# Hydrated Metal Ions in Aqueous Solution

<u>Models/Topics Covered</u>: Geometries of CN>3, Crystal Field Theory, Ligand Field Theory, Geometric Distortion in d-Block Complexes, Periodic trends in Metal-Ligand Bonding, Spectrochemical Series, (Brønsted-Lowry) Acidity



## Question 1 (s-Block Cations) [1-2]

For the alkali metals, hydrate Li(I) and Na(I) are thought to adopt octahedral coordination figures in aqueous solution, K(I), Rb(I) square antiprismatic, and Cs(I) a 12-coordinate geometry. Alkaline earth metals have better defined hydrated forms than the alkali metals, with Be(II) tetrahedral, Mg(II) octahedral and Ca(II), Sr(II), and Ba(II) square antiprismatic.

- (i). Draw an example of each of the above-named geometries (i.e. not 12-coordinate Cs). Assume no distortion.
- (ii). Explain the trend for increasing coordination number down the group. Indicate why only Be(II) is thought to be tetrahedral.

#### Question 2 (First Row d-Block Metals) [2,4-7]

- (i). Mid to late transition metal aqua complexes (Groups 7-10) are octahedral in most oxidation states, with the notable exception of Cu(I), which is thought to be tetrahedral. Give the d-splitting patterns and indicate the electron occupancy for Mn(II) to Zn(II) (octahedral) and Cu(I) (tetrahedral).
- (ii). Whilst still hexacoordinate and octahedral, the geometry of Cu(II) deviates from that typically expected. Indicate how and give the reason for this. Assuming octahedral complexation, which other d-electron count(s) is/are likely to demonstrate this same property?
- (iii). The species formed by hydration of early transition metal aqua complexes (in their group oxidation state) are affected by the potential for these ions to undergo additional reactions in water, in comparison to later transition metals. Indicate the reactions they undergo, the rationale for this, and suggest possible species formed.

# Question 3 (Heavier d-Block Metals) [2,8-9]

Hydrated platinum(II) and palladium(II) were long thought to be square planar, but have since been shown to have (very) weakly interacting water molecules in the axial positions for both hydrated Pd(II) and Pt(II), giving a heavily distorted octahedral geometry. The hydrated structures of Hg(II) and Ag(I) are also complex. Hydrated Hg(II) is thought to adopt a distorted octahedron, and Ag(I) is known to bind two molecules of water strongly with 2-4 thought to engage in long range interactions. Giving a distorted structure based on either a 2-coordinate linear complex or a 4-coordinate tetrahedron.

- (i). Draw the square planar splitting pattern. This geometry is very common for complexes of Pd(II), Pt(II), Rh(I), Rh(II), Ir(I) and Ir(III) (amongst others). Explain this observation.
- (ii). Suggest how the splitting pattern might be altered by the addition of the two weakly interacting water molecules in the axial positions.
- (iii). Ag(I) species often adopt a purely linear configuration. Give the d-splitting pattern for this geometry, and suggest what effect or effects are responsible for distortion in the hydrated Ag(I) cation.

# Question 4 (Rare Earth Metals) [1-2]

Hydrated lanthanide cations can be divided into four triads based on their hydrated structures in aqueous solutions (as shown below). All are based on the nonacoordinate tricapped trigonal prismatic geometry. Rationalise this observation.



Reproduced from Ref[2]: (left) Tricapped trigonal prismatic geometry (Fig. 2), (right) Tetrads indicating the different variants in hydrated Ln(III) structure (Fig. 5)

## Question 5 (Heavy p-Block Metals) [2,10]

Pb(II) adopts a very unusual hexacoordinate geometry referred to as a hemi-directed conformation, as shown. Preference for hemidirected or the opposite, holo-directed, conformation depend on a number of factors including number of coordinating ligands and resulting steric crowding, ligand flexibility, and additional repulsion between ligands that carry a formal charge.



Reproduced from Ref[2]: Hemi-directed structure of hydrated Pb(II) (Fig. 4)

- (i). Explain the electronic origin for the hemi-directed conformation of hydrated Pb(II) (note: hydrated Tl(I) and Sn(II) are also thought to demonstrate the same effect).
- (ii). By contrast, Bi(III) adopts an octacoordinate holo-directed conformation. Suggest a geometry for this species.
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