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## EFFECT OF pH ON THE ELECTROCHEMICAL REDUCTION OF Zn (II)- PYRIMIDINES COMPLEXES

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**ABSTRACT:** Electrochemical reduction can offer an attractive alternative to Birch reduction. The advantages could be: reduction in aqueous or mixed organic–aqueous media, possibility of isolating products not expected to be stable to metal ammonia conditions, ability to deal with base-sensitive substrates or products, etc. Electrochemical reduction describes the transformation in the electrochemical circuit of metallic cation to metals by electron transfer. A similar concept is used in the synthesis of NP, where metal cations are reduced to metals and transformed into NP

**KEYWORDS:** pH, electrochemical reduction, zinc, pyrimidines, complexes, metals, substrates

### I.INTRODUCTION

Two zinc(II) based metal complexes,  $[Zn(Pymox)Cl_2]$  (1) and  $[Zn_6(Pymox)_6(\mu_2-O)_3]$  (2), where Pymox = 3-[(4,6-dimethyl-pyrimidine-2-yl)-hydrazono]-butan-2-one oxime, have been synthesized and characterized by elemental analysis, IR, and single crystal X-ray diffraction studies. Single crystal X-ray analysis confirms that one of the synthesized products (1) is a mononuclear complex and another (2) is a hexanuclear Zn complex. The optical band gap energy in both the complexes (3.43 eV in 1 and 2.36 eV in 2) from solid state UV measurement explores semiconductor behavior of the synthesized materials. The dielectric parameters such as charge transfer resistance, room temperature dc conductivity and electron lifetime measurement shows the superiority of complex 2 over complex 1.<sup>1</sup> Therefore, the Schottky barrier diode (SBD) electronic devices were fabricated by using these two complexes with aluminum (Al) and indium tin oxide (ITO) in sandwich configuration—ITO/1 or 2/Al. Both the devices exhibit sound rectification behavior with better photosensing property for complex 2 based SBD under irradiation of light, in comparison to dark conditions. The electric current measurement for complex 2 based SBD also exhibits enhanced photoconduction properties under irradiation of light when current is measured several times under a constant bias voltage by putting light on and off with successive repetitions.<sup>2,3</sup> The detailed discussion of photo response properties of both the complexes in the solid state device have been reported along with their applicability in photosensitive devices. Finally, DFT calculations have been carried out to rationalize the experimental differences in band gap and conductivity observed for compounds 1 and 2.<sup>4,5</sup>

We demonstrated first that the electrochemical reduction of zinc phosphate in neutral phosphate buffer is possible and potentially applicable to bio-compatible rechargeable battery. The actual redox component is Zn(s)/Zn phosphate(s) and the future research about the control of crystal formation for the better cyclability is required. In lead-acid battery, the electrochemical redox reaction of Pb(s)/PbSO<sub>4</sub>(s) is used by reducing Pb(II) and oxidizing Pb(0) in sulfate rich solution. Since both reduced form and oxidized form are insoluble, they cannot diffuse to the opposite electrodes and react. It is a very common strategy to make a stable battery electrode that a metal element is reduced and oxidized in solution containing an abundance of anion readily precipitating with the metal ion. For the application of this strategy to construction of rechargeable battery using bio-compatible electrode materials and electrolytes, the use of phosphate ion can be considered as anion readily precipitating with metal ions. If phosphate buffer with neutral pH is used as electrolyte, the better bio-compatibility will be achieved than most of rechargeable battery using strong acid, strong base or organic solvent as electrolyte solution. There are many metal ions readily precipitating with phosphate ion, and zinc is one of them<sup>6,7,8</sup>

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Zinc is a chemical element with the symbol Zn and atomic number 30. Zinc is a slightly brittle metal at room temperature and has a shiny-greyish appearance when oxidation is removed. It is the first element in group 12 (IIB) of the periodic table. In some respects, zinc is chemically similar to magnesium: both elements exhibit only one normal oxidation state (+2)<sup>9,10</sup>, and the Zn<sup>2+</sup> and Mg<sup>2+</sup> ions are of similar size. Zinc is the 24th most abundant element in Earth's crust and has five stable isotopes. The most common zinc ore is sphalerite (zinc blende), a zinc sulfide mineral. The largest workable lodes are in Australia, Asia, and the United States. Zinc is refined by froth flotation of the ore, roasting, and final extraction using electricity (electrowinning).<sup>11,12</sup>

Zinc is an essential trace element for humans,<sup>[4][5][6]</sup> animals,<sup>[7]</sup> plants<sup>[8]</sup> and for microorganisms<sup>[9]</sup> and is necessary for prenatal and postnatal development.<sup>[10]</sup> It is the second most abundant trace metal in humans after iron and it is the only metal which appears in all enzyme classes.<sup>[8][6]</sup> Zinc is also an essential nutrient element for coral growth as it is an important cofactor for many enzymes.<sup>[11]</sup>

Zinc deficiency affects about two billion people in the developing world and is associated with many diseases.<sup>[12]</sup> In children, deficiency causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea.<sup>[10]</sup> Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans.<sup>[13]</sup> Consumption of excess zinc may cause ataxia, lethargy, and copper deficiency.<sup>13</sup>

## II.DISCUSSION

New series of metal(II) complexes of [Mn(L)(OAc)], [Co(L)(OAc)], [Ni(L)(OAc)], [Cu(L)(OAc)], and [Zn(L)(OAc)], where HL is Schiff base ligand as 2-[(4,6-dimethylpyrimidin-2-ylimino)methyl]-6-methoxyphenol and -OAc is acetate have been synthesized and characterized by physico-chemical and different spectral techniques.<sup>13,14</sup> The synthesized metal(II) complexes have square planar geometry which was proved from above listed characterization methods. The synthesized complexes have remarkable antimicrobial agents than ligand. Absorption titration and viscosity experiments results suggest that metal(II) complexes bind with calf thymus (CT) DNA via groove binding mode. CT-DNA cleavage activities of HL and complexes have been investigated by gel-electrophoresis method. Moreover, molecular docking analysis has been carried out using the DFT optimized geometries to understand the nature of interactions of the synthesized ligand and its metal complexes with DNA and BSA protein. Molecular docking analysis<sup>15,16</sup> reveals that the metal(II) complexes tend to show good binding affinity towards both DNA and BSA compared to Schiff base ligand. The effect of pH and hardness metal ions on the interactions between trace metals and both inorganic and organic complexing agents has been studied under conditions simulating natural aquatic conditions, by employing anodic stripping voltammetric titration techniques. The complexation of Bi(III), Cd(II), Cu(II), Pb(II), and Tl(I) with the hydroxo- and carbonato-ligands found in a carbonate medium has been observed to generally increase with increasing pH. Both labile and nonlabile interactions have been observed. Nonlabile interactions are predominant at low pH and labile interactions generally increase with increasing pH. Neither calcium nor magnesium affects these interactions. The complexation of humic acids with trace metals in a carbonate medium was found to be more intense than metal ion-inorganic complexation. Both labile and nonlabile complexation was found; however, no generalizations can be made concerning the type and extent of complexation because of the individual nature of the interactions of each trace metal. Calcium was found to be more effective than magnesium in inhibiting trace metal-organic complexation. The effect of calcium is to inhibit labile complexation and is most pronounced with the cadmium-humic acid system.<sup>17,18,19</sup>

Zinc makes up about 75 ppm (0.0075%) of Earth's crust, making it the 24th most abundant element. Typical background concentrations of zinc do not exceed 1 µg/m<sup>3</sup> in the atmosphere; 300 mg/kg in soil; 100 mg/kg in vegetation; 20 µg/L in freshwater and 5 µg/L in seawater.<sup>[26]</sup> The element is normally found in association with other base metals such as copper and lead in ores.<sup>[27]</sup> Zinc is a chalcophile, meaning the element is more likely to be found in minerals together with sulfur and other heavy chalcogens,<sup>20,21,22</sup> rather than with the light chalcogen oxygen or with non-chalcogen electronegative elements such as the halogens. Sulfides formed as the crust solidified under the reducing conditions of the early Earth's atmosphere.<sup>[28]</sup> Sphalerite, which is a form of zinc sulfide, is the most heavily mined zinc-containing ore because its concentrate contains 60–62% zinc.<sup>[27]</sup>

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Other source minerals for zinc include smithsonite (zinc carbonate), hemimorphite (zinc silicate), wurtzite (another zinc sulfide), and sometimes hydrozincite (basic zinc carbonate).<sup>[29]</sup> With the exception of wurtzite, all these other minerals were formed by weathering<sup>23,24,25</sup> of the primordial zinc sulfides.<sup>[28]</sup>

Identified world zinc resources total about 1.9–2.8 billion tonnes.<sup>[30][31]</sup> Large deposits are in Australia, Canada and the United States, with the largest reserves in Iran.<sup>[28][32][33]</sup> The most recent estimate of reserve base for zinc (meets specified minimum physical criteria related to current mining and production practices) was made in 2009 and calculated to be roughly 480 Mt.<sup>[34]</sup> Zinc reserves, on the other hand, are geologically identified ore bodies whose suitability for recovery is economically based (location, grade, quality, and quantity) at the time of determination. Since exploration and mine development is an ongoing process, the amount of zinc reserves is not a fixed number and sustainability of zinc ore supplies cannot be judged by simply extrapolating the combined mine life of today's zinc mines. This concept is well supported by data from the United States Geological Survey (USGS), which illustrates that although refined zinc production increased 80% between 1990 and 2010, the reserve lifetime for zinc has remained unchanged. About 346 million tonnes have been extracted throughout history to 2002, and scholars have estimated that about 109–305 million tonnes are in use.<sup>[35][36][37]</sup>

## III.RESULTS

Pyrimidine is an aromatic, heterocyclic, organic compound similar to pyridine (C<sub>5</sub>H<sub>5</sub>N).<sup>[3]</sup> One of the three diazines (six-membered heterocyclics with two nitrogen atoms in the ring), it has nitrogen atoms at positions 1 and 3 in the ring. The other diazines are pyrazine (nitrogen atoms at the 1 and 4 positions) and pyridazine (nitrogen atoms at the 1 and 2 positions).<sup>30,31,32</sup>

In nucleic acids, three types of nucleobases are pyrimidine derivatives: cytosine (C), thymine (T), and uracil (U). The pyrimidine ring system has wide occurrence in nature<sup>[5]</sup> as substituted and ring fused compounds and derivatives, including the nucleotides cytosine, thymine and uracil, thiamine (vitamin B1) and alloxan. It is also found in many synthetic compounds such as barbiturates and the HIV drug zidovudine. Although pyrimidine derivatives such as alloxan were known in the early 19th century, a laboratory synthesis of a pyrimidine was not carried out until 1879,<sup>[5]</sup> when Grimaux reported the preparation of barbituric acid from urea and malonic acid in the presence of phosphorus oxychloride.<sup>[6]</sup> The systematic study of pyrimidines began<sup>[7]</sup> in 1884 with Pinner,<sup>[8]</sup> who synthesized derivatives by condensing ethyl acetoacetate with amidines. Pinner first proposed the name “pyrimidin” in 1885.<sup>[9]</sup> The parent compound was first prepared by Gabriel and Colman in 1900,<sup>[10][11]</sup> by conversion of barbituric acid to 2,4,6-trichloropyrimidine followed by reduction using zinc dust in hot water.<sup>36,38,40</sup>

Replication is a fundamental aspect of cancer, and replication is about reproducing all the elements and structures that form a cell. Among them are DNA, RNA, enzymes, and coenzymes. All the DNA is doubled during each S (synthesis) cell cycle phase. This means that six billion nucleic acids must be synthesized in each cycle. Tumor growth, proliferation, and mutations all depend on this synthesis. Cancer cells require a constant supply of nucleotides and other macromolecules. For this reason, they must stimulate de novo nucleotide synthesis to support nucleic acid provision. When deregulated, de novo nucleic acid synthesis is controlled by oncogenes and tumor suppressor genes that enable increased synthesis and cell proliferation. Furthermore, cell duplication must be achieved swiftly (in a few hours) and in the midst of a nutrient-depleted and hypoxic environment.<sup>41</sup> This also means that the enzymes participating in nucleic acid synthesis must work efficiently. pH is a critical factor in enzymatic efficiency and speed. The enzymatic machinery working in nucleic acid synthesis requires a pH on the alkaline side in most cases. This coincides with many other pro-tumoral factors, such as the glycolytic phenotype, benefiting from an increased intracellular pH. An increased intracellular pH is a perfect milieu for high de novo nucleic acid production through optimal enzymatic performance.

### Implications

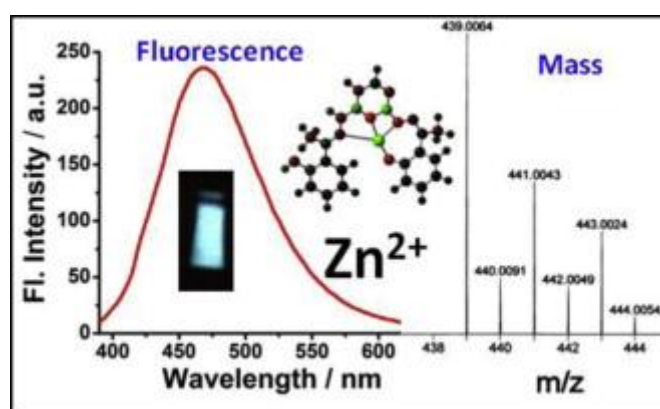
Barbiturase, which catalyzes the reversible amidohydrolysis of barbituric acid to ureidomalonic acid in the second step of oxidative pyrimidine degradation, was purified to homogeneity from *Rhodococcus erythropolis* JCM 3132. The characteristics and gene organization of barbiturase suggested that it is a novel zinc-containing amidohydrolase that should be grouped into a new family of the amidohydrolases superfamily. The amino acid sequence of barbiturase exhibited 48% identity with that of herbicide atrazine-decomposing cyanuric acid amidohydrolase but exhibited no significant homology to other proteins, indicating that cyanuric acid amidohydrolase may have evolved from

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barbiturase.<sup>42,43</sup> A putative uracil phosphoribosyltransferase gene was found upstream of the barbiturase gene, suggesting mutual interaction between pyrimidine biosynthesis and oxidative degradation. Metal analysis with an inductively coupled radiofrequency plasma spectrophotometer revealed that barbiturase contains ~4.4 mol of zinc per mol of enzyme. The homotetrameric enzyme had  $K_m$  and  $V_{max}$  values of 1.0 mM and 2.5  $\mu\text{mol}/\text{min}/\text{mg}$  of protein, respectively, for barbituric acid. The enzyme specifically acted on barbituric acid, and dihydro-L-ornotat, alloxan, and cyanuric acid competitively inhibited its activity. The full-length gene encoding the barbiturase (bar) was cloned and overexpressed in *Escherichia coli*. The kinetic parameters and physicochemical properties of the cloned enzyme were apparently similar to those of the wild-type.



Zinc has an electron configuration of  $[\text{Ar}]3d^{10}4s^2$  and is a member of the group 12 of the periodic table. It is a moderately reactive metal and strong reducing agent.<sup>[41]</sup> The surface of the pure metal tarnishes quickly, eventually forming a protective passivating layer of the basic zinc carbonate,  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ , by reaction with atmospheric carbon dioxide.<sup>[42]</sup>

Zinc burns in air with a bright bluish-green flame, giving off fumes of zinc oxide.<sup>[43]</sup> Zinc reacts readily with acids, alkalis and other non-metals.<sup>[44]</sup> Extremely pure zinc reacts only slowly at room temperature with acids.<sup>[43]</sup> Strong acids, such as hydrochloric or sulfuric acid, can remove the passivating layer and the subsequent reaction with the acid releases hydrogen gas.<sup>[43]</sup>

The chemistry of zinc is dominated by the +2 oxidation state. When compounds in this oxidation state are formed, the outer shell s electrons are lost, yielding a bare zinc ion with the electronic configuration  $[\text{Ar}]3d^{10}$ .<sup>[45]</sup> In aqueous solution an octahedral complex,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  is the predominant species.<sup>[46]</sup> The volatilization of zinc in combination with zinc chloride at temperatures above 285 °C indicates the formation of  $\text{Zn}_2\text{Cl}_2$ , a zinc compound with a +1 oxidation state.<sup>[43]</sup> No compounds of zinc in positive oxidation states other than +1 or +2 are known.<sup>[47]</sup> Calculations indicate that a zinc compound with the oxidation state of +4 is unlikely to exist.<sup>[48]</sup> Zn(III) is predicted to exist in the presence of strongly electronegative trianions;<sup>[49]</sup> however, there exists some doubt around this possibility.<sup>[50]</sup> But in 2015 another compound was reported with more evidence that had the oxidation state of +3 with the formula  $\text{ZnBeB}_{11}(\text{CN})_{12}$ .<sup>[49]</sup>

Zinc chemistry is similar to the chemistry of the late first-row transition metals, nickel and copper, though it has a filled d-shell and compounds are diamagnetic and mostly colorless.<sup>[50]</sup> The ionic radii of zinc and magnesium happen to be nearly identical. Because of this some of the equivalent salts have the same crystal structure,<sup>[50]</sup> and in other circumstances where ionic radius is a determining factor, the chemistry of zinc has much in common with that of magnesium.<sup>[43]</sup> In other respects, there is little similarity with the late first-row transition metals. Zinc tends to form bonds with a greater degree of covalency and much more stable complexes with N- and S- donors.<sup>[50]</sup> Complexes of zinc are mostly 4- or 6- coordinate, although 5-coordinate complexes are known.<sup>[43]</sup>

### IV.CONCLUSIONS

Human red cell pyrimidine-5'-nucleotidase (EC 3.1.3.5) was partially purified from the blood of normal subjects by ion-exchange and affinity chromatography. Red cells were lysed in 50 mmol/l Tris-Cl buffer at pH 7.5 containing 1.0

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mmol/l dithiothreitol and 0.5 mmol/l EDTA. The lysate was centrifuged and introduced onto a column of Sephadex A-50. After washing, the pyrimidine-5'-nucleotidase activity was eluted from the column with a NaCl gradient from 0 to 200 mmol/l in Tris buffer at pH 7.5. The pyrimidine-5'-nucleotidase was then desalted on Sephadex G-25 and introduced onto a UDP agarose column with a Tris buffer at pH 6.5 containing 150 mmol/l NaCl. This partial purification resulted in an approximately 80,000-fold increase in enzyme concentration. The  $K_m$  for the partially purified enzyme was 0.32 mmol/l for UMP, 0.16 mmol/l for CMP and 0.11 mmol/l for OMP with a pH maximum of 7.5. This partially purified pyrimidine-5'-nucleotidase was then dialyzed in 50 mmol/l Tris-Cl buffer at pH 7.5 with 0.01 mmol/l  $CaCl_2$  and NaCl against  $2 \times 10^{-3}$  mol/l 1,10-phenanthroline for 24 h at 4 °C. This incubation resulted in a 73% decrease in enzyme activity which could be restored by the addition of zinc into the mixture, but not by the addition of other divalent metal ions.<sup>50</sup>

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