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Research paper

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

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ABSTRACT

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

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 CO₂ and water using photosynthetic reactions. Thus, bioinspired CO₂-fixation alternatives could offer novel pathways for converting feedstock of atmospheric CO₂ to address future food and energy requirements [5] (Scheme 1).

In some of the living systems, the transformation of CO_2 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)₃Zn-OH₂, 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, CO₂ 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 CO₂ 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_2 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

 1 H and 13 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_{6} solution, and the chemical shifts were referenced with respect to

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Scheme 1. Proposed reaction mechanism of CO_2 hydration by carbonic anhydrase.

tetramethylsilane. High resolution (ESI⁺ 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 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 ($C_{14}H_{22}N_{10}O_9Zn$): calculated C, 31.15; H, 4.11; N, 25.95; found C, 30.95; H, 4.01; N, 26.15. ¹³C NMR: (500 MHz, DMSO- d_6 , 25 °C, TMS); δ (ppm) 46.49, 118.57, 142.70, 150.08, 152.75, 156.13, 172.65. IR (KBr, ν/cm^{-1}): 3522, 3277, 2971, 2693, 1692, 1609, 1425, 1295, 1079, 977, 792, 656, 620. HRMS: [L1+H]⁺ : 194.0674 (Calc.: 194.0678), [L1+H+Zn]⁺: 257.9989, (Calc.: 257.9969), [2L1-H +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.



Fig. 2. Secondary interaction of complex 1 (carboxylic groups are deleted for clearness). The inset shows a purine-purine trimer formed by N6-H—N1 and N6-H—N7 interactions (Distances shown are in Å).



Fig. 3. (a) Crystal lattice of complex 2 showing (H-atoms are deleted for clearness); (b) Carbonate anion creating μ_3 -bridge between three Zn-atoms; (c) Distance between carbonate of Oxo anions and Zn atoms are shown in Å.

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 7 days. (Yield: 84%). CHN Analysis ($C_{18}H_{26}N_{12}O_{16}Zn_3$): calculated C, 25.06; H, 3.04; N, 19.48; found C, 24.86; H, 2.95; N, 19.75. ¹³C NMR: (500 MHz, Solid, 25 °C); δ (ppm) 45.89, 109.46, 139.05, 149.70, 154.04, 159.21, 167.62, 172.36. IR (KBr, ν/cm^{-1}): 3477, 3438, 3352, 3225, 1646, 1617, 1479, 1291, 1220, 1183, 1080, 986, 970, 849, 711, 604. HRMS: [L2+H]⁺:

209.0782 (Calc.: 209.0787), $[2L2-H+Zn]^+$: 479.0628, (Calc.: 479.0631), HRMS: $[3L2-H+Zn]^+$: 687.1329 (Calc.: 687.1339). HRMS: $[2L2-H+2Zn+CO_3]^+$: 602.9944 (Calc.: 602.9770).

2.1.3. Complex 3

Ligand L3 (0.10 g, 0.44 mmol) and zinc acetate (0.162 g, 0.88 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



Fig. 4. ¹³C spectra of ligands (L1-L3) shown as (a), (c) and (e) respectively, and complexes 1 and 3 shown as (b) and (f) respectively, while (d) is solid state C¹³ NMR of complex 2; (g) µ₃-Carbonate binding is shown in the figure.

and kept for crystallization. Slow evaporation of the solution afforded the corresponding crystalline product within two days. Yield: (80%). CHN Analysis ($C_7H_{11}N_5O_5SZn$): calculated C, 24.54; H, 3.24; N, 20.44; found C, 24.39; H, 3.08; N, 20.62. ¹³C NMR: (500 MHz, DMSO- d_6 , 25 °C, TMS); δ (ppm) 46.85, 126.26, 140.72, 148.46, 159.88, 171.49, 173.21. IR (KBr, ν/cm^{-1}): 3612, 3324, 3112, 2924, 1592, 1558, 1514, 1462, 1377, 1265, 967, 940, 793, 694 HRMS: $[L3 + Zn/2]^+$: 256.9634 (Calc.: 256.9965).

2.1.4. Complex 4

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 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 in closed vial and obtained corresponding crystalline product in 20 days. (Yield: 45%). CHN Analysis ($C_{14}H_{22}N_{12}O_8Zn$): calculated C, 30.47; H, 4.02; N, 30.46; found C, 30.17; H, 3.89; N, 30.70. ¹³C NMR: (500 MHz, DMSO- d_6 , 25 °C, TMS); δ (ppm) 46.52, 113.46, 139.83, 152.12, 156.19, 160.37, 171.88.

3. Results and discussion

The primary objective of this work is a fixation of atmospheric carbon dioxide as carbonate with the help of zinc complexes of purine derivatives. Such studies basically explore the potential role of purines along with the role of zinc in catalyzing CO_2 transformation. Three different purine derivatives, with varied substitution pattern, were chosen to assess the possibility of CO_2 activation. Alkaline conditions were used for interaction of N9-carboxymethyl substituted adenine (L1), 2, 6-diaminoadenine (L2) and 2-amino-6-thiopurine (L3) with zinc acetate.

Ligands L1-L3 and zinc acetate were stirred in the presence of aqueous ammonium hydroxide in methanol at ambient temperature for 4 hrs (Fig. 1). Eldik and co-workers have described favourable carbonate-metal ion coordination between pH ranges 6–10, where an increase in pH beyond 10 leads to the displacement of carbonate ion [27]. Considering this point of view, all the reactions were conducted at pH 9 and at this pH carbonate is stable to bind to the metal ions. Slow evaporation of filtered solution, in open tubes, to enable interaction with



Fig. 5. 2D polymeric crystal lattice self-assemble with another layer to form 3D polymeric structure of complex **2** (Few H-atoms are deleted for clearness) and purine-purine interactions are shown in the dotted line and methanol molecules are shown in the center of the polymeric structure.

the atmosphere, afforded corresponding crystalline complexes 1-3, which possess different structural framework, although they crystallized in different space groups P21/c, P21/n, and C2/c of the monoclinic crystal system, respectively, while complex 4 exhibits triclinic system having space group P-1.Fig. 2.

The asymmetric unit of mononuclear complex 1 consisted of two L1 molecules, two water molecules, and one zinc atom. The zinc atom coordinated to four oxygen ions derived from two carboxylate ions and two coordinated water molecules to exhibit a distorted octahedral geometry (Fig. 1). Synthesis of ligand L3 favours increased binding sites and also brings changes in supramolecular structures by introducing exocyclic sulphur ion at C6 position. The asymmetric unit of 3 composed of one ligand L3, two water molecules and one zinc ion (Fig. 1). Other crystallographic details of these complexes are provided in the supporting information.

Notably, only modified diaminopurine ligand (L2) was successful in trapping atmospheric CO_2 in carbonate form (Fig. 3). Modified adenine (L1) did show coordination with zinc to afford a mononuclear complex and the substitution of C6-amino group with a thiol in L3 afforded zinc coordination via C6-thiol, albeit without incorporation of CO_2 . Such an outcome suggests that substitution patterns in the purine framework could be of significance in tuning CO_2 activation by zinc complexes of modified derivatives, due to changes in pKa causing altered metal ion coordinating ability of N7 nitrogen [28]. Ligand L2 reacts with zinc acetate in a closed system to give a discrete dimeric structure 4, having no μ -carbonate group (Figure S2), which suggest that carbon dioxide fixation did not occur, due to the absence of atmospheric CO_2 . This is in line with our observations concerning the design of metal–nucleobase supramolecular structures leading to novel coordination frameworks [29–34].

Notably, the asymmetric unit of complex 2 was composed of two Zn atoms, one ligand, water and a methanol molecule (Fig. 1). Zn ion coordinated to four oxygen atoms (three carbonate oxygen and one water molecule) form a tetrahedral structure. 2 also contained an

unusual associated connectivity of μ_3 -CO₃ group through CO₂ trapping (Fig. 3b). Some previous reports have documented di, tri and tetra nuclear μ_3 -carbonate complexes [35–37]. However, CO₂ was exogenously supplied for activation in most of these studies. IR spectra of L2 and complex 2 were measured in the solid state at ambient temperature. The sharp peak observed at 1479 cm⁻¹ could be ascribed to symmetrically bridged μ_3 -carbonate groups [38]. The existence of carbonate ligands in complex 2 was additionally confirmed by solid-state ¹³C NMR spectra, where a peak at 167.9 ppm, ascribed to coordinated carbonate group, was observed (Fig. 4) [15]. Notably, experimental PXRD patterns of 2 matched nicely with simulated ones, supporting the resemblance of produced majority materials to single crystals (Figure S11).

It is proposed that the carbonate anion is formed as a result of atmospheric carbon dioxide hydration, as decomposition of acetate ion is not feasible under the reaction conditions employed. Bermejo and coworkers have reported that zinc complex of heptadentate Schiff base ligand captures atmospheric carbon dioxide under basic medium when reacted with zinc acetate.³¹ Control reactions performed in the open air without added ligands did not reveal characteristic carbonate peak in ¹³C spectrum. From this experiment, it was concluded that CO₂ fixation is possible in the presence of ligand as well as all reaction conditions.

The purine-purine interaction leads 2D polymeric structure to 3D polymeric structure (Fig. 5). Interestingly one carbonate ion is coordinated to three different Zn atoms to form μ_3 -CO₃ bridge. The μ_3 -CO₃ ion coordinate to Zn atoms to form 1D polymeric bridge structure (Fig. 3b). It is noticed that in complex **2**, six metal atoms and two ligands **L2** form a macrocyclic (M₂L) ring composed of 30 atoms with a minimum distance of 4.41 Å between two metal ions and maximum separation between two zinc atoms is 13.84 Å. N7 nitrogen and Zn atom gets separated by a bond distance of 2.02 Å and shows a bond angle of 98.48°. The distance between carbonate oxygen and Zn atoms varies from 1.92 to 1.99 Å.

3.1. Morphological study

Samples to study autonomous, solution-phase self-organization of 2 was followed by two different methods (Fig. 6: M1 and M2). In M1, crystals of complex 2 were dissolved in 60% methanol-water (1 mM), followed by microscopy study; while in M2 ligand L2 alone was dissolved together with Zn(CH₃COO)₂ in methanolic solution (ammonia solution was added to make pH 9) and incubated for 2 hrs, followed by microscopy study. Spherical morphologies appeared within 2 hrs in M1 sample as confirmed by microscopy (Fig. 6), which upon further incubation of 7 days afforded formation of spherical clusters. Interestingly, spherical morphologies did not form in first 2 hrs of co-incubation (Fig. 6). However, spherical structures appeared when the solution was kept in contact with the atmosphere for 7 days. The presence of zinc ions in the spherical structures were confirmed by energy-dispersive X-ray spectroscopy (EDX) (Figure S10). This experiment suggests that uptake of CO₂ by the ligand lead to the formation of stable soft spherical structures.

Gross morphology of autonomously assembled complex 2 was analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Spherical properties of these assemblies might be ascribed to the self-assembly of complex **2**. These structures were further investigated by high-energy, focused ion-beam (FIB) experiments to visualize the core of these spherical structures (Fig. 7). These experiments suggested that spherical structures consisted of hollow inner core, proposing the formation of relatively stable, hollow vesicle-like structures that were amenable to ion-beam milling (Fig. 7) [39–40]. These spherical morphologies bear resemblance to metal–organic



Fig. 6. (a, b and c) Self-assembly study of complex 2 by two different methods M1 and M2; (d) and (e) AFM image of complex 2 after 2 h and 1 d incubation respectively. (Scale: 2.5 µm).

core–shell structures as well as nanocomposites [41–43], in particular to spherical and hollow ferrocenyl coordination polymers [44].

4. Conclusion

In summary, we have constructed three modified purine ligands (**L1-L3**). The design of the ligands shows the introduction of heteroatom at C6 position of the purine ring. As a result, we observed different types of supramolecular interactions in complex **1–4**. Interestingly, complex **2** fixes atmospheric CO_2 as carbonate but complex **4** fails to

fixed CO_2 which was put under a closed system. Studies with ligands L1 and L2 suggest that 2,6-diamino groups have an important role in CO_2 fixation in the basic medium. It is worth mentioning that 2,6-diaminopurine was unambiguously identified in carbonaceous meteorites and is known to be as stable as principal purine nucleobases, such as adenine and guanine [45]. It can also pair with thymine or uracil through three hydrogen bonds and supports pairing with 7-methyl oxoformycin B and T7 polymerase catalysed enzymatic incorporation of xanthosine [46]. Based on the results obtained in this study, we surmise that the possibility of generating hollow spherical structures,

a

Fig. 7. (a) SEM image of the sphere before ion-beam application (scale 2 µm); (b) SEM image of the sphere after ion beam application on silicon surface; (d) and (e) SEM image of the sphere after ion beam application on silicon surface (scale: 2.5 µm).

subsequent to CO₂ fixation, is intriguing and it allows us to propose that such morphologies could be considered as primordial protocell-like enclosures, without the involvement of lipids, for replication and proliferation [47,48].

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.ica.2018.09.041.

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