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Coordination Chemistry and Binding Properties with Zinc (II) Cations

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ABSTRACT

The solution and complexation chemistry of zinc ions is the basis for zinc biology. In living organisms, zinc is redox-inert and has only one valence state: Zn(II). Its coordination environment in proteins is limited by oxygen, nitrogen, and sulfur donors from the side chains of a few amino acids. In an estimated 10% of all human proteins, zinc has a catalytic or structural function and remains bound during the lifetime of the protein. However, in other proteins zinc ions bind reversibly with dissociation and association rates commensurate with the requirements in regulation, transport, transfer, sensing, signalling, and storage. In contrast to the extensive knowledge about zinc proteins, the coordination chemistry of the "mobile" zinc ions in these processes, i.e. when not bound to proteins, is virtually unexplored and the mechanisms of ligand exchange are poorly understood. Knowledge of the biological inorganic chemistry of zinc ions is essential for understanding its cellular biology and for designing complexes that deliver zinc to proteins and chelating agents that remove zinc from proteins, for detecting zinc ion species by qualitative and quantitative analysis, and for proper planning and execution of experiments involving zinc ions and nanoparticles such as zinc oxide (ZnO). In most investigations, reference is made to zinc or Zn^{2+} without full appreciation of how biological zinc ions are buffered and how the d-block cation Zn^{2+} differs from s-block cations such as Ca^{2+} with regard to significantly higher affinity for ligands, preference for the donor atoms of ligands, and coordination dynamics. Zinc needs to be tightly controlled. The interaction with low molecular weight ligands such as water and inorganic and organic anions is highly relevant to its biology but in contrast to its coordination in proteins has not been discussed in the biochemical literature. From the discussion in this article, it is becoming evident that zinc ion speciation is important in zinc biochemistry and for biological recognition as a variety of low molecular weight zinc complexes have already been implicated in biological processes, e.g. with ATP, glutathione, citrate, ethylenediaminedisuccinic acid, nicotianamine, or bacillithiol.

KEYWORDS: *coordination, zinc, cations, chemistry, binding, investigations, properties*

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INTRODUCTION

Zinc fingers (ZFs) are among the most structurally diverse protein domains. They interact with nucleic acids, other proteins and lipids to facilitate a multitude of biological processes. Currently, there are more than 10 known classes of ZFs, with various architectures, metal binding modes, functions and reactivity. The versatility, selectivity and stability of these short amino acid sequences is achieved mainly by (i) residues participating in Zn(II) coordination (mostly Cys and His), (ii) hydrophobic core and ZF structure formation, and (iii) variable residues responsible for inter- and intramolecular interactions. Since their discovery, ZFs have been extensively studied in terms of their structure, stability and

recognition targets by the application of various methodologies. Studies based on interactions with other metal ions and their complexes have contributed to the understanding of their chemical properties and the discovery of new types of ZF complexes, such as gold fingers or lead fingers. Moreover, due to the presence of nucleophilic thiolates, ZFs are targets for reactive oxygen and nitrogen species as well as alkylating agents. Interactions with many reactive molecules lead to disturb the native Zn(II) coordination site which further result in structural and functional damage of the ZFs. The post-translational modifications including phosphorylation, acetylation, methylation or nitrosylation frequently affect ZFs function via changes in the protein structure and dynamics. Even though the literature is replete with structural and stability data regarding classical (ββα) ZFs, there is still a huge gap in the knowledge on physicochemical properties and reactivity of other ZF types. In this review, metal binding properties of ZFs and stability factors that modulate their functions are reviewed. These include interactions of ZFs with biogenic and toxic metal ions as well as damage occurring upon reaction with reactive oxygen and nitrogen species, the methodology used for ZFs characterization, and aspects related to coordination chemistry.[1,2]

Observations

Zinc is required for the activity of > 300 enzymes, covering all six classes of enzymes. Zinc binding sites in proteins are often distorted tetrahedral or trigonal bipyramidal geometry, made up of the sulfur of cysteine, the nitrogen of histidine or the oxygen of aspartate and glutamate, or a combination. Zinc in proteins can either participate directly in chemical catalysis or be important for maintaining protein structure and stability. In all catalytic sites, the zinc ion functions as a Lewis acid. Researchers in our laboratory are dissecting the determinants of molecular recognition and catalysis in the zinc-binding site of carbonic anhydrase. These studies demonstrate that the chemical nature of the direct ligands and the structure of the surrounding hydrogen bond network are crucial for both the activity of carbonic anhydrase and the metal ion affinity of the zinc-binding site. An understanding of naturally occurring zinc-binding sites will aid in creating de novo zinc-binding proteins and in designing new metal sites in existing proteins for novel purposes such as to serve as metal ion biosensors.[3,4]

TABLE 1:Comparison of the zinc ligands (L_1, L_2, L_3 and L_4) and the spacers (X, Y and Z) between zinc ligands in catalytic and structural zinc sites[1]

	L_1	X	L_2	Y	L_3	Z	L_4	Solvent
Catalytic zinc								
Oxidoreductases[2]								
Alcohol dehydrogenase (horse liver)[3]	C_{37}	20	H_{59}	106	C_{174}			H_2O
Alcohol dehydrogenase (Thermoanaerobium brockii)[4]	C_{37}	21	H_{59}	90	D_{150}		NA[5]	
Hydrolases								
Carboxypeptidase A (bovine)[6,7]	H_{69}	2	E_{72}	123	H_{196}			H_2O
Thermolysin (Bacillus thermoproteolyticus)[8,9]	H_{142}	3	H_{146}	19	E_{166}			H_2O
DD carboxypeptidase (Streptomyces albus)[10]	H_{196}	2	H_{193}	40	H_{152}			H_2O
Astacin (crayfish)[11]	H_{92}	3	H_{96}	5	H_{102}			H_2O
β-Lactamase (Bacillus cereus)[12]	H_{86}	1	H_{88}	121	H_{210}			H_2O
Cytidine deaminase (Escherichia coli)[13]	C_{132}	2	C_{129}	26	H_{102}			H_2O
Alkaline phosphatase (E. coli)[14]	D_{327}	3	H_{331}	80	H_{412}			H_2O
Adenosine deaminase (murine)[15]	H_{15}	1	H_{17}	196	H_{214}	80	D_{295}	H_2O
Lyases								
Carbonic anhydrase II (human)[17,16]	H_{94}	1	H_{96}	22	H_{119}			H_2O
Carbonic anhydrase (spinach)[18]	C_{213}	2	H_{210}	59	C_{150}			H_2O
Carbonic anhydrase (Methanosarcina thermophila)[19]	H_{81}	35	H_{117}	NA[19]	H_{122}			H_2O

Novel catalytic zinc sites								
Transferases								
Protein farnesyltransferase (rat)[20]	D_{297}	1	C_{299}	62	H_{362}			H_2O
Cobalamin-dependent methionine synthase (E. coli)[21]	C_{247}	62	C_{310}		C_{311}		N/O atom	
Cobalamin-independent methionine synthase (E. coli)[21]	H_{641}	1	C_{643}	82	C_{726}		N/O atom	
Nonenzymatic								
Ada repair protein (E. coli)[22]	C_{38}	3	C_{42}	26	C_{69}	2	C_{72}	No
Structural zinc								
Alcohol dehydrogenase (horse liver)[3]	C_{97}	2	C_{100}	2	C_{103}	7	C_{111}	No
Aspartate carbamoyltransferase (E. coli)[23]	C_{109}	4	C_{114}	23	C_{138}	2	C_{141}	No
Zinc finger (Zif268) (mouse)[24]	C_7	5	C_{12}	12	H_{25}	4	H_{29}	No
Glucocorticoid receptor (rat)[25]	C_{440}	2	C_{443}	8	C_{457}	2	C_{460}	No
Ferrodoxin (Sulfolobus sp.)[26]	H_{16}	2	H_{19}	14	H_{34}	41	D_{76}	No

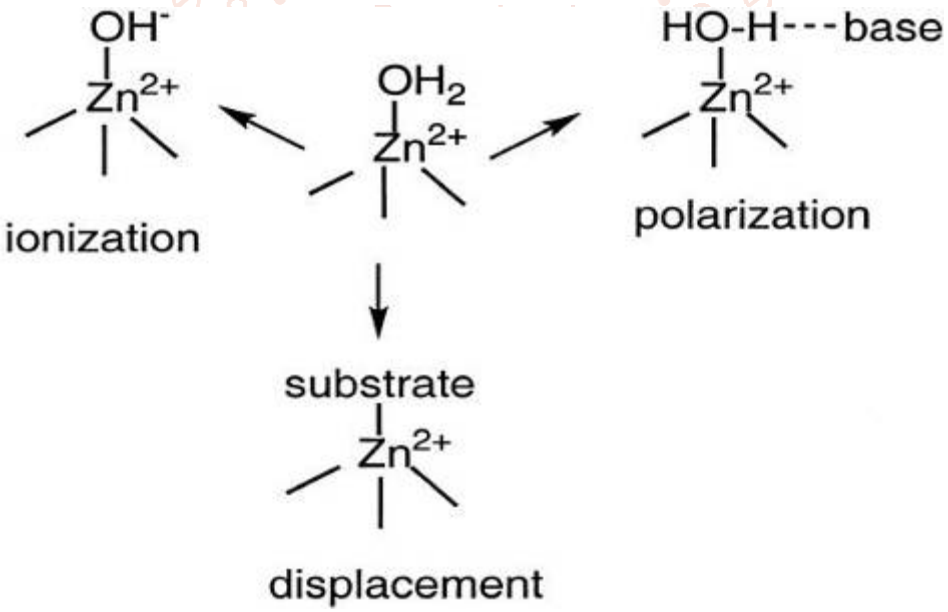
1.Included in this table are representative enzymes in which the active site ligands differ. The protein ligands are shown using the one-letter amino acid codes of: H, histidine; C, cysteine; D, aspartate; and E, glutamate.

2.The relatively long spacer between L_1 and L_2 is unusual, and it may be due to the requirements of NAD(H) cofactor binding at the active site.

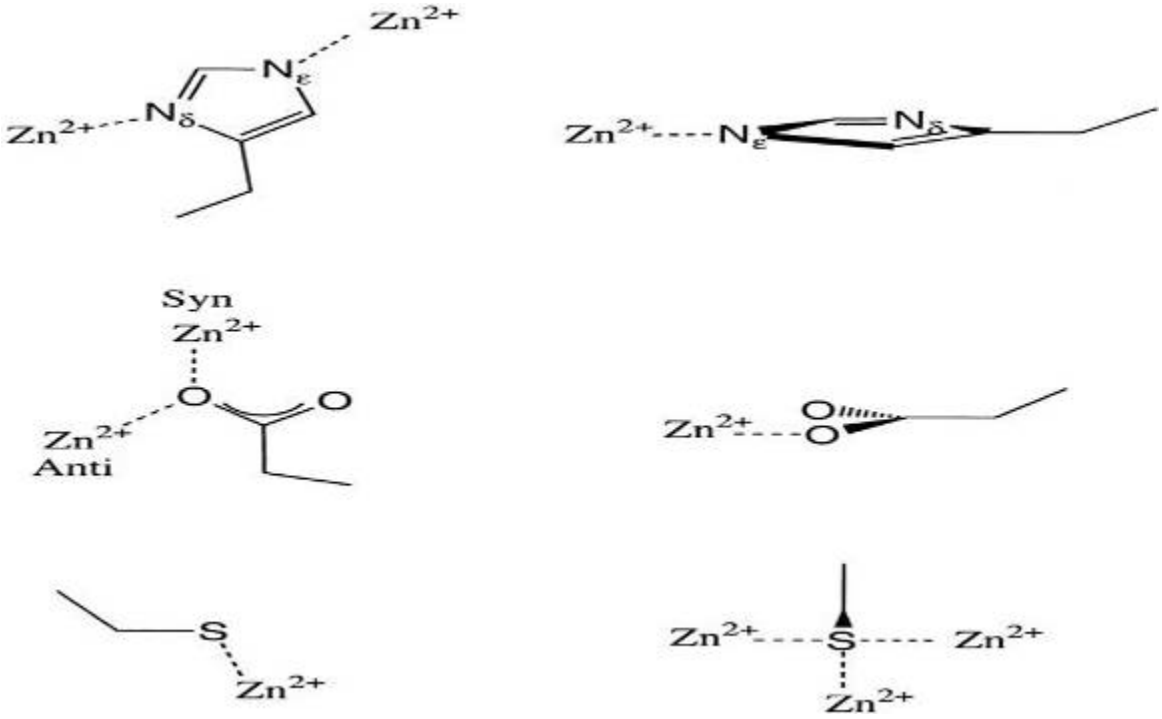
5.Not available. The zinc ligands were determined by mutations that abolish both the zinc-binding affinity and the catalytic activity.

19.The zinc site of carbonic anhydrase of M. thermophila is composed of three histidines: His_{81} and His_{122} from one subunit and His_{117} from the neighboring subunit.

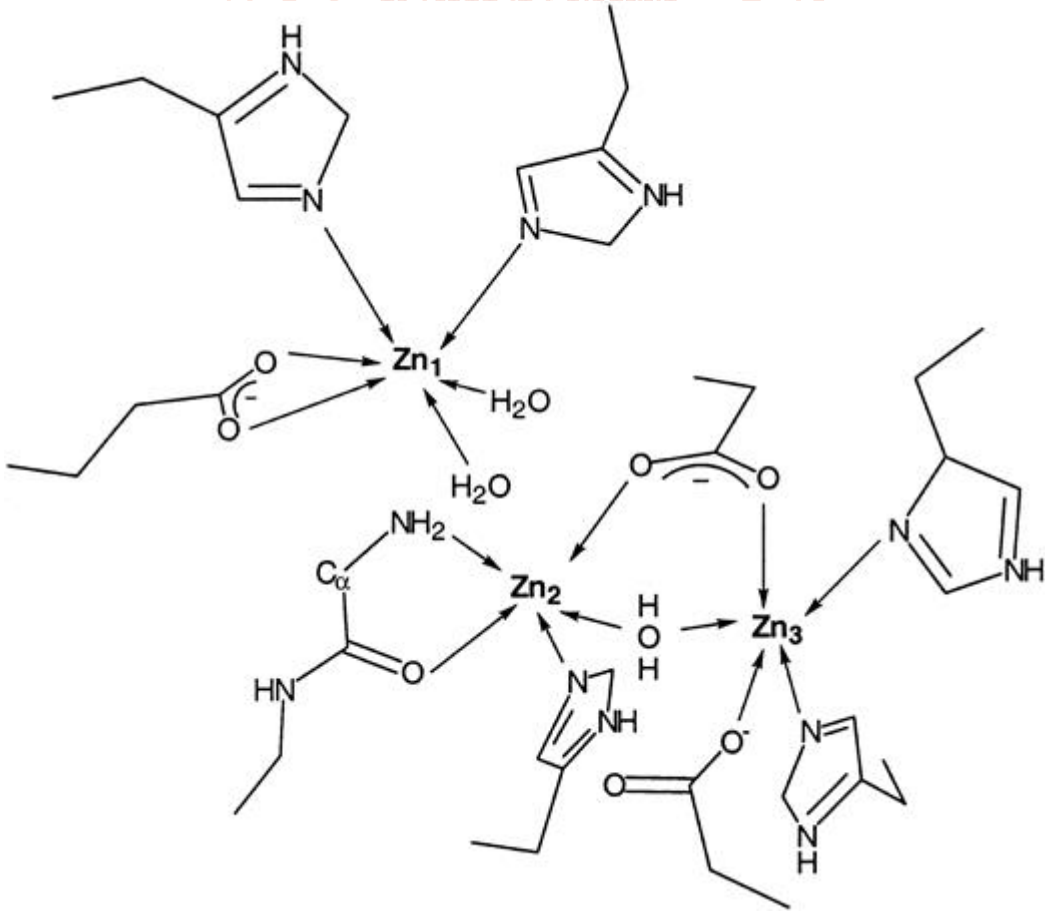
21.The type of zinc ligands of cobalamin-independent methionine synthase were determined by EXAFS to be a combination of two S atoms and two N/O atoms.[5,6]



The X-ray structures of catalytic zinc enzymes from four of the six classes of enzymes (oxidoreductases, transferases, hydrolases and lyases) have been determined, and they define the features of catalytic zinc-binding sites. Unlike the structural sites, the metal ion in catalytic sites is generally coordinated to the side chain of three amino acid residues, a combination of histidine, glutamate, aspartate and cysteine, and a solvent molecule completes the tetrahedral coordination sphere. However, the zinc polyhedra of adenosine deaminase (EC 3.5.4.4)



The majority of histidine zinc ligands found in zinc protein structures coordinate zinc through the N_ε atom although coordination with N_δ atoms has also been observed. For these interactions, the metal ion prefers a head-on and in-plane approach to the sp^2 lone pair of the nitrogen atom Carboxylate-zinc interactions with syn-stereochemistry are observed more frequently than those with anti-stereochemistry, and the zinc ion displays a preference to be in the plane of the carboxyl. A stereochemical analysis of cysteine-zinc interactions in the Brookhaven Data Bank revealed that the average sulfur-zinc distance is 2.1 Å, the average C_β-S-zinc angle is 112 degrees and the C_α-C_β-S-zinc torsion angle distribution is trimodal with peaks at ± 90 and 180 degrees.



Example of cocatalytic zinc site: phospholipase C. In phospholipase C, as in nuclease P1, the backbone amino and carbonyl groups of N-terminal Trp_1 coordinate Zn_2.[7,8]

Discussion

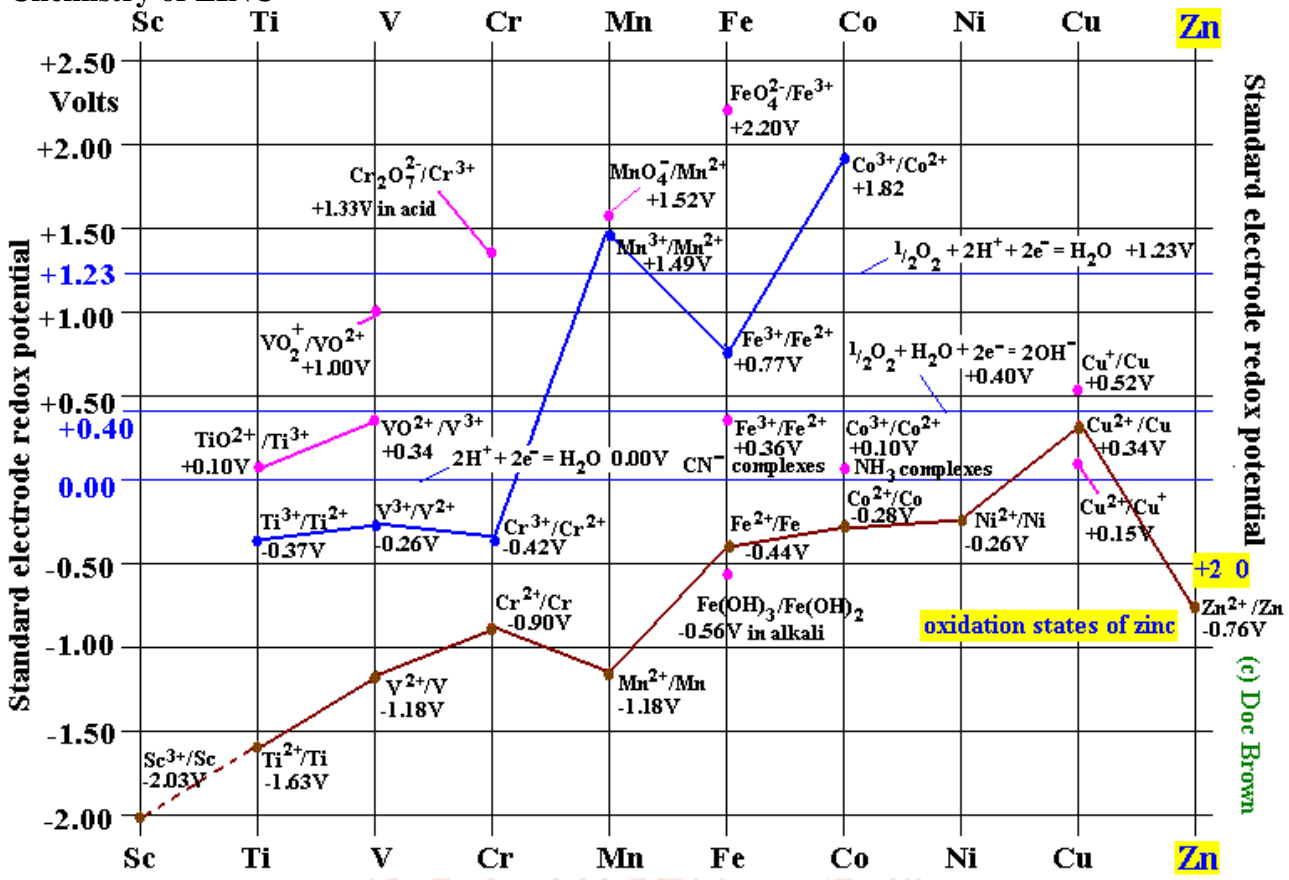
In natural waters, zinc speciation has been investigated widely and Zn2þ (aq), ZnCO3 o , ZnSO4 o , Zn(OH)2 , ZnClþ, ZnCl2, ZnCl3 , and ZnCl4 2 have been identified. In this literature, the supscript (o) refers to the soluble forms, ie. Zn(OH)2 ¼ Zn(OH)2(aq). The chemical formulae do not indicate the bound water molecules. Thus, ZnClþ is actually [ZnCl(H2O)x-1] þ according to the speciation and nomenclature discussed above. [9,10] The concentrations of these species depend on the pH of the aqueous solution, the anion concentrations and the presence of dissolved organic matter (DOM), which on average contributes with a logK of 6.4e7.0 with ligands such as humic and fulvic acid. Chloride species become important with increasing salinity. The concentrations of zinc hydroxo and carbonato complexes increase above pH 7.5 and become the predominant species above pH 8. Sulfide also contributes, even in oxic water. In anoxic water, ZnS nanoparticles and Zn-S clusters have been identified: [Zn3S3(H2O)6] and [Zn4S6(H2O)4] 4- [30,31]. It is quite remarkable that the nuclearity of these complexes with regard to zinc is exactly what is found in the two zinc-sulfur clusters of mammalian metallothioneins. Distribution of elements in blood often reflects their distribution in sea water. However, within cells, a different milieu is maintained as the concentrations of chloride and hydrogen sulfide (HS) are kept relatively low, though the latter is a signalling substance and a component of the structure of Fe-S clusters. Whether these anions [11,12] are involved in coordinating zinc ions or the presumable coordination changes during zinc transport from/into cells is not known. In the cell, these anions are also buffered, ie. there is a controlled equilibrium between free and bound, though the term buffering is not used in this context. Hydrogen sulfide is kept at very low concentrations, but hydrogen phosphate (HPO4 2), sulfate (SO4 2), hydrogen carbonate/carbonate (HCO3), and chloride are all present at millimolar concentrations .Hydrogen sulfide, hydrogen phosphate, and sulfate are the strongest inorganic anions for zinc [13] There is also diphosphate (pyrophosphate, P2O7 4), triphosphate (P3O10 5), tetraphosphate (P4O13 6), and inositol phosphate , all of which bind zinc much more efficiently with apparent dissociation constants (pKd) of 2.7, 6.9, 7.2 and 10.4, respectively [32e35]. Acetate, carbonate, and chloride are ligands with intermediate strength for coordinating with zinc ions, and some anions are biological ligands of zinc in proteins. Free acetate is expected to be very low as it is mainly in the form of acetyl-CoA. Other organic acids that are metabolites can also serve as potential ligands. Hydrogen carbonate is a ligand in the zinc enzyme carbonic anhydrase. Chloride has been identified as a ligand of zinc in the crystal structures of some zinc proteins. Chloride is likely to be a ligand in ternary complexes with other ligands if expansion of the coordination sphere is possible. Hydrogen phosphate interacts with zinc sites in metallophosphatases. Chloride complexes are likely significant in the stomach, which contains up to 0.1 M HCl, whereas carbonate complexes likely play a role in the duodenum where Brunner's glands provide an alkaline secretion high in bicarbonate to neutralize the acid from the stomach. When preparing zinc salt solutions for biological experiments the possibility of these anions forming zinc complexes and affecting the outcome of the experiment(s) is significant and should be considered, in particular in the absence of other ligands with competing affinity for zinc. Physiological salt solutions are often based on phosphates and so are cell culture media, which provide ligands for zinc in the absence of serum. Considering speciation of complexes with anions is not only important for bioavailability of zinc ions but also for interactions with proteins, which may be very specific and lead to either activation or inactivation of a biological process. Sodium or potassium chloride added to biological buffers to adjust their ionic strength will change zinc speciation, especially in the absence of other ligands with high affinity for zinc. Perchlorate does not occur naturally in biological systems and nitrate concentrations are very low [14]Other negatively charged metal anion or oxoanion complexes may also form insoluble zinc complexes. Examples are [Fe(CN)6] 4- or [Hg(SCN)4] 2- used in analytical chemistry to precipitate zinc ions.

Results

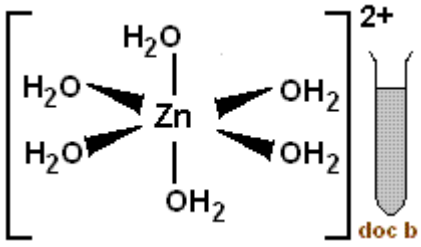
Zinc cannot form an ion with an incomplete d sub–shell and is therefore not a true transition element. Zinc's chemistry is determined solely by the formation of compounds in its +2 oxidation state, but it does form many complexes, though not as many as other transition metals.

principal oxidation states of zinc, redox reactions of zinc, ligand substitution displacement reactions of zinc, balanced equations of zinc chemistry, formula of zinc complex ions, shapes colours of zinc complexes, formula of compounds[15]

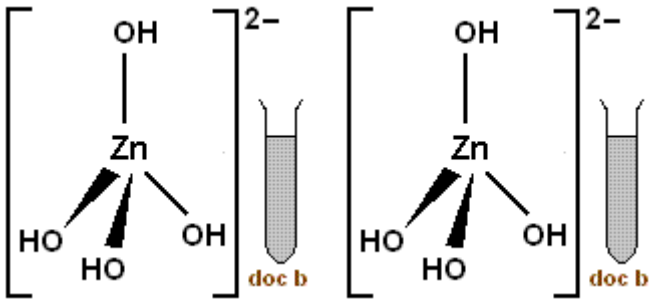
The Chemistry of ZINC



- The electrode potential chart highlights the value for the one positive oxidation state of zinc.
- Although a member of the 3d–block, zinc is NOT a true transition metal.
- Zinc metal readily dissolves in dilute hydrochloric acid or dilute sulfuric acid reducing hydrogen ions to hydrogen gas.



- $Zn_{(s)} + 2H^+_{(aq)} \Longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$
- The Zn^{2+} ion has a full sub–shell, $3d^{10}$, which does not allow the electronic transitions which account for the colour in transition metal compounds.
- See Appendix 4. complex ion colour theory
- In aqueous solution zinc forms the colourless stable hydrated zinc ion, $[Zn(H_2O)_6]^{2+}_{(aq)}$ and most complexes of the zinc ion have a co–ordination number of 6.
- Solutions of zinc sulfate $ZnSO_{4(aq)}$ or zinc chloride $ZnCl_{2(aq)}$ are suitable for laboratory experiments for investigating the aqueous chemistry of the zinc ion..
- The alkalis sodium hydroxide or ammonia, produce the hydrated white gelatinous zinc hydroxide precipitate. There is a further reaction with excess of NaOH or NH_3.
- $Zn^{2+}_{(aq)} + 2OH^-_{(aq)} \Longrightarrow Zn(OH)_{2(s)}$ (can be written as $[Zn(OH)_2(H_2O)_2]$)
- or $[Zn(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Zn(OH)_{2(aq)} + 6H_2O_{(l)}$
- A precipitation reaction which you can expression via various equations!
- Zinc ions with excess sodium hydroxide:
- (i) $[Zn(H_2O)_6]^{2+}_{(aq)} + 4OH^-_{(aq)} \rightleftharpoons [Zn(OH)_4]^{2-}_{(aq)} + 6H_2O_{(l)}$ (from original aqueous ion)
- or (ii) $Zn(OH)_{2(s)} + 2OH^-_{(aq)} \rightleftharpoons [Zn(OH)_4]^{2-}_{(aq)}$ (from hydroxide ppt.)



- For (i) the formation of tetrahydroxozincate ion is a ligand exchange reaction (hydroxide ion for water) with change in shape (octahedral to tetrahedral), change in co-ordination number (from 6 to 4), but no change in oxidation state of zinc (+2). However the overall charge on the zinc complex changes from 2+ to 2- (2+ 4x-1).
- In fact zinc oxide is a classic amphoteric oxide e.g. giving a 'zincate' with alkali and a chloride salt with hydrochloric acid.
- $ZnO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} ==> Na_2Zn(OH)_{4(aq)}$
- $ZnO_{(s)} + 2HCl_{(aq)} ==> ZnCl_{2(aq)} + H_2O_{(l)}$
- Zinc ions with excess ammonia:
- $[Zn(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Zn(NH_3)_4]^{2+}_{(aq)} + 6H_2O_{(l)}$ (formation from original aqueous ion)
- The formation of the tetraammine zinc(II) ion is a ligand exchange reaction (ammonia for water) with change in shape (octahedral to tetrahedral), co-ordination number changes (from 6 to 4), but no change in the oxidation state of zinc (+2) or overall change in the net charge on the zinc complex ion (2+, since both ligands involved are neutral).
- or $Zn(OH)_{2(s)} + 4NH_{3(aq)} \rightleftharpoons [Zn(NH_3)_4]^{2+}_{(aq)} + 2OH^-_{(aq)}$ (or from hydroxide precipitate)
- The ammonia ligand displaces the water/hydroxide ion ligands.
- With aqueous of sodium carbonate zinc ion solutions produce a precipitate of white zinc carbonate, but its a basic carbonate, i.e. the carbonate precipitate is mixed with the hydroxide, $Zn(OH)_2$.
- $Zn^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} ==> ZnCO_{3(s)}$
- better prepared using $NaHCO_3$: $Zn^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} ==> ZnCO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$
- Some examples of zinc complex ion formation
- The variation of the stability constant with change in ligand is illustrated with the zinc ion.[16]
- The data set for zinc compares five different monodentate ligands and the polydentate ligand EDTA.
- Apart from the EDTA complex the stability constant (Kstab) equilibrium expression is
- $K_{stab} = \{[ZnL_4]^{2+/2-}_{(aq)}\} / \{[Zn(H_2O)_4]^{2+}_{(aq)}\} \{[L_{(aq)}]^4\}$ $mol^{-4}dm^{12}$

Table 2: Ligand substitution reaction to give new complex ion

Ligand substitution reaction to give new complex ion	K_{stab}	lg K_{stab}
$[Zn(H_2O)_4]^{2+}(aq) + 4CN^-(aq) ==> Zn(CN)_4]^{2-}(aq) + 4H_2O(l)$	5.0×10^{16}	16.7
$[Zn(H_2O)_4]^{2+}(aq) + 4NH_3(aq) ==> Zn(NH_3)_4]^{2-}(aq) + 4H_2O(l)$	3.8×10^{9}	9.58
$[Zn(H_2O)_4]^{2+}(aq) + 4Cl^-(aq) ==> [ZnCl_4]^{2-}(aq) + 4H_2O(l)$	1.0	0.0
$[Zn(H_2O)_4]^{2+}(aq) + 4Br^-(aq) ==> [ZnBr_4]^{2-}(aq) + 4H_2O(l)$	10^{-1}	–1.0
$[Zn(H_2O)_4]^{2+}(aq) + 4CN^-(aq) ==> [Zn(CN)_4]^{2-}(aq) + 4H_2O(l)$	10^{-2}	–2.0
$[Zn(H_2O)_4]^{2+}(aq) + EDTA^{4-}(aq) ==> [ZnEDTA]^{2-}(aq) + 4H_2O(l)$	3.2×10^{16}	16.5

- The very value for the tetracyanozincate(II) in reflects the strong of central metal ion (Zn^{2+}) – ligand (CN) bond.
- The lower Kstab value for ammonia indicates on average a weaker dative covalent bond.
- The ligand bonds are even weaker for the halide ions possibly due to their larger radius, since there is a steady decrease in Kstab as the halide radius increases, making the Zn–X dative covalent bond longer and weaker.
- The stability constant for the zinc–EDTA complex is a very high value, typical for a polydentate ligand .[17]

Conclusion

- Zinc is extracted from either zinc blende/sphalerite ore (zinc sulfide) or sometimes calamine/Smithsonite ore (zinc carbonate).
- (1) The zinc sulfide ore is roasted in air to give impure zinc oxide.
- $2ZnS_{(s)} + 3O_{2(g)} ==> 2ZnO_{(s)} + 2SO_{2(g)}$

- Note: calamine ore can be used directly in a zinc smelter because on heating it also forms zinc oxide.

➢ $ZnCO_{3(s)}$ ==> $ZnO_{(s)}$ + $CO_{2(g)}$ (endothermic thermal decomposition)

➢ (2) The impure zinc oxide can be treated in two ways to extract the zinc:

- It is roasted in a smelting furnace with carbon (coke, reducing agent) and limestone (to remove the acidic impurities).

➢ $C_{(s)}$ + $O_{2(g)}$ ==> $CO_{2(g)}$ (very exothermic oxidation, raises temperature considerably)

➢ $C_{(s)}$ + $CO_{2(g)}$ ==> $2CO_{(g)}$ (C oxidised, CO_2 reduced)

➢ $ZnO_{(s)}$ + $CO_{(g)}$ ==> $Zn_{(l)}$ + $CO_{2(g)}$ (zinc oxide reduced by CO, Zn undergoes O loss)

➢ or direct reduction by carbon: $ZnO_{(s)}$ + $C_{(s)}$ ==> $Zn_{(l)}$ + $CO_{(g)}$ (ZnO reduced, C oxidised)

➢ The carbon monoxide acts as the reducing agent i.e. it removes the oxygen from the oxide.[18]

➢ The impure zinc is then fractionally distilled from the mixture of slag and other metals like lead and cadmium out of the top of the furnace in an atmosphere rich in carbon monoxide which stops any zinc from being oxidised back to zinc oxide.

➢ The slag and lead (with other metals like cadmium) form two layers which can be tapped off at the base of the furnace.

➢ The zinc can be further purified by a 2nd fractional distillation or more likely by dissolving it in dilute sulfuric acid and purified electrolytically as described below.

- (b)Two stages

➢ It is dissolved and neutralised with dilute sulfuric acid to form impure zinc sulfate solution.

➢ $ZnO_{(s)}$ + $H_2SO_{4(aq)}$ ==> $ZnSO_{4(aq)}$ + $H_2O_{(l)}$

➢ or using calamine ore/zinc carbonate directly:

➢ $ZnCO_{3(s)}$ + $H_2SO_{4(aq)}$ ==> $ZnSO_{4(aq)}$ + $H_2O_{(l)}$+ $CO_{2(g)}$

➢ Quite pure zinc is produced from the solution by electrolysis. It can be deposited on a pure zinc negative electrode (cathode) in the same way copper can be purified. The other electrode, must be inert e.g. for laboratory experiments, carbon (graphite) can be used and oxygen is formed.

➢ $Zn^{2+}_{(aq)}$ + $2e^-$ ==> $Zn_{(s)}$

➢ A reduction process, electron gain, as zinc metal is deposited on the (–) electrode.

➢ You can't use solid zinc oxide directly because its insoluble and the ions must free to carry the current and migrate to the electrodes in some sort of solution.[19]

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