Coordination Geometry Primer

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Introduction

Bioinorganic chemistry is a field that examines the interactions between metals and metalloproteins, and coordination geometry, which focuses on understanding coordination complexes, is a subfield that lies in the heart of this study. Coordination geometry is important because it characterizes the interactions between metals and ligands, and many derived rules can be used to predict the structure/stability of a coordination complex and answer questions like, “Does Mn(IV) prefer six-coordination or four-coordination?”, or “Does Cu(II) or Mn(II) have a stronger tendency towards six-coordination?”. In a synthetic biology context, knowing the answers to these questions can be largely beneficial towards protein design and engineering, because we can then obtain preliminary predictions, without having to do excessive lab work or modelling, to questions of the form “Given that the protein has this binding site, can it bind to this metal?” This document thus aims to cover the basics in coordination geometry so that we can provide an answer to “why does this metal bind to this protein” at least at a high level.

Compared to most fields of chemistry, coordination geometry is relatively new, with deliberate efforts to prepare and characterize “modern-day” coordination complexes only beginning in the nineteenth century. So the first question is, what makes coordination geometry so special? One of the largest factors is the uniqueness of bonds involving metals, particularly transition metals. We are all familiar with the story about Lewis structures, octet rules and covalent bonds. Unfortunately, this model only works for a selective few atoms (not even the first 20, which is often what is taught in high school; the expanded octet has to be invoked in a few cases). But where it really starts to fail is when we reach the transition metals, which are most of the d-block elements. Why are these different? Well, if we think back to electronic structures, we realize that interesting things happen between the 3d and 4s orbitals. According to the Aufbau principle, the 4s orbital is lower in energy than the 3d orbital (although they are in fact fairly close in energy levels, if one performs the calculations; this is why transition elements can lose both 3d and 4s electrons to have variable oxidation states), so we should fill in the 4s electrons first. However, once 3d orbitals are occupied by electrons, as in transition metals, since 3d electrons are closer to the nucleus (lower principal quantum number), they will repel the 4s electrons away from the nucleus, causing it to become higher in energy level. This is why even though the 4s orbitals are filled before 3d, we ionize the 4s electrons before 3d electrons. In addition, their closeness in energy levels dictates that the electrons in both subshells can easily be involved in bond forming, as well as the 4p electrons, resulting in potentially 18 electrons (2+6+10) in total. This is what makes the bond formation of transition metals different from other main group elements, and the 18-electron rule (also known as the Effective Atomic Number rule, EAN) is used to predict complex stability as opposed to the octet rule.

Coordination Complexes

In most main group element compounds, the valence electrons of the atoms combine to form chemical bonds to satisfy the octet rule. For example, the 4 valence electrons of C overlap with electrons from 4 H atoms to form CH_4 with covalent bonds; the one valence electron leaves Na and adds to the 7 valence electrons of Cl to form the ionic formula unit NaCl. On the other hand, transition metals primarily form coordinate covalent bonds, which is a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). We refer to the resulting compound as a coordination complex. The Lewis acid in the coordination complex is often called a central metal ion, and it is often a transition metal or inner transition metal (although main group elements can also form coordination compounds, like diborane). The Lewis base is called a ligand and can be atoms, molecules, or ions; the only requirement is that they have one or more electron pairs that can be donated to the central metal. A key observation is that the properties and reactivity of a bound ligand differ substantially from that of a free ligand, which results in a change in the properties of the central metal ion. This modification of the character of the molecular components upon binding of the ligand to the metal ion is at the heart of the importance of the field.

The coordination sphere consists of the central metal ion or atom plus its attached ligands. We usually use brackets in a formula to enclose the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The most common coordination numbers are 2, 4 and 6, but complexes with coordination numbers from 1 to 15 are known.

The ligands can coordinate to the metal in various fashions. Many common ligands are monodentate, which means that there is only one atom on the ligand that coordinates to the metal centre. Bidentate ligands have two atoms on the ligand that coordinate to the metal centre. For example, the ligand ethylenediamine ($H_2NCH_2CH_2NH_2$) is bidentate, since it has two nitrogen atoms, each with a lone pair and can act as a Lewis base. Any ligand that binds to a central metal ion by more than one donor atom is a polydentate ligand. In fact, many polydentate ligands are chelating ligands (also known as a chelating agent), and a complex consisting of one or more of these ligands and a central metal is a chelate. What chemists refer to as chelation is exactly the process in which a polydentate ligand bonds to a metal ion, forming a ring. For example, the single ligand heme contains 4 N atoms that coordinate to Fe in hemoglobin to form a chelate. This formation of polydentate ligand-metal complexes is how chelating agents are used to sequester metal ions.

Structures of Coordination Complexes

In principle, there is no limit to the size of a molecule that may bind metal ions; however, as molecules get larger they become less soluble, which places a limit on their ability to coordinate to metal ions in solution. Interestingly, even solids carrying groups that can form complexes with metal ions are able to adsorb metal ions from a solution with which they are in contact onto a solid surface, effectively removing them from solution via complexation in a process called chemisorption. (This means that complexation is not limited to the liquid phase, but can in fact, occur in both the solid phase and gas phase)

Many biomolecules are composed of complex polymeric units (peptides or nucleotides) and have the potential to bind metal ions; in fact, the metal ions may contribute to the shape and chemical activity of the polymer. What remains true even in these macromolecules is that the rules of coordination do not change, and any particular type of metal ion tends to demand the same type of coordination environment or number of donors irrespective of the size of the ligand. In other words, if a metal ion prefers to form 6 bonds to 6 donor groups, it will typically achieve this whether only one donor group is offered by a molecule (in which case it binds to 6 separate molecules) or whether 100 donor groups are offered by a molecule (by binding selectively only 6 of the 100 donors available).

The most common structures of the complexes in coordination compounds are octahedral, tetrahedral, and square planar. For transition metal complexes, the coordination number determines the geometry around the central metal ion.

The chemical and physical properties of the transition elements are determined by the partly filled nd subshells. In the simple atomic model of the first row d-block elements, as discussed before, the set of closely-spaced levels involving 4s, 4p and 3d orbitals can be considered as the valence orbitals, providing 9 orbitals (18 electrons) for bonding, giving rise to the nine-orbital (or 18-electron) rule that attempts to explain metal-donor coordination numbers up to 9.

There are two main theories to explain the properties of metal complexes: a crystal field theory that is a useful holistic ionic bonding model, and a molecular orbital theory that is a useful holistic covalent bonding model. Both models have obvious limitations, one of which being that they both assume a purity in the bonding character that is unlikely. Even so, they are both very important as they offer a certain level of understanding for the physical and chemical properties of complexes, as well as a means of prediction of properties where changes or new species are involved.

Ionic Bonding Model - Crystal Field Theory (CFT)

Crystal field theory for transition metal complexes simplifies the complex species to one featuring point charges involved in purely ionic bonds. It focuses on the usually partly filled d subshell valence electrons, with the key idea being that in the isolated metal ion (or atom), the 5 nd orbitals all have the same energy level, or they are degenerate. However, in a ligand environment this is lost, leading to a non-equivalence of energies between the nd orbitals.

Due to this non-equivalence of energies of the nd orbitals, we need to consider how the electrons occupy these levels, as variation in this occupancy can be associated with variation in properties. Towards this end, we make some assumptions to reduce the complexity of the model, including:

1. We reduce the spherical metal ion to a point positive charge.
2. We reduce the ligand donor groups each to a point negative charge that represents the electron pair. Even though ignoring the ligand bulk and shape aspects is a huge leap, the model does yield useful outcomes in terms of interpreting physical properties such as colour and magnetic properties in the metal complexes.
3. We consider bonding to arise dominantly through electrostatic forces between cation and anion point charges in the ionic array. These primary electrostatic interactions are responsible for a stable assembly, but they actually have little direct influence on properties; the key lies in the effect of ionic interactions on the set of valence electrons (p orbitals for main group elements, d electrons for most transition metal ions, f for lanthanoids).
4. The valence orbitals of the central atom are assumed to be influenced by the close approach of the ligands acting simply as points of negative charge.

Why do the orbitals behave differently when approached by ligands? This is because the electric fields associated with the ligands cause repulsions in the d orbitals and that raises their energies. But it also affects the various d orbitals differently depending on how they are arranged in space. Imagine the ligands approaching along the x, y and z axes, each attaching to the metal ion via a lone pair of electrons. However, two of the d orbitals have lobes pointing along these axes; from the 3d orbitals shown above, you can see that it is the $3d_{x\hat{}2-y\hat{}2}$ and $3d_{z\hat{}2}$ orbitals. Thus they will experience a stronger repulsion than the other three, which have lobes in-between the axes, due to a shorter distance and less spatially restricted negative charge. That means that two of the d orbitals will now have a higher energy than the other three, with the weights 2/5 and 3/5 allowing the overall effect to be balanced.

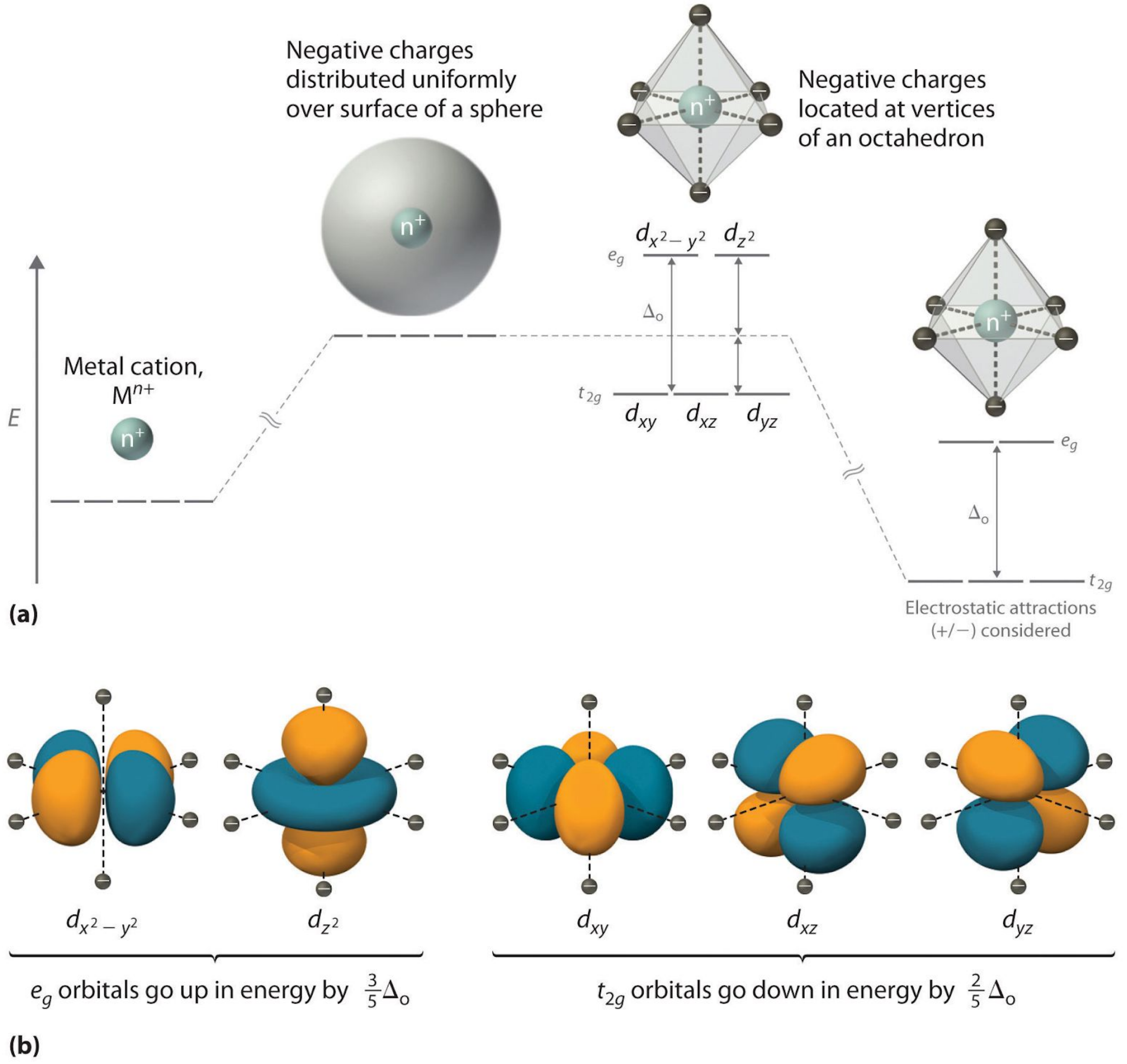


Figure 1: CFT Overview (Figure Taken from [1])

The formation of doubly and triply degenerate orbitals shown above is characteristic of the octahedral field, due to the spatial location of the set of negative point charges approaching from both directions along the x, y and z axes. In fact, every different shape arrangement of point charges will lead to a different characteristic outcome. Going back to the octahedral case diagram, the lower energy set of three orbitals (d_{xy}, d_{xz}, d_{yz}) is called the diagonal set (t_{2g} from group theory), and the higher energy set of two orbitals is called the axial set (e_g from group theory). The energy difference between these two levels is called Δ_o, where o stands for octahedral. Some also refer to this energy gap as 10Dq, with the diagonal set lowered by 4 Dq and the axial set raised by 6 Dq.

Now the question is, what factors dictate the size of Δ_o? If we know this, we would be able to predict certain spectroscopic properties. If we fix the metal's identity and focus on the ligands, we note that for the octahedral complexes of most of the first-row transition metal ions, the presence of colour suggests that part of the visible light spectrum is being removed. This can be envisaged if the energy gap between the diagonal and axial levels equates with the visible region, leading to absorption of a selected part of the visible light that occurs to cause the complex to undergo electron promotion from the lower to the higher energy level. Simply by monitoring the change in colour as ligands are changed, we can determine the energy gap Δ_o applying for any ligand set: the stronger the crystal field, the larger Δ_o is, and hence more energy is required to promote an electron, leading to a higher energy transition, which shows as a shift of the absorbance peak maximum to shorter wavelength. This allows us to rank particular ligands in terms of their capacity to separate the diagonal and axial energy levels. This has been done to produce what is called the spectrochemical series.

Unfortunately, this empirical trend does not sit well with the crystal field model. For example, this trend suggests that an ion like Br^- is far less effective than a neutral molecule like CO at splitting the d-orbital set, which contradicts a model based on electrostatic repulsions, in which we would expect a charged ligand to be more effective than a neutral one, even considering size, dipole effects and electronegativities. Other strange cases include the O-donor anion HO^- turns out to be a weaker ligand than its larger, neutral O-donor parent water, and ammonia is a stronger ligand than water despite having a smaller dipole moment and larger molar volume.

These discrepancies mostly arise from the fact that CFT is based on a concept of point charges. Real ligand donors have size, and along with size comes the strong possibility of the donor group or atom undergoing deformation of its electron density distribution simply as a result of being placed near a positive charge centre. This is essentially a shift of electron density towards the region between the metal and the donor, or what would happen when a covalent bond forms. While the outcome here is far from covalent bond formation, there is an introduction of some covalency into the otherwise purely ionic bonding model. The outcome of allowing some covalency in the model is a fairly minor perturbation, not a drastic change, except the theory morphs into ligand field theory to distinguish the changes introduced.

Covalent Bonding Model - Molecular Orbital Theory

First, we will do a quick overview of the Molecular Orbital theory. The key is that it involves the combinations of orbitals from components to produce a new set of orbitals of different energy from those of the separate components. However, the number of orbitals in the molecular assembly matches the number in the components exactly. For example, if we are combining one orbital from atom A and one orbital from atom X, we obtain two orbitals; one stabilized (i.e., of lower energy) compared to the parent orbitals, called the bonding orbital, and the other destabilized (i.e., of higher energy), called the antibonding orbital. These names reflect the character of the orbitals, as electrons inserted in the former lead to a more stable conformation when A and X are linked by a bond, while electrons in the latter destabilize the assembly. An excess of electrons in bonding compared to antibonding orbitals leads to a stable compound AX. The model can accommodate sigma and pi bonding, as well as orbitals that may not participate directly in bonding, called nonbonding orbitals.

Once again, we study the main octahedral model by considering six of the nine available bonding orbitals on the metal interacting or mixing with the six lone pairs on the ligands to form six bonding and six antibonding orbitals. Originally, there were 9 orbitals of similar energy on the metal considered (one s, three p, and five d), and yet to form bonds to six ligand orbitals, only six are required. This means that three of the nine are not involved in forming bonds to the ligands, and are thus designated as nonbonding orbitals, which essentially correspond to the t_{2g} orbitals from the CFT. Overall, we have 15 orbitals of interest in the diagram, which can accommodate up to 30 electrons. In addition, the number of participating orbitals in the components must equal the number of MOs in the assembly; also, equal numbers of bonding and antibonding orbitals must form.

The 12 electrons from the 6 ligands' lone pairs are used to occupy the 6 bonding orbitals created, defined by their symmetry labels as a_{1g} (singlet), t_{1u} (triplet), and e_g (doublet), which lie lower but fairly close in energy to the initial ligand orbital energy levels, with the metal d electrons then inserted in the next highest energy levels, e.g., t_{2g} orbitals. This set of three nonbonding levels along with the six bonding orbitals provide an upper limit of 18 electrons before antibonding orbitals are employed, which would lead to a reduced stability of the system, which gives rise to the so-called "18-electron rule".

Note that in the MO theory, it is not essential to limit bonding to linkages between only two atoms at a time; rather, it allows a MO to spread out over any number of atoms in a molecule, from two to even all atoms. It applies mathematical group theory to determine the allowed combinations of metal orbitals and ligand orbitals that can lead to bonding situations. One example of a combination involving many centres is the overlap of the metal s orbital with all six of the lone pair orbitals from the ligands at once. This seven-centre combination produces both a bonding MO (a_{1g}) and a complementary antibonding orbital (a^*_{1g}).

The 3 p orbitals only differ in spatial orientation, and so their interactions with donor orbitals are energetically equivalent, leading to a set of three degenerate levels (t_{1u}). The 5 d orbitals interact as two sets due to their spatial arrangement into two groups; those lying along axes and those between axes, same as in CFT. The key to forming allowed bonding interactions is orbital orientation: the lobes of the orbitals need to point along a line joining the atomic centres. This is readily achieved by the $d_{x^2-y^2}$ and d_{z^2} orbitals, which interact with ligand orbitals to form a degenerate set of two bonding levels (e_g) and two degenerate antibonding levels (e^*_g). However, with an orbital like d_{xy}, this cannot occur due to its spatial orientation relative to the lone pair orbitals, and so the three remaining d orbitals d_{xy}, d_{xz}, d_{yz} with lobes oriented between the axes become nonbonding orbitals, as a degenerate set (t_{2g}).

Ligand Field Theory (LFT)

Molecular orbital theory has given us another perspective on the d-orbital set, with the t_{2g} level being dominantly nonbonding in character, and so its energy is not particularly influenced by changing ligands, and the e_g^* level being responsible for altering the size of Δ_o as it responds to the different ligands. With just two energy levels involved, increasing the size of Δ_o can be done in two ways – either by raising the energy of the e_g^* level, or by lowering the energy of the t_{2g} level. The crystal field model solely focused on modifying the e_g^* level through electrostatic interactions between ligands and metal d electrons. On the other hand, the key to any interaction involving t_{2g} d orbitals is whether the ligand donor has p or even pi orbitals directed orthogonal to the metal–donor bond direction. If so, then a further interaction between metal t_{2g} d orbitals and ligand donor p (or pi) orbitals can occur, which would lead to two MOs, one bonding and one antibonding orbital of lower and higher energy than the parent orbitals respectively. This thus provides a mechanism that depends on the properties of the ligand for manipulating the energy of the t_{2g} set.

Stability

The stability of complex formation is measured with the stability constant, which is essentially the equilibrium constant for the formation of a complex. A larger stability constant generally indicates a favourable complex formation. We can identify a number of factors that contribute to the size of stability constants, some in relation to the metal and some associated with the ligand.

Metal Factors for Stability

Size and Charge

Since a complex consists of a positively-charged metal ion and anionic or polar neutral ligands carrying high electron density in their lone pairs, there is a purely electrostatic contribution. As the charge on cations, all of similar size, varies from 1+ to 4+ across the series, the stability constant increases. When the metal ion charge is fixed but the metal ion size is increased, the surface charge density decreases as the ionic radius increases, which means the attractive force for the ligand is less effective, which leads to a fall in the size of the stability constant. As a conclusion, the smaller the ion and the larger its charge, the more stable its metal complexes are.

Metal Class and Ligand Preference

This is essentially the “hard likes hard, soft likes soft” rule from before, which is reiterated as follows: Electropositive metals (lighter and/or more highly charged ones from the s, d and f block belonging to Class A) tend to prefer lighter p-block donors (such as N, O and F donors); less electropositive metals (heavier and/or lower-charged ones belonging to Class B) prefer heavier p-block donors from the same families (such as P, S and I donors).

The Natural Order of Stabilities for Transition Metal Ions

For transition metal ions with incomplete sets of d electrons, there is a contribution to stability from the crystal field stabilization energy (CFSE), whereas for d^{10} metal ions, with a full set, there is no such stabilization energy. Crystal field stabilization energies of metal ions in complexes have a key influence on stability constant values for transition metals. This effect is overlaid on the general “upward” trend from left to right across the row with increasing Z_{eff}, associated with imperfect shielding of the nucleus, and leads to what is usually called the natural order of stabilities. This experimentally-based order states that the accessible water-stable M^{2+} octahedral first-row transition metal ions exhibit an order of stabilities with any given ligand which is essentially invariant regardless of the ligand employed, that is:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}.$$

This means the same trend in stability constant values is seen regardless of ligand (unless some other special effect overrides it). This trend identifies copper(II) as the metal ion that forms the most stable complexes, irrespective of the ligand; it also predicts a fall in stability constant values in each direction from Cu^{2+}, irrespective of the ligand. The trend is preserved for the series of metal ions with bidentate chelates even when the type of donor atom or the size of the chelate ring is varied.

Ligand Factors for Stability

Base Strength

There is a significant effect of the Bronsted base strength of a ligand on its ability to form strong complexes, since base strength essentially measures the capacity to bind a proton. We can say with some certainty that the greater the base strength of a ligand (that is, its affinity for H^+), the greater its affinity for (and hence stability of complexes of) at least Class A metal ions. Unfortunately, this is not true of Class B metal ions. Some interfering factors include increased covalent character in the M-L bond as the electropositivity of the ligand increases. The steric bulk of ligands also introduces an influence that can act counter to a pure base strength effect.

Chelate Effect

When we employ molecules as ligands where they offer more than one donor group capable of binding to metal ions, there is the strong possibility that more than one donor group will coordinate to the one metal ion, resulting in a polydentate ligand, or a chelating ligand. In general, chelation is beneficial for complex stability, and chelating ligands form stronger complexes than comparable monodentate ligand sets. Of course, this is not very common in proteins, since most ligands interacting with the metal ions are amino acid residue side chains, each of which is generally limited to one electron donor.

Chelate Ring Size

The size of the stability constant depends on the number of atoms or bonds in the ring. For saturated rings, five-membered rings where ligand donor “bite” and preferred angles within the chelate ring are optimized are preferred for the lighter metal ions, with smaller or larger rings being of lower stability. Again, this is of less relevance in a protein engineering context, since there are generally not many large ring structures within a binding pocket.

Steric Strain

The effects of ligand bulk, resulting from molecules being necessarily required to occupy different regions of space and thus required to avoid “bumping” against each other when confined around a central metal ion, tend to be termed steric effects. As a general rule, the bulkier a molecule, the weaker the complex formed when there is a set of ligands involved. In the gas phase, where there is no metal ion solvation and usually only low coordination number complexes form due in part to a low probability of metal–ligand encounters, discrimination in complex stability based more on base strength than steric bulk may apply. Since gas phase coordination chemistry is quite uncommon, even outside of protein engineering, we will only consider solution chemistry, where inherently sterically less demanding ligands can display stability constants that reflect basicity effects more. Overall, large, bulky groups that interact sterically when attempting to occupy coordination sites around a central metal ion usually leads to lower stability. The strain in such systems is seen in distortions of bond lengths and angles away from the ideal for the particular stereochemistry applying. Ligand bulk is particularly significant with regard to its introduction in the immediate region around the donor atom, as congestion will become greater the closer bulky groups approach the central atom.

Selectivity

Now we try to tackle the question: what dictates the preference of ligands for metals and metals for ligands? First, consider the preference of the ligand for forming coordinate bonds to metal ions that are more ionic versus those purely covalent in character. Small, highly charged entities will have a high surface charge density and a tendency towards ionic character. A large, low-charged entity tends to have more diffuse and expanded electron clouds, making it less dense or “soft”, and better suited to orbital overlap. This concept, applied to donor atoms and groups, leads to us defining “hard” donors as those with a preference for ionic bonding, and “soft” donors as those preferring covalent bonding. Note that the “hard” donor atoms are also the most electronegative.

Any individual metal ion will display preferential binding when presented with a range of different ligands, and so similar to the “hard-soft” characterization of ligands, by convention, we define the least electronegative as “hardest” and the most electronegative as “softest”. For the metals, they grow increasingly “soft” from left to right across the Periodic Table, and also increase in softness down any column of the table. This results in the principle of hard and soft acids and bases (HSAB) that “hard” ligands (bases) prefer “hard” metals (acids) and “soft” ligands (bases) prefer “soft” metals (acids). We can characterize the metal ions more specifically as follows:

“Class A” Metal Ions (“hard”): small, compact and not very polarizable; this group includes alkali metal ions, alkaline earth metal ions, and lighter and more highly charged metal ions such as Ti^{4+}, Fe^{3+}, Co^{3+}, Al^{3+}. These ions show a preference for ligands that are also small and less polarizable.

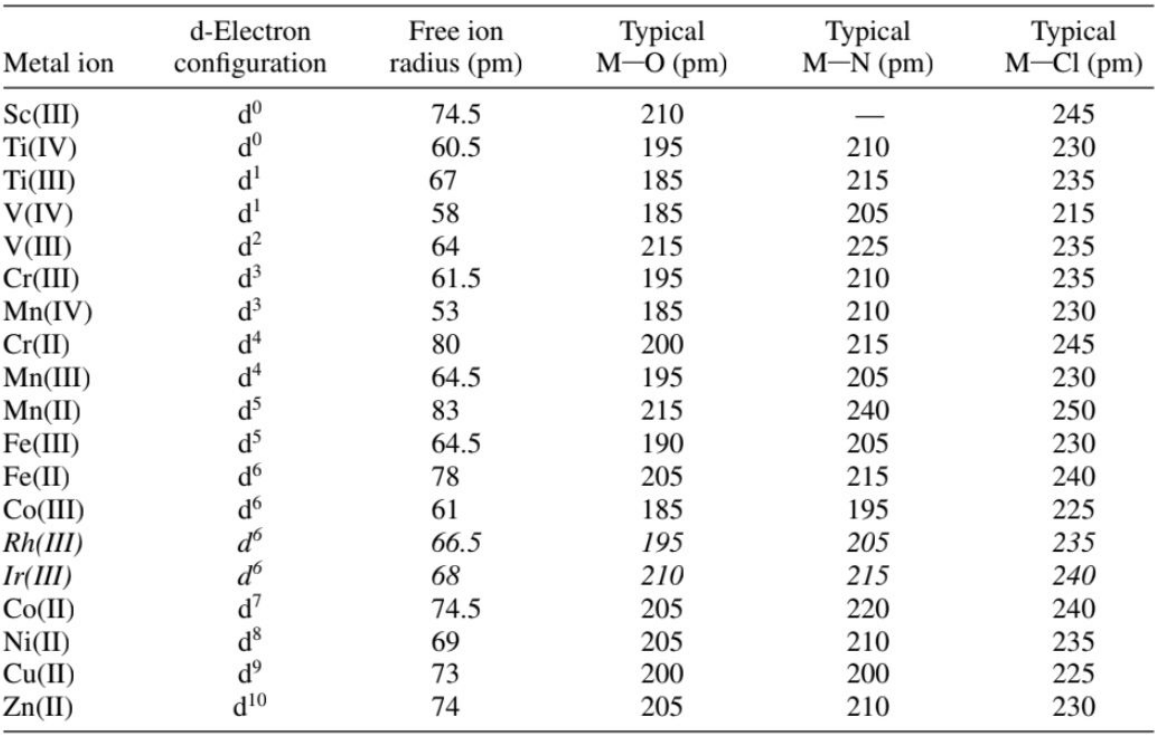
“Class B” Metal Ions (“soft”): larger and more polarizable; this group includes heavier transition metal ions such as Hg^{2+}, Pt^{2+}, Ag^{+}, as well as low-valent metal ions including formally M(0) centres in organometallic compounds. These ions exhibit a preference for larger, polarizable ligands.

This leads to a changing preference order seen across the Periodic Table, with Class A showing a trend from weaker to stronger from left to right, and Class B showing the opposite trend of stronger to weaker, in terms of the measured stability of ML complex formation.

Shape

Since we are mainly concerned with the specificity of one binding pocket in the protein for multiple metals, or in other words, fixed ligands and varying metals, we will only discuss the metal-centric factors that affect complex shape: (1) the number of d electrons on the metal ion; and (2) metal ion size and preferred metal ion–ligand donor group bond length.

Each metal in a particular oxidation state brings a unique character into its complexes. There are also other influences, including the specific type of donor group for a particular type of donor atom, the ligand shape and associated strain energy, as well as the effects of other donors in the coordination sphere. Some trends include the fall in M-L distance with increasing charge on central metal ions with the same number of d electrons, the increase in metal cation size from the first to third rows of the Periodic Table accompanying longer M-L distances, and a higher spin state of the central metal resulting in a greater M-L distance. Some M-N, M-O and M-Cl distances for various metal ions are shown in the following figure. This can be helpful for predicting if a binding pocket is potentially the right size for different metals to bind.

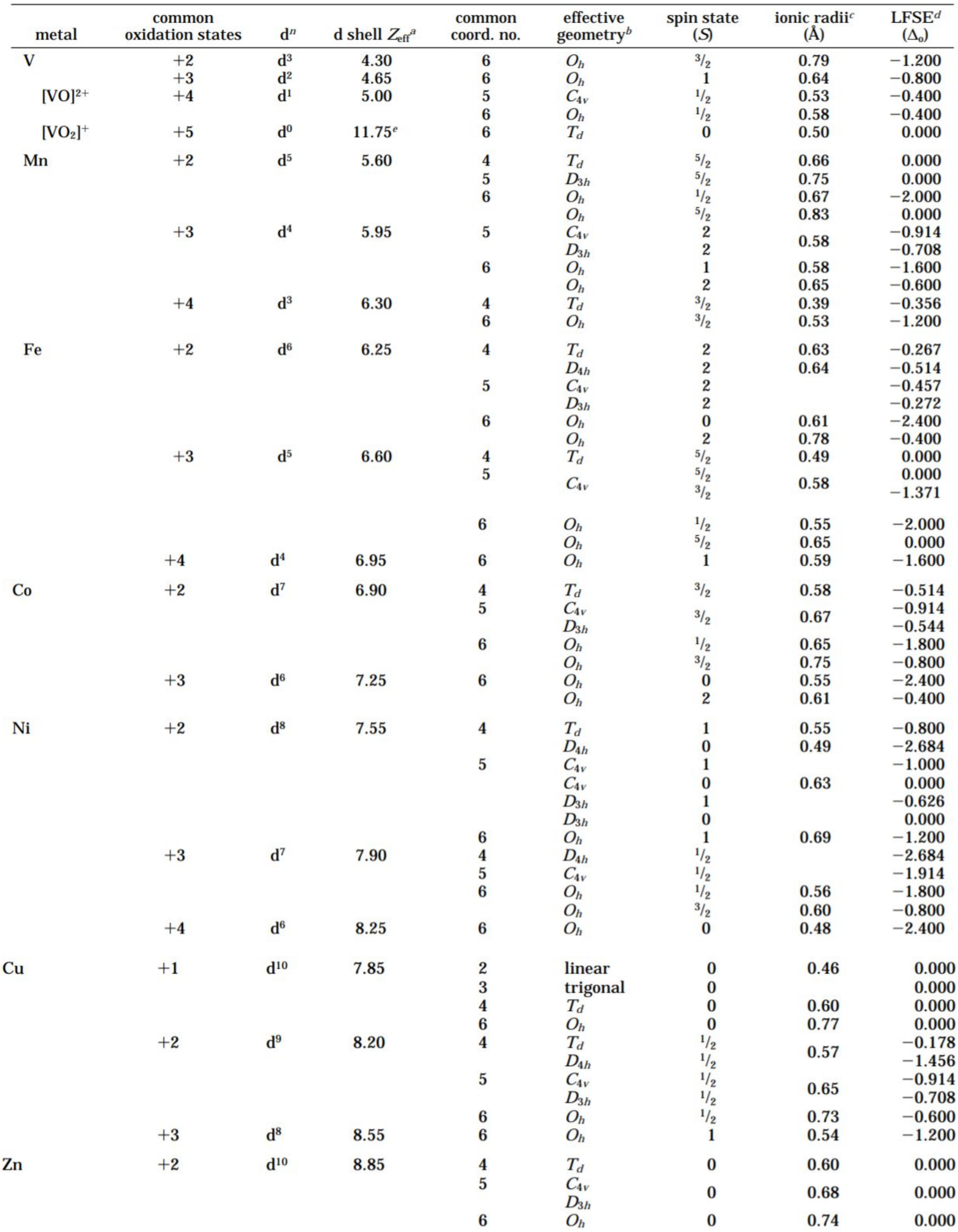


Metal ion	d-Electron configuration	Free ion radius (pm)	Typical M—O (pm)	Typical M—N (pm)	Typical M—Cl (pm)
Sc(III)	d^0	74.5	210	—	245
Ti(IV)	d^0	60.5	195	210	230
Ti(III)	d^1	67	185	215	235
V(IV)	d^1	58	185	205	215
V(III)	d^2	64	215	225	235
Cr(III)	d^3	61.5	195	210	235
Mn(IV)	d^3	53	185	210	230
Cr(II)	d^4	80	200	215	245
Mn(III)	d^4	64.5	195	205	230
Mn(II)	d^5	83	215	240	250
Fe(III)	d^5	64.5	190	205	230
Fe(II)	d^6	78	205	215	240
Co(III)	d^6	61	185	195	225
Rh(III)	d^6	*66.5*	*195*	*205*	*235*
Ir(III)	d^6	*68*	*210*	*215*	*240*
Co(II)	d^7	74.5	205	220	240
Ni(II)	d^8	69	205	210	235
Cu(II)	d^9	73	200	200	225
Zn(II)	d^{10}	74	205	210	230

Figure 2: Some Metal Ions and Their Corresponding Bond Lengths in M-O, M-N and M-Cl Coordination Complexes (Figure Taken From [2])

Conclusion

This document provides a general overview for basic concepts and theories in coordination geometry, with a focus on formulating models of coordination complexes, and explaining the stability/specificity of metal-ligand complexes. This is particularly relevant for metalloprotein engineering. However, since this document was more theory-focused, it is often more important to find more specific data for metalloprotein design from scientific documentation. For example, the following diagram shows a list of metal ions and their preferred complex states, which can be very helpful towards a preliminary determination of whether or not a theoretical active site would bind to the target metal ion without having to run any simulations or try out mutations in the lab.



metal	common oxidation states	d^n	d shell Z_{eff}^{a}	common coord. no.	effective geometry^b	spin state (S)	ionic radii^c (Å)	LFSE^d (Δ_o)
V	+2	d^3	4.30	6	O_h	$3/2$	0.79	−1.200
	+3	d^2	4.65	6	O_h	1	0.64	−0.800
[VO]$^{2+}$	+4	d^1	5.00	5	C_{4v}	$1/2$	0.53	−0.400
				6	O_h	$1/2$	0.58	−0.400
[VO$_2$]$^+$	+5	d^0	11.75^e	6	T_d	0	0.50	0.000
Mn	+2	d^5	5.60	4	T_d	$5/2$	0.66	0.000
				5	D_{3h}	$5/2$	0.75	0.000
				6	O_h	$1/2$	0.67	−2.000
					O_h	$5/2$	0.83	0.000
	+3	d^4	5.95	5	C_{4v}	2	0.58	−0.914
					D_{3h}	2		−0.708
				6	O_h	1	0.58	−1.600
					O_h	2	0.65	−0.600
	+4	d^3	6.30	4	T_d	$3/2$	0.39	−0.356
				6	O_h	$3/2$	0.53	−1.200
Fe	+2	d^6	6.25	4	T_d	2	0.63	−0.267
					D_{4h}	2	0.64	−0.514
				5	C_{4v}	2		−0.457
					D_{3h}	2		−0.272
				6	O_h	0	0.61	−2.400
					O_h	2	0.78	−0.400
	+3	d^5	6.60	4	T_d	$5/2$	0.49	0.000
				5	C_{4v}	$5/2$	0.58	0.000
						$3/2$		−1.371
				6	O_h	$1/2$	0.55	−2.000
					O_h	$5/2$	0.65	0.000
	+4	d^4	6.95	6	O_h	1	0.59	−1.600
Co	+2	d^7	6.90	4	T_d	$3/2$	0.58	−0.514
				5	C_{4v}	$3/2$	0.67	−0.914
					D_{3h}			−0.544
				6	O_h	$1/2$	0.65	−1.800
					O_h	$3/2$	0.75	−0.800
	+3	d^6	7.25	6	O_h	0	0.55	−2.400
					O_h	2	0.61	−0.400
Ni	+2	d^8	7.55	4	T_d	1	0.55	−0.800
					D_{4h}	0	0.49	−2.684
				5	C_{4v}	1		−1.000
					C_{4v}	0	0.63	0.000
					D_{3h}	1		−0.626
					D_{3h}	0		0.000
				6	O_h	1	0.69	−1.200
	+3	d^7	7.90	4	D_{4h}	$1/2$		−2.684
				5	C_{4v}	$1/2$		−1.914
				6	O_h	$1/2$	0.56	−1.800
					O_h	$3/2$	0.60	−0.800
	+4	d^6	8.25	6	O_h	0	0.48	−2.400
Cu	+1	d^{10}	7.85	2	linear	0	0.46	0.000
				3	trigonal	0		0.000
				4	T_d	0	0.60	0.000
				6	O_h	0	0.77	0.000
	+2	d^9	8.20	4	T_d	$1/2$	0.57	−0.178
					D_{4h}	$1/2$		−1.456
				5	C_{4v}	$1/2$	0.65	−0.914
					D_{3h}	$1/2$		−0.708
				6	O_h	$1/2$	0.73	−0.600
	+3	d^8	8.55	6	O_h	1	0.54	−1.200
Zn	+2	d^{10}	8.85	4	T_d	0	0.60	0.000
				5	C_{4v}	0	0.68	0.000
					D_{3h}			
				6	O_h	0	0.74	0.000

Figure 3: Selected Biological Metals and Their Common Coordination Geometries (Figure Taken from [3])

Of course, there is much more to coordination geometry than this document even touched upon. This is an extremely exciting field, with applications beyond simply metalloprotein engineering. It is my hope that this document has been informing in terms of a general coordination geometry introduction, as well as intriguing towards further studies.

References

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