

## Macrocyclic molecular square complex of zinc(II) self-assembled with a carbohydrazone ligand

Easwaran potti Manoj <sup>a</sup>, Maliyeckal Ramakrishna Panicker Prathapachandra Kurup <sup>a,\*</sup>,  
Hoong-Kun Fun <sup>b</sup>

<sup>a</sup> Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682022, Kerala, India

<sup>b</sup> X-ray Crystallography Unit, School of Physics, Universiti Sains, Malaysia, 11800 USM, Penang, Malaysia

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### Abstract

A novel N<sub>4</sub>O coordination mode offers carbohydrazone ligands as a building block for interesting frameworks through self-assembly. Bridging mode of oxygen of bis(2-benzoylpyridine ketone) carbohydrazone (H<sub>2</sub>L) with metal centers facilitates the formation of the macrocyclic molecular square [Zn(HL)]<sub>4</sub>(BF<sub>4</sub>)<sub>4</sub> · 10H<sub>2</sub>O, offers wide range of applications for carbohydrazones.

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Metallosupramolecular squares have been considered as versatile substitutes of the conventional organic macrocycles [1]. Strategies to produce molecular square grids of transition metal centers include design and synthesis of a polyfunctional ligand and judicious utilization of its organizing ability to suitable metal ions. The first step towards this direction was explored by Fujita et al. [2] by making use of the cis-protected square planar Pd<sup>II</sup> and linear bidentate ligand 4,4'-bipyridine. Self-assembly and kinetically controlled macrocyclization are major strategies for the construction of such building blocks. Of these, self-assembly is a powerful and simple approach to build up interesting multidimensional frameworks like macrocyclic molecular squares often having versatile magnetic properties and endowed with special functional properties such as luminescence, redox activity, etc. [3–7]. The most frequently used metal ions for octahedral centers include Fe(II), Co(II) and Ni(II) [8] and are rare for self assembled molecular squares of multidentate ligands [9].

In order to achieve a desired situation, the building blocks must be designed properly [1]. Owing to the presence of different kinds of potential donor sites [10], we selected carbohydrazones as building blocks in the self-assembly of macrocyclic molecular architectures. Hitherto reported complexes of carbohydrazones are all mononuclear or dinuclear in nature and only two crystal structures have been reported, which are copper(II) [10] and dioxomolybdenum(VI) [11] complexes. Somewhat similar kind of ligands *N'*, *N'*<sup>2</sup>-bis[(1E)-1-(2-pyridyl)ethylidene]ethanedihydrazide (L1) and *N'*, *N'*<sup>2</sup>-bis[(1E)-1-(2-pyridyl)ethylidene]propanedihydrazide on equimolar reaction with Zn(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O yielded only mononuclear complexes [12] though these compounds possess two N, N, O pockets, without any crystal studies. However the reaction with Fe(ClO<sub>4</sub>)<sub>3</sub> · 6H<sub>2</sub>O, L1 undergoes an oxidative degradation of the side chain (–CO–CO–) and a reduction of Fe(III) to Fe(II) to form a complex, as evidenced by crystallographic study. However we anticipated carbohydrazones can act as building blocks for self-assembly, like thiocarbohydrazones [13–16], when suitable conditions are employed. Here in our study the reaction conditions were in such a way that H<sub>2</sub>L behaves as a building block for self-assembly. Here we report

\* Corresponding author. Tel.: +91 484 2575804; fax: +91 484 2577595.  
E-mail address: [mrp@cusat.ac.in](mailto:mrp@cusat.ac.in) (M.R.P. Prathapachandra Kurup).

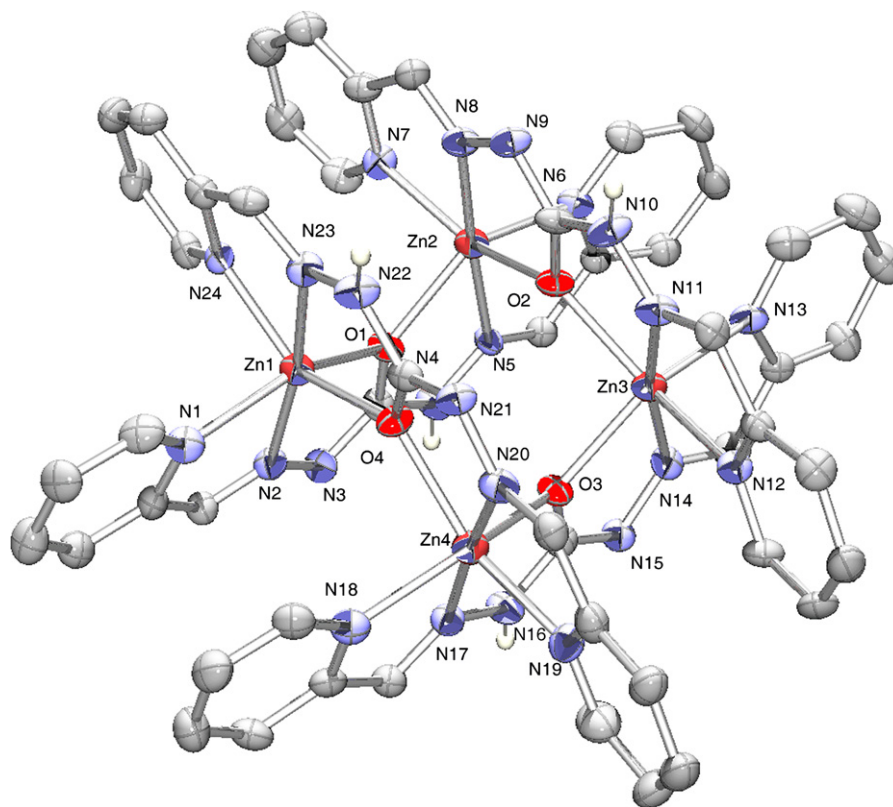


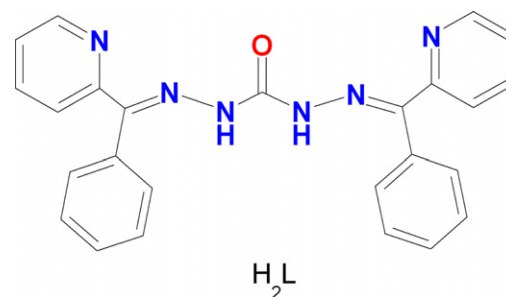
Fig. 1. ORTEP diagram for the compound (**1**) in 70% probability ellipsoids. Benzyl groups, carbon bound hydrogen atoms, anions and water molecules are omitted for clarity. The hydrogen atoms on N(4), N(10), N(16) and N(22) of ligand H<sub>2</sub>L are retained in the complex, while their counterparts are deprotonated on coordination after enolization.

the first molecular square [Zn(HL)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub> · 10H<sub>2</sub>O of a carbohydrazone, where HL is the monodeprotonated form of bis(2-benzoylpyridine ketone) carbohydrazone (H<sub>2</sub>L), a known ligand (Scheme 1) [17]. The reaction of H<sub>2</sub>L with Zn(II) and Fe(II) metal salts produced mononuclear complexes, which lacks crystal studies. Also its reaction with CuCl<sub>2</sub> suffers degradation of –CO– and cyclization to form a copper complex of 3-phenyltriazolo[1,5-*a*]-pyridine. However our study is the first report of carbohydrazone derivatives behaving as the building blocks for self-assembly, and thereby offers a new dimension to supramolecular chemistry.

When H<sub>2</sub>L was treated<sup>1</sup> with Zn(BF<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O, the macrocyclic [Zn(HL)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub> · 10H<sub>2</sub>O, **1**, was formed as yellow

crystalline solids *via* self-assembly. Complex **1** is found to be soluble in solvents like DMF, DMSO and acetonitrile and less soluble in methanol, ethanol, chloroform etc. The compound **1** in acetonitrile shows absorbance features at λ<sub>max</sub> (ε) = 260 (56,600), 335 (77,000) and 399 nm (37,000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) against the λ<sub>max</sub> at 235, 267 and 317 nm of free ligand. An X-ray crystallographic study [18] has unequivocally confirmed the formation of a tetranuclear molecular square. The molecular structure of **1** with relevant atom numbering scheme is given in Fig. 1. Crystal structures of only two carbohydrazone ligands reported so far [10,19] were in amidoketone tautomeric form. The enol tautomer can adopt a *syn* or *anti* configuration as a consequence of the double-bond character of the central N–C linkage. The *syn* configuration is essential for

<sup>1</sup> All reagents were used as received from Aldrich. The ligand bis(2-benzoylpyridine ketone) carbohydrazone was prepared according to reported procedure [17], except that a 2 h reflux could yield 67%, against 70% yield for 60 h. [Zn(HL)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub> · 10H<sub>2</sub>O, **1**: A solution of the H<sub>2</sub>L (0.2153 g, 0.5 mmol) in chloroform (10 ml) was added to a solution of Zn(BF<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O (0.12 g, 0.5 mmol) in methanol (20 ml) and refluxed for 1 h. The yellow crystalline solid which formed after a week was filtered, washed with methanol and ether, and dried over P<sub>4</sub>O<sub>10</sub> *in vacuo* to give **1** (0.180 g, 68%). Elemental analysis (%): calcd for C<sub>100</sub>H<sub>96</sub>B<sub>4</sub>F<sub>16</sub>N<sub>24</sub>O<sub>14</sub>Zn<sub>4</sub>: C, 48.69; H, 3.92; N, 13.63; found: C, 48.87; H, 4.12; N, 13.60. IR(KBr): ν 3410 br, 3058 s, 1664 s, 1626 s, 1570 s, 1525 vs, 1465 s, 1443 s, 1262 s, 1324 s, 1213 s, 1083 vs, 1069 vs, 767 w, 796 s, 703 vs, 535 w, 522 s, 410 s, 355 w, 234 s cm<sup>-1</sup>. Crystals suitable for X-ray structure determination were obtained from slow evaporation of a chloroform:methanol mixture solution (1:1 v/v) of **1** in air.



Scheme 1.

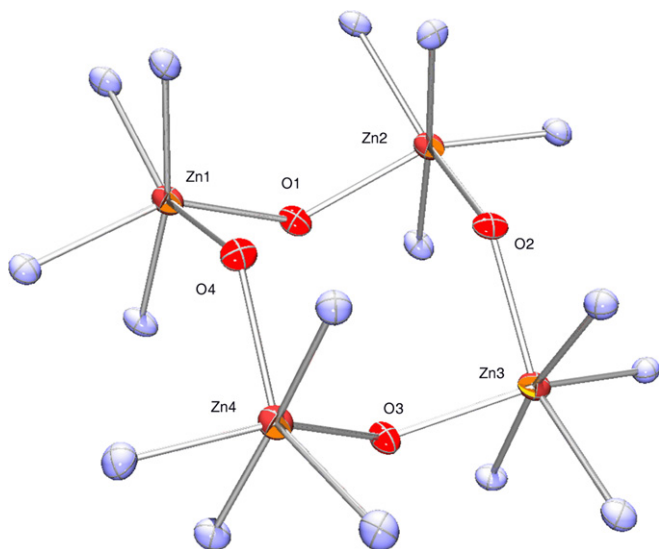


Fig. 2. The coordination core about the Zn(II) centers showing the metal centers are connected through oxygen atoms.

getting molecular square architectures of octahedral centers like compound **1**.

In the tetranuclear cation  $[\text{Zn}(\text{HL})]_4^{4+}$ , the ligands are coordinated in the monoanionic form by deprotonation after enolization. The hydrogen atoms on N(3), N(9), N(15) and N(21) are deprotonated on coordination, while their counterparts retained. This is confirmed by the C(13)–O(1) bond distance of 2.288(5) Å, and a decrease of 0.026(7) Å for C(13)–N(3) bond compared to C(13)–N(4) bond, for example. Two  $\text{HL}^-$  ligands bind to a Zn(II)

in the *mer* configuration (with pairs of O atoms and pyridyl N atoms each bearing a *cis* relationship, whereas the azomethine N atoms are *trans* to each other) to form distorted octahedral metal centers, similar to sulfur counterpart of oxygen [16] but different from the *cis-mer* configuration seen in Zn(II) semicarbazone complex [20]. Thus the molecule comprises four octahedral Zn(II) centers connected through oxygen atoms (Fig. 2). This alternate zinc and oxygen atoms form a boat like structure of eight atoms. The angles subtended at Zn(1) and Zn(3) are  $\sim 92.7^\circ$  and at Zn(2) and Zn(4) are  $\sim 90^\circ$ , while those subtended at oxygen atoms varies from  $133.90^\circ$  to  $136.06^\circ$ . Yet, the four Zn(II) atoms are in a plane with a maximum deviation of  $-0.1654(5)$  Å for Zn(3). The nearby Zn(II)···Zn(II) distances are  $\sim 3.96$  Å and Zn(II)···Zn(II)···Zn(II) angles are  $\sim 89^\circ$ . The Zn(II)···Zn(II) distances along the corners of the square are 5.5158(7) Å for Zn(1)–Zn(3) and 5.6664(7) Å for Zn(2)–Zn(4). But no water or solvent molecules are present in the mid cavity space of square grid. However all tetramers are interconnected by a number of hydrogen bonding interactions including water and  $\text{BF}_4^-$  anions (Fig. 3) to form a three dimensional motif in the lattice, which includes some C–H··· $\pi$  and very weak  $\pi$ ··· $\pi$  interactions in the packing.

The MALDI mass spectrum of the complex **1** as DCTB mix on positive ion mode shows peaks at  $m/z$  757, 1031, 1514.9, 1711.9 and 1934.9 along with well resolved isotropic peaks (Fig. 4). The molecular ion peak 1934.9 assigned to  $[\text{Zn}_4(\text{HL})\text{L}_3]^+$ , 1514.9 corresponds to  $[\text{Zn}_4\text{L}_3]^{2+}-\text{H}^+$  and 1031 corresponds to  $[\text{Zn}_3\text{L}_2]^{2+}-\text{H}^+$ . The peak at  $m/z$  757 is due to  $[\text{Zn}_4\text{L}_3]^{2+}$  species. These results suggest the existence

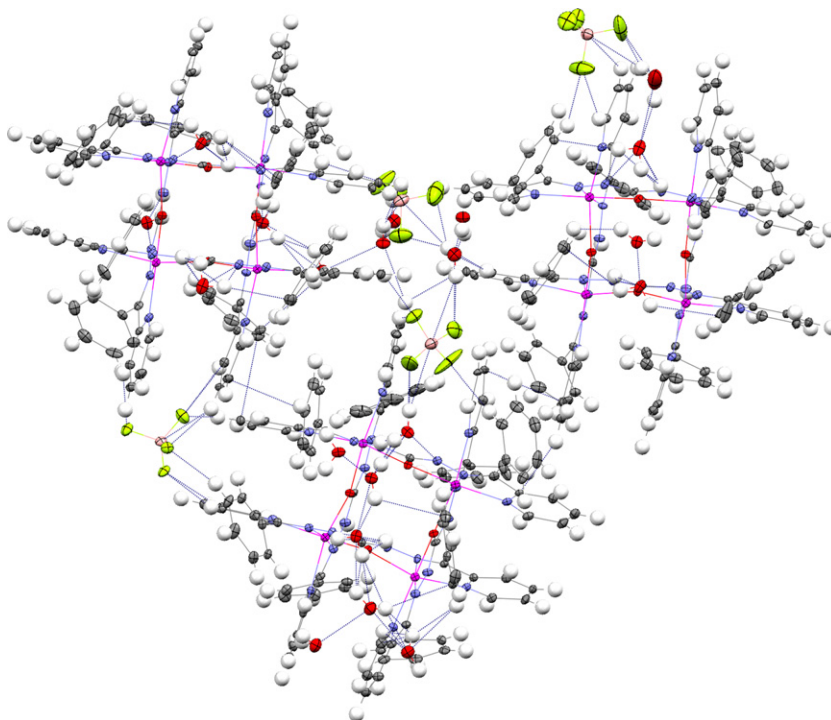


Fig. 3. Extended network of Zn(II) tetramers in the lattice showing the formation of 3D motif through various hydrogen bonding interactions.

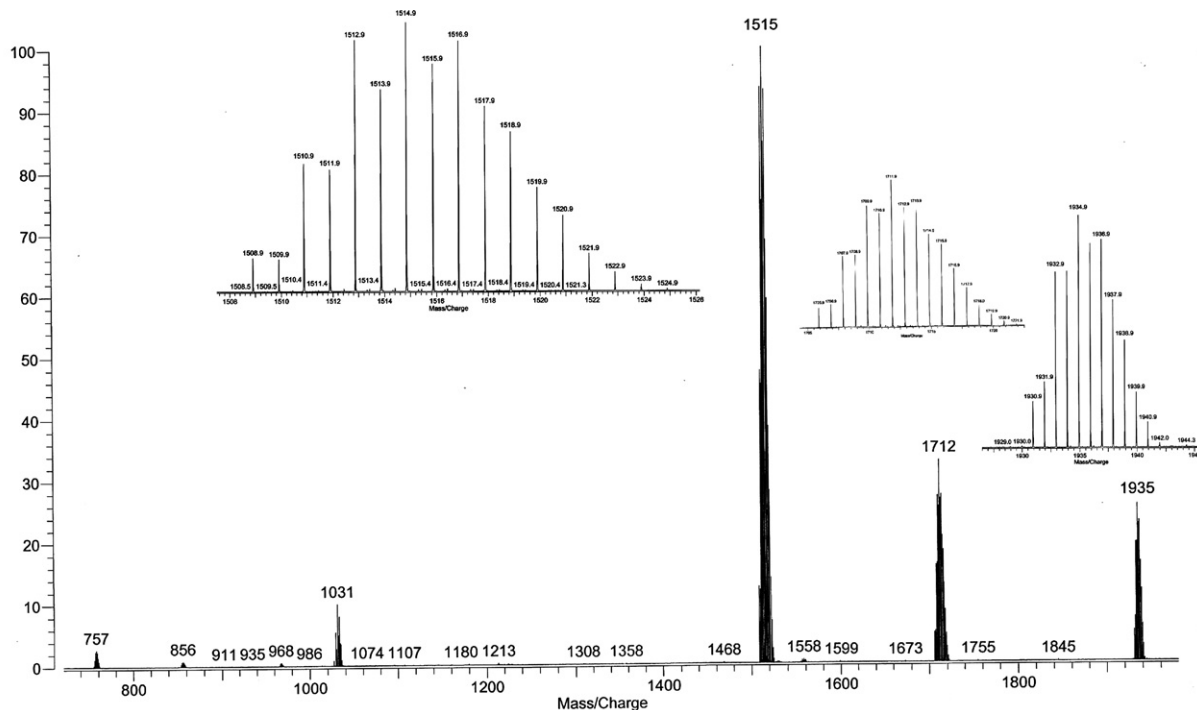


Fig. 4. MALDI mass spectra of compound **1** in dichloromethane; the inserts show the isotopic distributions for the main peaks.

of molecular square structure in the solution phase as well. The presence of  $[\text{Zn}_3\text{L}_2]^{2+}-\text{H}^+$  species indicates that the complex **1** may lose one metal ion under ionization condition. Also, calculation of isotopic distribution of peaks shows that the peak at 1711.9 corresponds to a dissociated species  $\text{C}_{87}\text{H}_{64}\text{N}_{21}\text{O}_3\text{Zn}_4^+$  (calc 1712.2592) formed by the degradation of one of the ligand in the tetrameric species  $[\text{Zn}_4(\text{HL})\text{L}_3]^+$ . Its structure along with calculated isotopic distribution pattern are attached in the appendix.

The carbohydrazones are not much studied like thiocarbohydrazones perhaps due to a possibility of an oxidative degradation of the carbonyl group. The compound **1** consists of carbonyl oxygen as the connecting atoms between metal centers. Hitherto reported carbohydrazone complexes show either mononuclear or binuclear metal complexes coordinated through N, N, O and N, N, N atoms. The work reported here is novel in several respects. This is the first report where the carbonyl group is involved in the bridging mode for carbohydrazone ligands. The novel  $\text{N}_4\text{O}$  coordination mode offers carbohydrazone ligands as a building block for interesting frameworks through self-assembly. The carbohydrazone inner core thus offers a wide range of possibilities with suitable substituents having different coordination properties to build novel coordinating ligands for designing multinuclear coordination complexes of desired metals, which would find applications in various fields.

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#### Appendix A. Supplementary data

CCDC 621124 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2006.11.009](https://doi.org/10.1016/j.inoche.2006.11.009).

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