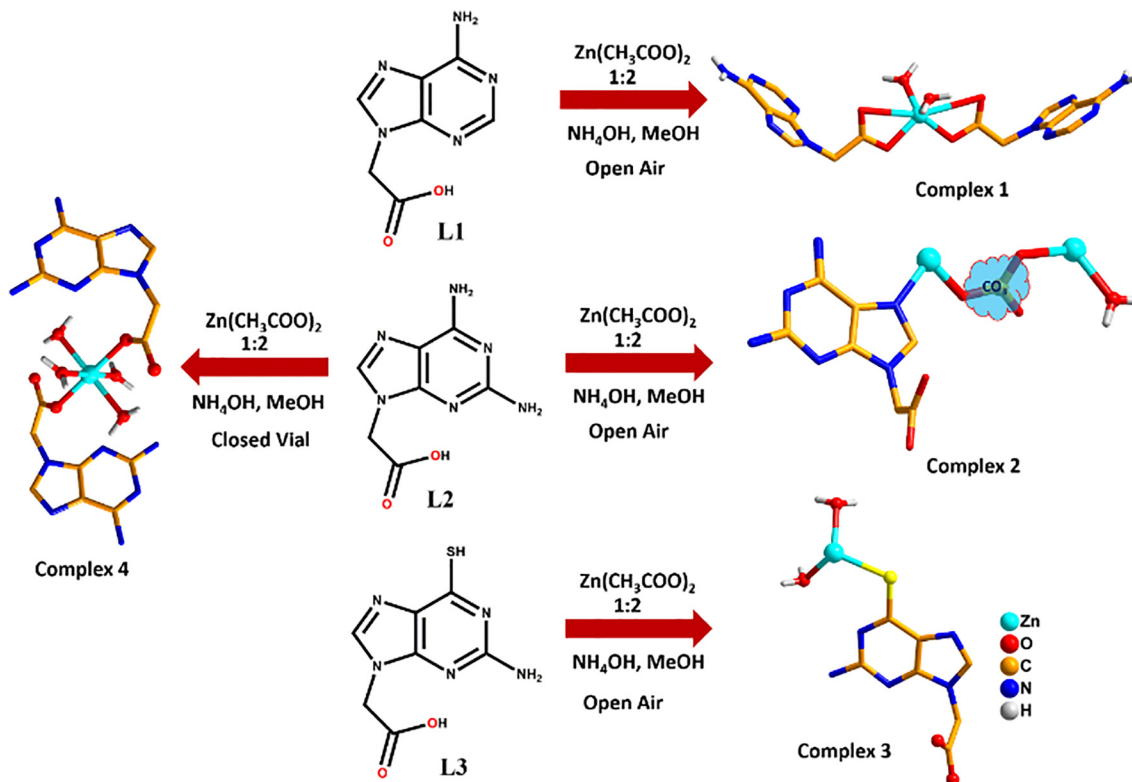
## 2.1. Synthesis of complex 1–4

### 2.1.1. Complex 1

Ligand **L1** (0.10 g, 0.52 mmol) and zinc acetate (0.096 g, 0.52 mmol) were stirred in the presence of aqueous ammonium hydroxide (1 mL) in methanol at room temperature for 4 hrs. The reaction mixture pH value 9 was maintained. The resulting solution was filtered and kept for crystallization. Slow evaporation of the solution afforded the corresponding crystalline product in 3–4 days. (Yield: 51%). CHN Analysis ( $\text{C}_{14}\text{H}_{22}\text{N}_{10}\text{O}_9\text{Zn}$ ): calculated C, 31.15; H, 4.11; N, 25.95; found C, 30.95; H, 4.01; N, 26.15.  $^{13}\text{C}$  NMR: (500 MHz,  $\text{DMSO}-d_6$ , 25 °C, TMS);  $\delta$  (ppm) 46.49, 118.57, 142.70, 150.08, 152.75, 156.13, 172.65. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3522, 3277, 2971, 2693, 1692, 1609, 1425, 1295, 1079, 977, 792, 656, 620. HRMS:  $[\text{L1}+\text{H}]^+$ : 194.0674 (Calc.: 194.0678),  $[\text{L1}+\text{H}+\text{Zn}]^+$ : 257.9989, (Calc.: 257.9969),  $[\text{2L1-H}+\text{Zn}]^+$ : 449.0401, (Calc.: 449.0413).

### 2.1.2. Complex 2

Ligand **L2** (0.10 g, 0.48 mmol) and zinc acetate (0.176 g, 0.96 mmol) were stirred in the presence of aqueous ammonium



**Fig. 1.** Synthetic scheme of complexes 1–4.

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