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B. Sc. Chemistry (CBCS) C-401
Semester-4 – Chapter 2
Bioinorganic chemistry

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❖ **General Introduction**

- Among these element Na, Mg, K, Ca are called main group metals, the biometals having atomic number exceeding 30, only Mo & Sn are essential for the living organism.
- These inorganic elements especially elements at trace & ultra-trace quantities play roles at the molecular level in a living system & thus, the boundary between bio-chemistry & molecular.
- Biology on one side & inorganic chemistry on the other side has generated a new science called bio-inorganic chemistry.
- It is a living & expanding subject which offers both interest & challenge.

❖ **Give the Classification of essential element**

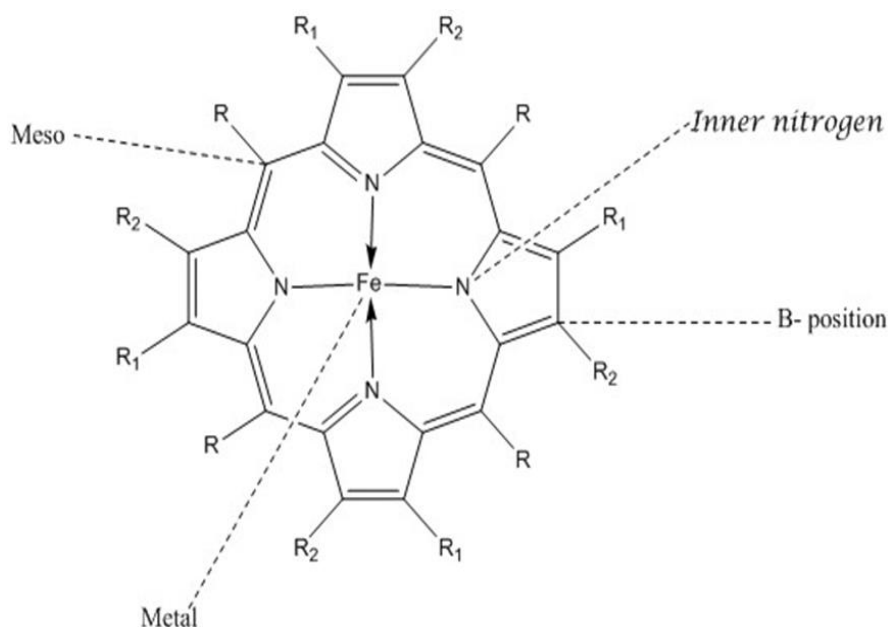
- The classification of the essential elements is based on what amount of an element is needed, required in macroscopic amount & some other are require in the trace amount. So in these criteria these thirty (30) essential elements have been classified into the...
 - ✓ Six (6) bulk OR structural element
 - ✓ Five (5) macrominerals
 - ✓ Nineteen (19) trace elements
 - ✓ Bulk / structural element : C, H, O, N, S, P
 - ✓ Macrominerals : Na, K, Mg, Ca, Cl
 - ✓ Trace elements : Fe, Cu, Zn
 - ✓ Ultratrace elements : 1) Non Metal : F, I, Se, Si, As, Br
 2) Metal : Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VII B	
(H)																	He
Li	Be											B	(C)	(N)	(O)	(F)	Ne
(Na)	(Mg)											Al	Si	(P)	(S)	(Cl)	Ar
(K)	(Ca)	Sc	Ti	(V)	(Cr)	(Mn)	(Fe)	(Co)	(Ni)	(Cu)	(Zn)	Ga	Ge	As	(Se)	(Br)	Kr
Rb	Sr	Y	Zr	Nb	(Mo)	Tc	Ru	Rh	Pd	Ag	Cd	In	(Sn)	Sb	Te	(I)	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	

○ – Bulk Elements
 □ – Trace Elements
 △ – Ultratrace Elements

❖ Metalloporphyrins

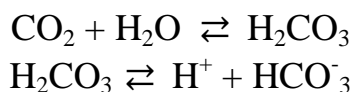
- Metalloporphyrins in association with protein globule performs several important biochemical functions in nature, haemoglobin, myoglobin, chlorophyll, cytochromes catalase.
- Peroxidases are well known example, Metalloporphyrins are widely & intensely investigated in the area of catalysis & also as models & mimics of enzymes like catalyses, peroxidases, p-450, and cytochrome or as trans membrane electron transport agents.
- They have also been used as NMR image enhancement agent, nonlinear optical materials & DNA-binding or cleavage agents, radio diagnostic agents in photodynamic therapy (PDT) foodstuff antioxidants, semiconductors or electrochromic materials, beauty shop as body deodorants and stimulants of hair growth.
- The porphyrin is an ubiquitous (everywhere) molecule present in almost all living organism in one form or other.
- The basic unit of porphyrin consists of four pyrrole unit linked by four methine bridges.
- It is an 18-electron system & hence exhibits aromaticity.
- Porphyrin ring provides a vacant site at the its center ideally suited for metal incorporation



- Here generally R = phenyl & ortho metal or para substituted phenyl. The important pyrrole substituted porphyrin includes octaethyl porphyrin (R₁ = R₂ = ethyl) & etioporphyrin (R₁ = ethyl, R₂ = methyl)

❖ **Haemoglobin & myoglobin**

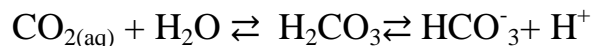
- The function of oxygen transport & storage in higher animals is provided by haemoglobin & myoglobin.
- The former transport dioxygen from its source (lungs, gills or skin) to the site of use inside the muscle cells.
- There the oxygen is transferred to myoglobin for use in respiration. Myoglobin may serve as a simple storage in living organism functioning of myoglobin include facilitation of O₂ flow within the cell and buffering of the partial pressure of dioxygen within the cell.
- The iron in haemoglobin & myoglobin is in the +2 oxidation state. The oxidation forms Fe (III) called metmyoglobin & methemoglobin will not find oxygen.
- The free heme is immediately oxidised in the presence of oxygen & water & thus renders useless for O₂ transport.
- Vertebrates when uses iron porphyrin, the other mentioned classes uses by nuclear metal arrangement (haemocyanin) & ironprotein (hemerythrin) complex O₂ transport is not a catalytic but a stoichiometric function about 65% of iron in human body is used for O₂ transporting in the form of haemoglobin.
- Nearly 30 times more solubility for O₂ than in H₂O. Haemoglobin was the first protein crystallized with a recognised physiological purpose such as O₂ transport & CO₂ transport.
- It was the first protein whose tertiary & quaternary structures were determined by X-ray at crystallography. Haemoglobin (haem=iron porphyrin + globin=polypeptide chain) M.W. = 645 myoglobin consists of one polypeptide chain (globin) with one haem embedded therein the peptide chain contain 150 to 160 amino acid residues.
- The position of oxygen molecule In Myoglobin its occupied by H₂O molecule the globin (protein) absorbs H⁺ ions this helps to removal of CO₂ from tissue



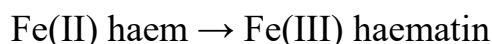
- In lungs H⁺ ions is again released by globin due to oxygenation, that helps in converting in soluble HCO₃⁻ ion in blood to CO₂



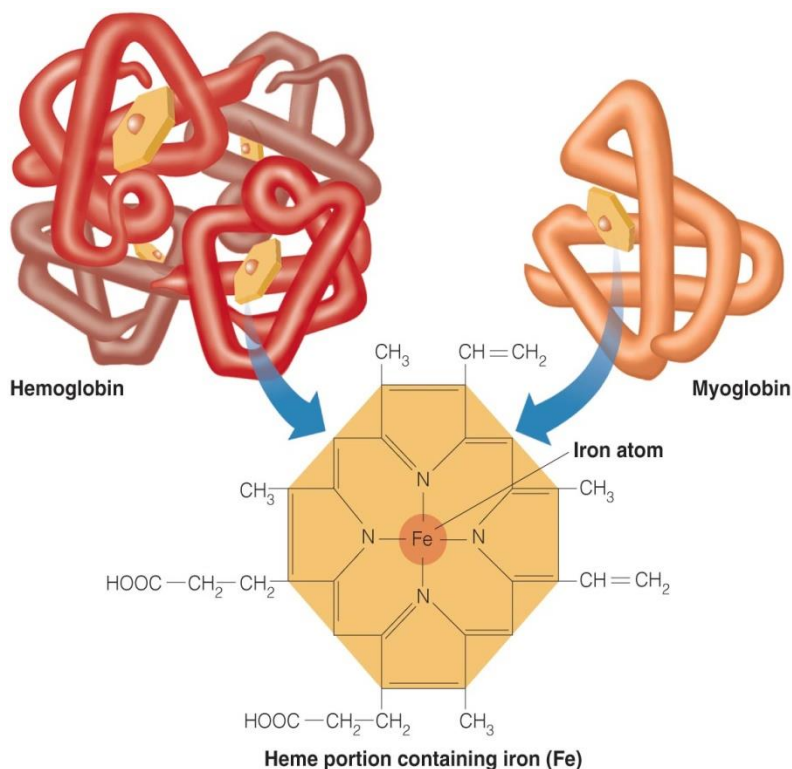
- Within the cell (RBC) a zinc containing enzyme called carbonic anhydrase facilitates the transport of CO₂ from the tissue to the lungs. This enzyme is responsible for catalysing the reaction for formation of H₂CO₃



- The oxidized forms of myoglobin & haemoglobin are known as methemoglobin & methaemoglobin contain Fe (III) & do not bind O₂. The naked 'haem' the Fe-porphyrin complex without the accompanying protein is oxidized irreversibly to Fe (III) by molecular O₂ to give a M-O₂ bridge dimeric product.
- This would seem to be a fatal flaw for its biological function however this unproductive reaction is prevented by the protein environment



- In Mb porphyrin ring is converted in Polypeptide chain the polypeptide is formed from amino acid residues with nonpolar side groups & is there for hydrophobic.
- The same groups block access of larger molecules to the Fe atom neighbourhood & so prevent the formation of the Fe-O₂-Fe bridged species involved in the oxidative reaction of protein free haem.
- The structural information gained from the analysis of myoglobin served as the basis for hypothesis on tertiary cysteinyl residue (no disulphide bonds) & β-conformation but contains a very large proportion of α-helical structure.
- Between each identical subunit there are only a few electrostatic connections. Although there are two cysteinyl residue per α-chain & one per β-chain, no covalent bonding occurs between the four subunits.
- Between one α & one β subunit there are longer regions of electrostatic interactions which produce two identical dimers α₁β₁ and α₂β₂, which are capable of integrated movement.

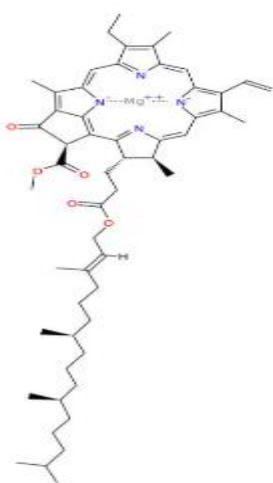


❖ Chlorophyll

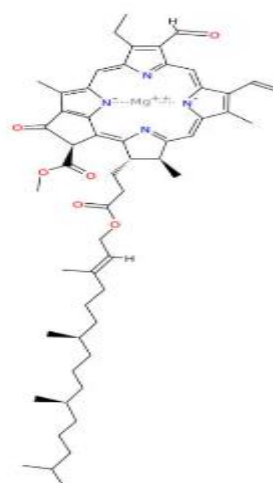
- The word "chlorophyll" comes from the Greek words chloros, which means "green", and phyllon, which means "leaf". Joseph Bienaimé Caventou and Pierre Joseph Pelletier first isolated and named the molecule in 1817.
- Chlorophyll is the name given to a group of green pigment molecules found in plants, algae, and cyanobacteria.
- Chlorophyll is an essential pigment molecule for photosynthesis, the chemical process plants use to absorb and use energy from light. It's also used as a food coloring (E140) and as a deodorizing agent. As a food coloring, chlorophyll is used to add a green color to pasta, the spirit absinthe, and other foods and beverages. As a waxy organic compound,
- The two most common types of chlorophyll are chlorophyll a, which is a blue-black ester with the chemical formula $C_{55}H_{72}MgN_4O_5$, and chlorophyll b, which is a dark green ester with the formula $C_{55}H_{70}MgN_4O_6$. Other forms of chlorophyll include chlorophyll c1, c2, d, and f. The forms of chlorophyll have different side chains and chemical bonds.
- All are characterized by a chlorin pigment ring containing a magnesium ion at its center.

➤ **Key Takeaways: Chlorophyll**

- ✓ Chlorophyll is a green pigment molecule that collects solar energy for photosynthesis. It's actually a family of related molecules, not just one.
- ✓ Chlorophyll is found in plants, algae, cyanobacteria, protists, and a few animals.
- ✓ Although chlorophyll is the most common photosynthetic pigment, there are several others, including the anthocyanins.
- ✓ Chlorophyll is known to be fat-soluble organic molecules having tetrapyrrole ring and due to this reason they are called the “Tetrapyrrole pigments or Magnesium chlorine”.
- ✓ They are known to be food producers of the cell found in green plants, and they are mainly located in the chloroplast
- ✓ Chlorophyll works as a factor for the proper growth of healthy and green plants.
- ✓ Chlorophyll is also present in the mesophyll cells in the leaves of green plants.
- ✓ Chlorophyll has a tendency to reject green colour by absorbing red and blue wavelengths of light from sun rays.
- ✓ It is also known as power of the cell-like mitochondria, as they help in the production of ATP.
- ✓ Chlorophyll structure is similar to that of heme group of haemoglobin and cytochromes, which is derived from protoporphyrin.
- ✓ Chlorophyll is not soluble in water. It is mixed with a small amount of oil when it's used in food.



Chlorophyll a



Chlorophyll b

Also Known As: The alternate spelling for chlorophyll is chlorophyl.

➤ **Role of Chlorophyll in Photosynthesis**

- ✓ The overall balanced equation for photosynthesis is:
- ✓ $6 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$
- ✓ Where carbon dioxide and water were react to produce glucose and oxygen.
- ✓ Plants and other photosynthetic organisms use chlorophyll to absorb light (usually solar energy) and convert it into chemical energy.
- ✓ In plants, chlorophyll surrounds photosystems in the thylakoid membrane of organelles called chloroplasts
- ✓ Chlorophyll absorbs light and uses resonance energy transfer to energize reaction centers in photosystem I and photosystem II.
- ✓ Electrons that enter the electron transport chain are used to pump hydrogen ions (H^+) across the thylakoid membrane of the chloroplast.
- ✓ The chemiosmotic potential is used to produce the energy molecule ATP and to reduce NADP^+ to NADPH. NADPH, in turn, is used to reduce carbon dioxide (CO_2) into sugars, such as glucose.

❖ **Toxic effect of trace elements**

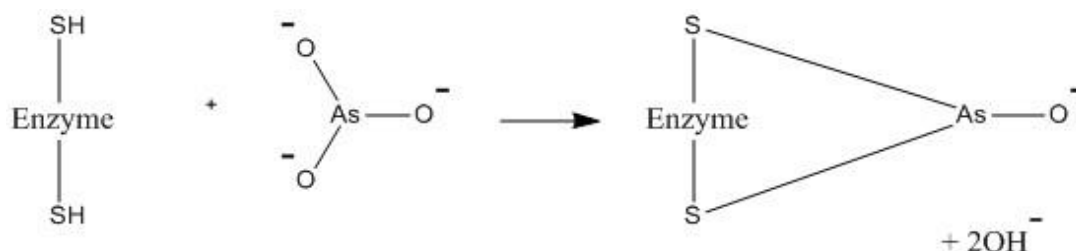
➤ **1) lead**

- ✓ Lead is widely distributed in our environment from automobiles & lead based panits.
- ✓ Most of the victims are childrens because of their property for chewing object those very often contain lead.
- ✓ It produced undesirable. Physiological effect such as the inhibition of synthesis of human red cells.
- ✓ Inhibition of activities in chronic intoxication. It increases pressure within the brain which many cause coma, convulsions, mental retardation even death.
- ✓ It may also damage the central nervous system. It is probably the most serious toxic metal around 70-90 % of the lead assimilated goes into the bones the next major accumulator is the liver, then kidneys.

➤ **2) Arsenic**

- ✓ Arsenic has some similar toxic properties to Pb, Hg & Cd as regards bonding to sulphate & inhibiting enzyme action such as pyruvate dehydrogenase.

- ✓ The order of toxicity of arsenic compound is Arsenes (As (III)) > Arsenite (As(III)) > Arsenate (As(v)) & arsenic organic acid As(v).
- ✓ Arsenic, which is found mainly in the kidneys, lungs & intestinal walls is readily absorbed if water soluble arsenic is also toxic by replacement of phosphorus in ATP & coagulation of protein.
- ✓ The toxic action of As(III) is by attacking –SH groups of an enzyme. Thereby inhibiting enzyme action.



➤ 3) Cadmium

- ✓ Cadmium is more toxic than lead. i.e. lower levels have an adverse effect on human beings. Tobacco product is a potential source of Cd-poisoning on smoking cigarette 1.4 g cadmium comes into our ecosystem as cadmium oxide which is in the more immediately toxic form.
- ✓ Cadmium accumulates in the liver & kidneys. Assessment of the cadmium body burden is difficult as level in both blood & urine are not good indicators.
- ✓ The main portion of Cd ingested into our body gets trapped in the kidneys & eliminated.
- ✓ A small amount is bound most effectively by the body protein metallothionein present in the kidneys while the rest gets stored in the body & gradually gets accumulated with age.
- ✓ When excessive amount of Cd^{+2} are ingested it replaces Zn^{+2} at key enzyme site.

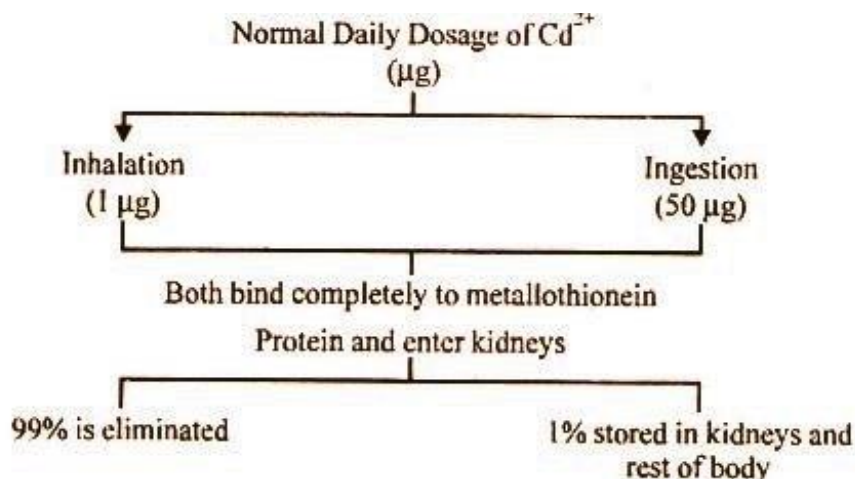


Fig. 3.15 : Metabolism of normal daily dosage of Cd^{2+} .

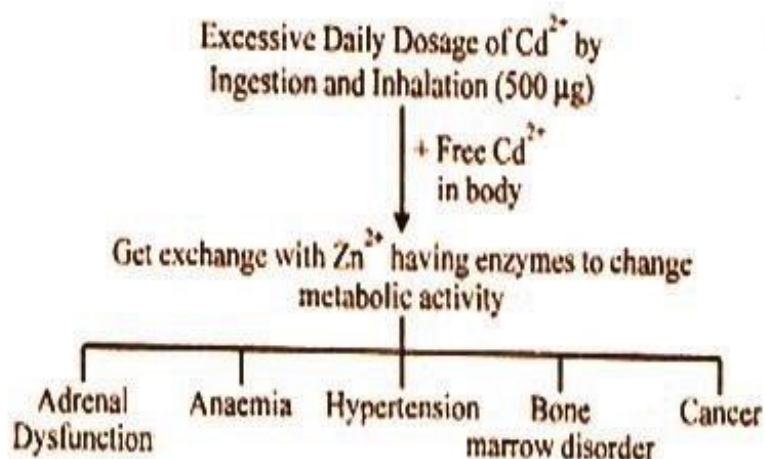


Fig. 3.16 : Metabolism of Excessive Dosage of Cd^{2+} .

➤ 4) Mercury

- ✓ Mercury is the most toxic heavy metal & many serious incident have resulted from mercury poisoning.
- ✓ An average daily intake of mercury is hard to estimate because of the contribution from fish.
- ✓ Around 1 g per person perday is taken in from air containing 50 $\mu\text{g m}^{-3}$ depending on its chemical form up to 80 % of this will be absorbed into the body mercury from fish is almost entirely as methyl mercury.
- ✓ The toxicity of mercury is related to the chemical form liquid mercury appears to have little effect but mercury vapour is readily absorbed into the blood stream producing brain damage. Hg (I) salts are relatively non-toxic compared with Hg (II) compounds because of their low solubility.
- ✓ Element Hg has been fairly inert & non-toxic if it is swallowed it gets excreted without causing serious damage.

- ✓ Hg should be handled only in well ventilated areas & spills must be cleaned up as early as possible to avoid vapors contact.
- ✓ Hg vapours when an inhale enters the brain through the blood stream giving rise to severe damage of the central nervous system.
- ✓ **Chemical species of mercury & biochemical properties**

Species	Chemical & biochemical properties
Hg	It is relatively inert & non-toxic, its vapour is highly toxic when inhaled
Hg ₂ ⁺²	It is insoluble as chloride its toxicity is low
Hg ⁺²	It is non-toxic but easily gets transported across biological membrane
RHg ⁺	It is highly toxic especially CH ₃ Hg ⁺ (Methyl mercury), it is brings about irreversible nerve & brain damage, it is readily transported across biological membrane, it is stored in fat tissue
HgS	It is insoluble & non-toxic, it is trapped in soil in this form

❖ Questionary

- 1) What is Bio-inorganic chemistry?
- 2) Give structure of Porphyrin.
- 3) How many heme units are arranged in Haemoglobin?
- 4) In mankind 1000ml of blood contains how many grams of haemoglobin?
- 5) What is the difference in structure of Chlorophyll a and chlorophyll b
- 6) Give photosynthesis reaction
- 7) Which metal is very toxic for human being?
- 8) Write short note on myoglobin.
- 9) Discuss the role of chlorophyll in photo synthesis.
- 10) Discuss about structure of haemoglobin and their importance
- 11) Explain effect on human of any two toxic metals.