

POST TRANSITION METAL CHEMISTRY NOTES

Definition:

Elements following the 2 transition series' which exhibit metallic character i.e. Group 12 onwards.

General decrease in metallic character on moving right across the periods.

Summary of Characteristics

- ❖ Post-TMs are the metallic elements which follow the completion of each d-shell.
- ❖ Metallic character (structures, conductivity, chemistry) decreases across each post-TM period and generally increases down the groups.
- ❖ The chemistry of the post-TMs is that of the ns and np orbitals; the (n-1)d shell is complete and plays no direct role in the chemistry.
- ❖ Compared to their pre- and early-transition metal counterparts, the post TMs are much less electropositive and show correspondingly less ionic and "softer" chemistry.
- ❖ Trends in atomic and ionic properties down the groups is complex, partly due to the effects of the 1st d-block and Lanthanide contractions.

Occurrence –

| | | | | | | |
|------------------------------------|--|-----------------------------------|--------------------------|-----------------------------|-------------------------|---|
| Cu – sulphate, oxide and carbonate | Zn – ZnS, ZnCO ₃ | Ga – impurity in Zn ores, bauxite | Ge – impurity in Zn ores | As – TM and S and O | Se – mainly with S | Br – sea water |
| Ag – S, Cl native | Cd – sulphide, and impurity in Zn ores | In – impurity in Zn ores | Sn – SnO ₂ | Sb – soft TMs and sulphides | Te – mainly with S | I – iodates |
| Au – native | Hg – HgS | Tl – impurity in PbS | Pb - PbS | Bi – oxides, sulphides | Po – impurity in U ores | At – rarest naturally occurring element |

| | | | | | | |
|----------|--------------------|--------------------------------------|--|----------------------------|--|--|
| Cu – CCP | Zn – distorted HCP | Ga – metallic Ga ₂ dimers | Ge – diamond | As – α - As | Se – 2 coordinate chain and rings structures | Br – Br ₂ |
| Ag – CCP | Cd – distorted HCP | In – distorted CCP | Sn – 2 forms – diamond and high T 4+4 coordinate (metal) | Sb – α - As and HCP | Te – 2 coordinate helical chain | I – I ₂ , metallic under pressure |
| Au – CCP | Hg – distorted HCP | Tl – HCP | Pb - CCP | Bi – α - As, BCC at high P | Po – simple cubic | At – ? |

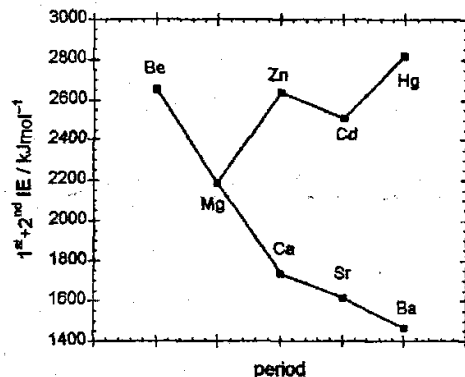
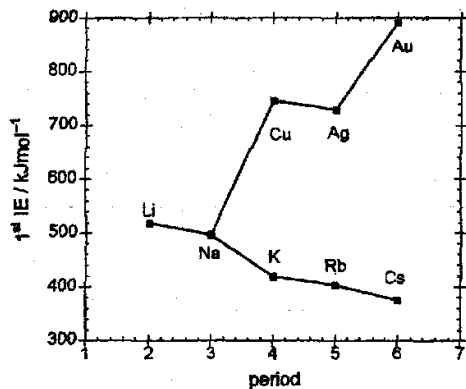
Atomic properties of the elements

Many physical and chemical properties vary irregularly down the group.

In some cases, the irregularity leads to a genuine alternation – "the alternation effect".

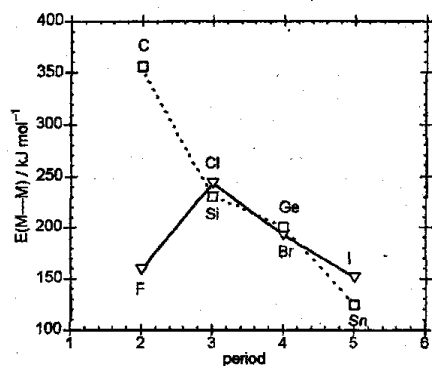
Ionisation energies

IEs are higher than for corresponding pre or early TMs, and zig-zag down the group (alternation effect):

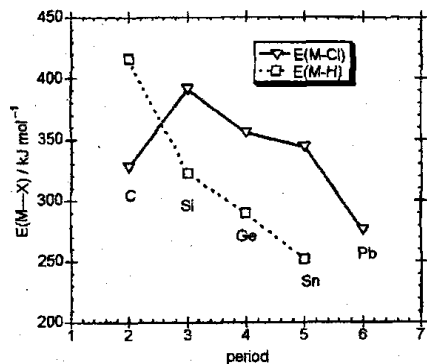


Bond enthalpies

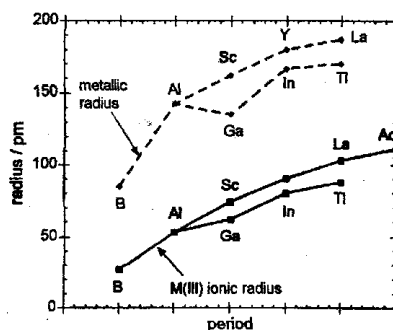
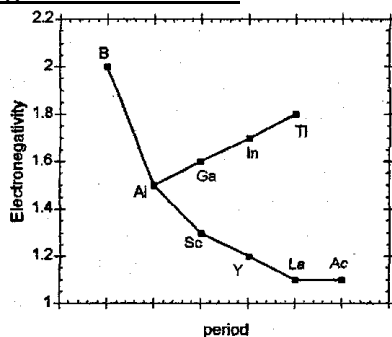
$E(\text{M}-\text{M})$ tends to decrease irregularly down the group. There is some correlation with sublimation energies, but this is not straightforward as the structures change.



Trends in $E(\text{M}-\text{X})$ are more complex. Values vary with X and oxidation state of M. Most trends can be rationalised in terms of overlap, combined with ionic contributions to bonding.

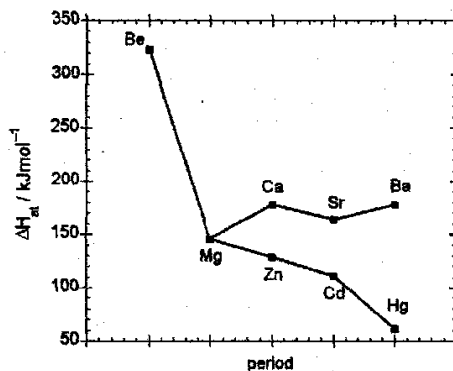
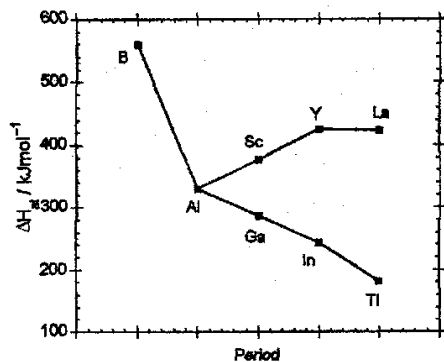


Electronegativities and radii



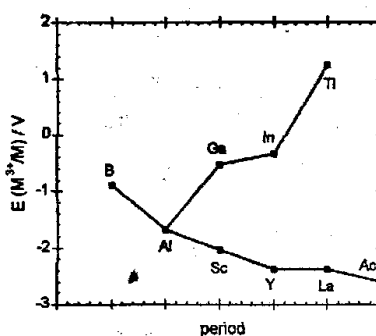
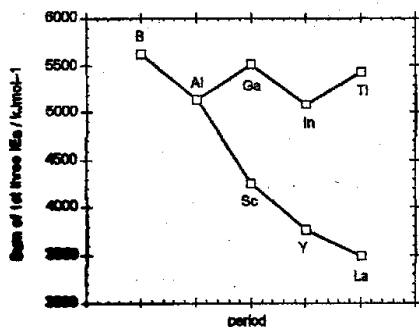
Radii are smaller than earlier elements in the same period. Trends are also subject to the alternation effect.

Sublimation/atomisation



Electrode potentials

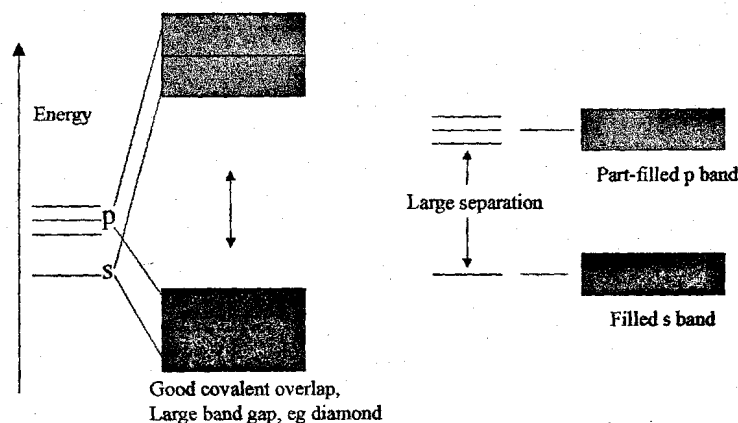
Somewhat complex to interpret. Consider M³⁺/ M shown below. Here, potentially, Tl₃ could recover more solvation energy than its pre transition metal counterpart, La. Tl should also be easier to atomise. However, the sum of IEs for Tl is much greater than for La. This is dominant and post transition couples are more oxidising than their pre transition metal counterparts. Any irregularities reflect the interplay of several contributing energetic processes.



The Alternation effect

Consider the sum of the first 2 IEs of group 2 and group 12 shown earlier. The pattern Be to Ba is familiar – electrons are increasingly far from the nucleus on average, and better shielded by core electrons from increased Z. If we compare Ca and Zn, then we are looking at ionisation from the same orbitals (4s). Zn has an additional 10 protons, plus 10 electrons occupying poorly shielding 3d orbitals. Thus, has a much larger effective nuclear charge and hence increased IEs. The relationship between Sr and Cd is similar to that between Ca and Sr. Due to the poor shielding of the full 4f orbitals, the IEs of Hg are larger than would be expected by extrapolating from Zn and Cd.

Group 14 elements with the diamond structure



The usual forms of Ge and grey Sn are isostructural with diamond and Si. They are general rationalised as giant covalent nets, with each atoms forming 4 sp^3 hybrid orbitals. A band model is needed to explain the electronic properties. The band gap for isostructural C, Si, Ge and Sn decreases from 5.5 eV to 0.1 eV, so the materials are increasingly good intrinsic semi-conductors as the group is descended. This can be related to decreased covalent overlap. When s and p orbital energies are large, orbital overlap leads to separate s and p bands. At the other extreme (c), substantial s-p mixing and good overlap leads to bonding and anti-bonding bands.

Tin and Lead –

The other allotrope of Sn (white, β) and Si and Ge at high pressure, has 4+2 coordination and can be regarded as a distortion of the grey Sn structure. It is the form of Sn thermodynamically stable at higher temperatures. This is unusual as it is also the denser form – usually higher temperature forms are less dense due to longer bond lengths. With Sn, the four individual bonds are, in fact, longer in the higher temperature form, but the longer (“+2”) bond lengths are decreased. This allotrope is metallic and can be regarded as $Sn^{2+} + 2e^-$ i.e. with two electrons being donated to the conduction band with two remaining on the Sn.

Lead has a more “normal” metallic structure than white Sn and is well described by $Pb^{2+} + 2e^-$. The more normal metallic structure is explainable by the reluctance of this element in indulge in tetravalent bonding (“inert pair effect” and/or weakness of Pb-Pb covalent bonds).

Group 15

Structures of α -(As, Sb, Bi) can be considered as puckered layers of 3 coordinate atoms, as expected if each atom forms three covalent bonds and a lone pair. There are also three other atoms at a somewhat longer distance. The disparity between the two distances decreases (i.e. coordination approaches octahedral) as we descend from As to Bi.

Group 16

Se has sulphur-like polymorphs, a conducting polymorph composed of helical chains and a black vitreous, disordered form.

Te has a helical chain structure like that of Se.

Po has several six-coordinate forms, the room temperature form being primitive cubic, with Po at the origin of each cubic cell.

Uses

Ge, GeAs, GaN, InP – important semiconductors.

Cu – wires, pipes, alloys (brass, bronze, coinage alloys, etc.). Proteins.

Ag – halides in photography, metal in jewellery, mirrors.

Au – jewellery, dentistry.

Zn – alloys (brass), dry batteries, oxides in the vulcanisation of rubber, enzymes, anti-corrosion coating e.g. galvanising (immersion in molten Zn).

Hg – electrolysis of NaCl, vapour lamps, barometers, thermometers, extraction of precious metals e.g. Au by amalgamation.

Ga – semiconductors (LED's, lasers).

In – alloys, semiconductors (InP, InAs, InSb).

Tl – formally used as a pesticide.

Sn – tins, anti-fouling paint, reagent in organic chemistry, pewter, bronze and solder alloys.

As – fungicides, drugs, pesticides.

Sb – semiconductors.

Bi – alloys, drugs, nuclear synthesis.

Pb – alloys, solder, roofing, formerly “anti-knock” petrol additive.

Biochemistry

Important:

Cu, Zn – very important.

As – fungicide and essential trace element.

Bi and As used in some drugs.

Dangerous:

Hg, Cd, Tl, Pb, As, Sb toxic – will bind to sulphur-containing amino acids. Antidotes are sulphur-containing ligands such as $\text{CH}_2(\text{OH})\text{CH}(\text{SH})\text{CH}_2\text{SH}$.

Cd, Hg – toxic (both will displace Zn). Elemental Hg is converted to MeHg^+ by micro-organisms – this is extremely toxic.

Sn – toxic to fungi and insects, but believed to be ok for mammals. Alkyl tin – protects ship hulls from barnacles. Poisonous to shellfish and fish.

| Metal | Deficiency | Toxicity |
|--------------|---|--|
| Al | Non-essential | Neurological disturbance. |
| Cd | Non-essential | Kidney and liver necrosis. |
| Co | Anaemia, growth retardation. | Polycythemia. |
| Cr | Glucose intolerance. | Gastroenteritis, Dermatitis. |
| Cu | Menkes disease. | Neurological disturbance. Wilson's disease. |
| Fe | Anaemia. | Liver necrosis. Heart failure. |
| Hg | Non-essential. | Kidney failure. Mental disturbance, coma, death. |
| Mn | Skeletal abnormalities. Connective tissue defects. | Neurological and mental disturbance. |
| Pb | Non-essential. | Kidney failure. Encephalopathy. |
| Zn | Gonadal failure. Stunted Growth | Metal fume fever. Kidney failure. |

General Chemical Features

Orbitals:

- The filled (n-1)d orbitals have profound effects on the chemistry, but these are indirect (shielding properties, etc.) and these orbitals are not involved in bonding, except in Group 11 (and perhaps to a small extent in Group 12).
- Valence orbitals are ns and np – the more covalent compounds tend to obey the 8e rule.
- Contrast to transition metals where ns, np and (n-1)d are the valence orbitals (and the more covalent compounds tend to obey the 18 electron rule).

Oxidation States:

- Highest oxidation state possible is that where all ns and np electrons are ionised to give a [core] (n-1)d¹⁰ ion or all ns and np are involved in covalent bonding.
- Often referred to as the “group oxidation state” – “old” nomenclature. The value of this group (N) oxidation state is simple N = group number – 10.
- Group 11 forms N+1, ... N+4 (Au^V) oxidation states, by ionising the (n-1)d electrons or involving the (n-1)d orbitals in covalent bonding (transition metal character).
- The most important oxidation states are N and N-2.
- Other intermediate oxidation states are usually either mixed valence or contain M-M bonds.
- For the latter, less metallic, post-transition elements, we also find N-4 etc, even N-8 in the halogens.
- Post-transition metal compounds are almost always diamagnetic. Contrast with transition metals which are often paramagnetic when in oxidation states below their group oxidation states (cf. N-2 compounds of Sb^{III} and V^{III}).
- The stability of the N oxidation state varies down the group irregularly (“alternation effect”).
- There are two basic patterns:
 - a) the 5s5p member of a group resembles the 4s4p, whilst the 3s3p and 6s6p members are rather different. The occurrence of oxidation states I and III in Group 13 is a good example. In terms of stability wrt reduction:
$$\text{B}^{\text{III}} \sim \text{Al}^{\text{III}} \gg \text{Ga}^{\text{III}} \sim \text{In}^{\text{III}} \gg \text{Tl}^{\text{III}}; \text{C}^{\text{IV}} \sim \text{Si}^{\text{IV}} \gg \text{Ge}^{\text{IV}} > \text{Sn}^{\text{IV}} \gg \text{Pb}^{\text{IV}}$$
 - b) The 4s4p member can show more similarities to the 6s6p than to the 5s5p. Thus, As shows marked reluctance to form As^V; Bi^V is also strongly oxidising. Sb^V is much less so. This is a genuine “alternation” and also applies to Group 17, where BrO₄⁻ is more oxidising than ClO₄⁻ or IO₄⁻.

“Softness” / Covalency:

- The chemistry of the post-transition metals is largely that of ionic compounds greatly affected by tendencies to directional/covalent bonding and polarising effects. These effects can be traced to the greater effective nuclear charge of these elements in comparison to their pre/early transition metal analogues.
- The Ionic Model is not accurate in predicting lattice energies, with deviation being greatest with “soft” polarisable anions such as sulphide or iodide.
- Post-transition metals are usually “softer” Lewis Acids compared to their pre/early transition metal analogues. Some of the ions, especially the larger ions in low oxidation states are very soft indeed (Au⁺, Hg²⁺).

Relativistic Effects

Special Relativity: $m = m_0/\sqrt{(1-v^2/c^2)}$

Significant for electrons.

These effects are greatest for s electrons and scale with Z.

Orbiting speed affects the radius of orbit.

- ❖ Relativistic effects lead to contraction and lowering of orbital energies.
- ❖ The same effects are observed with p orbitals, but lesser.
- ❖ Contraction increases shielding ability – relativistic effects on less penetrating orbitals may be reversed, i.e. relativistic expansion.

The Group Oxidation State, N

Definition:

The highest oxidation state possible for the post-transition elements where all the ns and np electrons are ionised to give a [core](n-1)d¹⁰ ion, or all ns and np are involved in covalent bonding.

Often referred to as the “group” oxidation state.

Summary

- ❖ N oxidation state becomes increasingly oxidising down each group and from left to right within each period.
- ❖ Structures of halides, oxides, chalcogenides, etc can be rationalised by a combination of ionic / size configurations with the effects of directional bonding and polarisation.
- ❖ Some features of the chemistry appear to alternate between successive periods.
- ❖ Extensive Organometallic chemistry; generally covalent η^1 bound structures.

Occurrence and Stability:

All the post-transition metals form the group oxidation state.

The group oxidation state becomes more oxidising as one moves right or down; there is some alternation in stability down group 15, and also in the non-metal groups 16 and 17. In particular, Tl^{III}, Pb^{IV}, Bi^V, Sb^V, As^V are all rather oxidising. PbCl₄ is stable only <0°C, the tetrabromide and tetraiodide are even less stable. AsCl₅ decomposes at -50°C, the only Sb pentahalides are the fluoride and the chloride. The only pentahalide of Bi is the fluoride.

Bottom right of this section of the Periodic Table → more oxidising in their Group Oxidation State, i.e. Bi^V >> Zn^{II}.

In the borderline post-transition metal group 11, the “group” oxidation state can be exceeded (transition metal character); indeed Cu^I and Au^I are often unstable wrt disproportionation; CuF, Au, Cu⁺(aq), Au⁺(aq) not known.

AgI somewhat more stable due to increased 2nd IE (from 4d).

M^I in group 11 is often stabilised wrt disproportionation by π -acceptors: Au(CN)₂⁻, CuCl(CO), AuCl(CO), Cu(CO)₄⁺ (some backbonding from the filled d-orbitals).

Structures, Polarisation Effects, etc.

Post- and pre-/early-transition metal compounds with similar structures

Many fairly ionic post-transition group oxidation state compounds (oxides, halides, sulphides) have the same or similar structures to the pre- and early-transition metal analogues with similar sized ions.

e.g. NaCl and AgCl – NaCl structure.

CaO and CdO – NaCl structure.

TiO₂ and SnO₂ – rutile structure.

TiS₂ and SnS₂ – CdI₂ structure.

Even when structures are the same, the post-transition metal compound is less well described by the ionic model than its pre-/early-transition metal analogue.

Discrepancies can be calculated (using a sophisticated ionic model). Similar discrepancies exist in electrode potentials if hydration energies are estimated on a purely electrostatic model.

Experimental lattice energies are larger in magnitude than calculated ones due to covalent contributions – this discrepancy is greatest for most polarisable anions (S²⁻, I⁻, etc).

Covalency means that fractional ionic characters of compounds are lower for post-transition elements.

Solubilities – reflect deviations from ionic model, e.g. AgCl vs NaCl and KCl.

Structural Differences from pre-/early-transition metal analogues

In some cases covalency / polarisation effects do lead to structural differences: post-transition metal compounds often have lower coordination number and/or less ideal ionic structures than their pre-/early-transition analogues.

Examples:

CuX – Zinc Blende structure vs. LiCl – NaCl structure.

ZnO (wurtzite) vs. MgO (NaCl).

CaCl₂ (dist. rutile) vs. CdCl₂.

Na₂O (antifluorite) vs. Cu₂O (cuprite).

Many coordination complexes, as well as solid state structures, of post-transition metals in the group oxidation state feature linear coordination of the metal.

Colour/Band Gap

Most post-transition group oxidation state compounds are coloured, whereas few pre-/early-transition group oxidation state compounds are.

Examples:

CdS (orange), CaS, SrS (white).

PbO₂ (red or black), MO₂ (M = Sn, Ti, Zr) – white.

AgBr cream-coloured, AgI yellow; NaBr, NaI (white).

The simplest model assumes a purely ionic structure and a HOMO-LUMO transition. Since this is from an anion-based to metal-based orbital, it is often referred to as ligand-

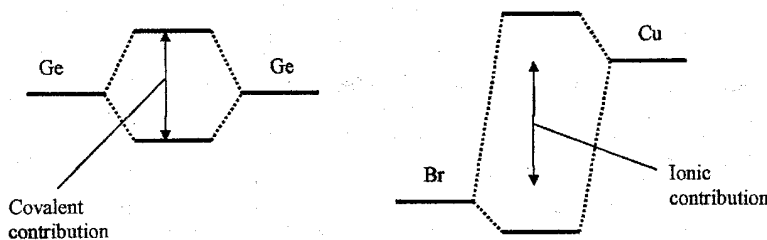
to-metal-charge-transfer. If the energy gap is low enough (metal ion easily reduced/anion easily oxidised) the appropriate energy can be in the visible.

The energy at which the compound begins to absorb light is called the band gap; this is the gap between the highest filled and lowest unfilled levels and dependent on both difference in electronegativities and covalent overlap. The size of the band gap is important in determining whether the material is an insulator or a semiconductor.

This is well-illustrated in the isostructural and isoelectronic series: Ge, GaAs, ZnS, CuBr. In this series, the M-X distance doesn't change much so we can assume the covalent contribution to be fairly constant. In Ge (a semiconductor) where there is no difference in electronegativity between the partner atoms, the band gap must be solely due to covalency. The observed band gap of 0.7eV corresponds to an onset of absorption of light at a wavelength of 1770nm, i.e. in the near-IR. CuBr on the other hand has a band gap of 3.5eV (ca. 350nm, in the near UV) and is colourless and an insulator. The difference is due to ionic contributions to the bonding in CuBr (arising from electronegativity differences). GaAs and ZnSe have intermediate band gaps of 1.5 and 2.8eV respectively (ca. 830 and 440nm) due to the considerable difference in electronegativity between the elements.

Band gaps decrease down the groups due to decreased covalent overlap.

Schematic showing covalent and ionic contributions to the band gaps in Ge and CuBr:



Linear Coordination in d^{10} Species

Linear coordination is quite common among some of the post-transition metals in their group oxidation states. Examples include:

- ✚ AuI has 2-coordinate chain structure.
- ✚ CuO and AgO have the cuprite structure, where the metal has linear coordination, and the oxide ions are tetrahedral.
- ✚ HgX_2 are linear molecules. Solid state structures feature 2+4 coordination (i.e. octahedral very strongly distorted towards linear, although HgI_2 also has a tetrahedral form). The fluoride has a more typically ionic fluorite structure.
- ✚ Many complexes of Cu^+ , Ag^+ , Au^+ and Hg^{2+} ions are linear.
- ✚ R_2Hg , $[\text{R}_2\text{Tl}]^+$, $[\text{R}_2\text{Pb}]^{2+}$ are all linear, where R = alkyl.

Explanation of Linear Coordination

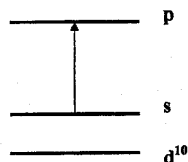
Several explanations have been advanced and it is likely that no one explanation is applicable to all compounds in which it is observed. Clearly some sort of covalency is important.

- ✚ Perhaps the simplest explanation is one of the metal using one ns and one np orbital in bonding, i.e. equivalent to sp hybridisation. This might arise because, at

least in some of the heavy post-transition metals, there is a large sp gap meaning, that for certain combinations of metal and ligand, the p-orbitals may be a little high in energy to get involved in covalent bonding, given that the heavier post-transition elements form rather weak M-X bonds.

Alternative explanations involve the (n-1)d orbitals. One way to view this involvement is to regard the linear complex as a second order Jahn-Teller distortion of an octahedral complex.

1. **Hybridisation.**



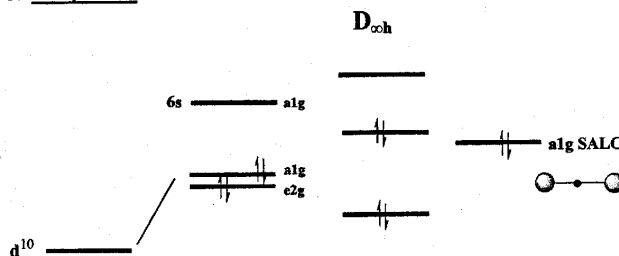
sp hybridization most favourable

2. **Deformation of d^{10} electron density.**



squeezing of electron density in xy plane

3. **MO picture.**



4. **Non-spherical space occupation by Hg core electrons**

Examples of Compounds

Group Oxidation State Halides

Monohalides of Group 11

As previously mentioned, include good examples of the effects of polarisation (insolubility of AgX) and directed covalency (T_d coordination of CuX). Linear coordination observed in AuI.

Dihalides of Group 12

Further examples of effects of polarisation and covalency: tetrahedral coordination in Zn halides (apart from ZnF_2 which has rutile structure), layer structures of CdX_2 (except CdF_2 which has the fluorite structure, tendency towards molecular structure in HgX_2 (again, apart from fluoride).

Trihalides of Group 13

A number of interesting trends observed.

- ✚ AlCl_3 , InCl_3 , InBr_3 and TiCl_3 all have layered structures based on close packed X^- with alternate layers of octahedral holes $2/3$ filled (i.e. related to CdX_2 structures but with incomplete metal layers). Interplay of size and covalency factors and the alternation effect leads to trichloride melting points of 192, 78, 586 and 155°C for Al through to Tl.
- ✚ Like BX_3 and AlX_3 , the heavier trihalides are Lewis Acids, forming species such as GaX_3L , GaX_3L_2 , InX_3L , InXL_2 , $[\text{InL}_4]^{3+}[\text{X}]_3^-$.
- ✚ Tl^{3+} is too oxidising to coexist with iodide and TlI_3 is, in fact, Tl^+I_3^- .

Tetrahalides of Group 14

- ✚ Pdl_4 is unknown. Even the bromide and chloride are easily decomposed to dihalide and halogen and are strong oxidants. They are stabilised by complexation, e.g. as PbCl_6^{2-} .
- ✚ The lighter $\text{M}[\text{Hal}]_4$ are volatile molecular liquids. Other examples are solids with higher coordination number achieved by formation of halide bridges, e.g. PbF_4 is formed from chains of edge-sharing PbF_6 octahedra.
- ✚ Like Group 13 halides, the Group 14 halides are Lewis acidic though are generally “harder” in character in complex formation.
- ✚ There are a number of parallels in terms of structure and reactivity with early-transition metal analogues of Group 4, especially when ions of like size are compared. e.g. both TiCl_4 and SnCl_4 are Lewis Acid molecular (T_d) liquids with mp of -24 and -33°C respectively. Both are readily hydrolysed.

Pentahalides of Group 15

- ✚ The group oxidation state halides from Group 15 onwards are molecular and “hypervalent”, i.e. the bonding can no longer be interpreted in terms of $2c2e$ bonding using only s and p orbitals. As in the case of PF_5 , SF_6 and XeF_4 , and other “hypervalent” p-block species, d orbitals are not needed to explain the bonding in these species, although the d orbital has the conceptual advantage of allowing the $2c2e$ model to be retained. In fact, it seems that the empty nd orbitals are too high in energy to make a significant contribution (and the full $(n-1)d$ orbitals too low). The bonding is well-described using MO Theory (multi-centre, multi-electron picture).
- ✚ The highly-oxidising nature of these elements in their group oxidation state means that pentabromides and pentaiodides are unknown. BiCl_5 is also unknown and AsCl_5 decomposes at ca. -50°C .
- ✚ $\text{AsF}_5(\text{g},\text{s})$, $\text{AsCl}_5(\text{s})$, $\text{SbCl}_5(\text{l})$ are all trigonal bipyramidal, as predicted by VSEPR. SbF_5 is comprised of SbF_6 octahedra with bridging fluorides (like NbF_5 and TaF_5).
- ✚ MX_5 are good Lewis Acids, with a preference for “hard” donors.

Group Oxidation State Oxides and Chalcogenides

Group 11 Oxides and Chalcogenides

- ✚ No Au^{I} oxide. Cu^{I} and Ag^{I} oxides have linear coordination about the metal.
- ✚ All three elements form M_2S .

Group 12 Oxides and Chalcogenides

- ✚ ZnO – wurtzite structure, white, amphoteric.
- ✚ CdO – NaCl structure.
- ✚ HgO – linear chains (linearly coordinated metal).

- ✚ ZnZ and CdZ (Z = S, Se, Te) all have the zinc blende / wurtzite structures.
- ✚ Cinnabar, the usual form of HgS, has a chain structure with linear metal coordination.

Group 13 Oxides and Chalcogenides

- ✚ Most stable form of Ga₂O₃ contains somewhat more tetrahedral cations than Al₂O₃. This is consistent with the increased covalency of Ga^{III} chemistry.
- ✚ Indium and Thallium analogues have the so-called C-M₂O₃ structure.
- ✚ Group Oxidation State Sulphides are known for Ga and In but not Tl.

Group 14 Oxides and Chalcogenides

- ✚ GeO₂ – a number of polymorphs, like its Si analogue, but with both T_d and O_h coordination.
- ✚ SnO₂ has the rutile structure and is the main ore of tin.
- ✚ The normal polymorph of PbO₂ also has the rutile structure. Whilst SnO₂ is white, PbO₂ is maroon due to LMCT.
- ✚ GeS₂ has a couple of polymorphs based on T_d coordination; SnX₂ (S, Se) have the CdI₂ structure and easily undergo redox-driven intercalation reactions.

Group 15 Oxides and Chalcogenides

- ✚ AsO₅ has equal numbers of O_h and T_d. It readily dissolves in water to give acidic H₃AsO₄, decomposes near its melting point and is a strong oxidising agent. Arsenates show a range of structures similar to that exhibited by phosphates, but with a somewhat lower tendency to catenate.
- ✚ Antimony(V) oxide is poorly characterised though has similar chemistry to its arsenic analogue.
- ✚ Bismuth(V) oxides are also not well characterised.
- ✚ The group oxidation state of the group 15 elements is too oxidising to coexist with sulphide and other chalcogenides.

Group Oxidation State Aqueous Chemistry

- ✚ The following group oxidation states form aquated cations: Ag⁺, Zn²⁺, Cd²⁺, Hg²⁺, Ga³⁺, In³⁺, Tl³⁺, although some undergo marked hydrolysis. Zn²⁺ and Ga³⁺ are amphoteric, giving anionic species at high pH.
- ✚ The cations are generally more acidic than the corresponding pre/early-TM analogues.
- ✚ Several group oxidation state ions are stable only in basic conditions as anions, e.g. [Sn(OH)₆]²⁻, [Sb(OH)₆]⁻.
- ✚ Cu^I and Au^I only stable in aqueous solution wrt disproportionation when complexed with certain ligands, e.g. [CuX₄]³⁻, [Au(CN)₂]⁻.

Group Oxidation State Hydrides

In general:

- ✚ The hydrides are only marginally stable.
- ✚ Thermal stability tends to decrease down a group.
- ✚ Some are stabilised within complex anions; no simple In or Tl hydride known but LiMH₄ isolatable.
- ✚ Group 15 M^V hydrides unknown.
- ✚ Group 13 trihydrides; interesting alternation of structure: gallane volatile dimeric molecules (like borane), AlH₃ extended solid.

- ✚ Group 14 Tetrahydrides; tetrahedral molecular species, thermal stability decreases down the group. Some chemical properties alternate, e.g. stability wrt hydrolysis $\text{CH}_4 \gg \text{SiH}_4 \ll \text{GeH}_4 > \text{SnH}_4$.
- ✚ Silane and stannane are pyrophoric in air whilst methane and germane are not.

Group Oxidation State Organometallics

In general:

- ✚ Organometallics in the group oxidation state are more plentiful and stable than the analogous hydrides.
- ✚ σ -coordination dominates. π -coordination, common in transition metals and low oxidation state (N-2) post-transition metal organometallics, is rare.

Group 11 Organometallics

- ✚ Extensive chemistry with σ -ligands. CO complexes also. A few π -complexes known, e.g. Ag^I with olefins, but tend to be labile due to weak backbonding. In CuR_2 , the Cu is often linearly coordinated. LiCuR_2 commonly used in synthetic organic chemistry. Known as cuprates though contain a covalent Cu-R bond.

Group 12 Organometallics

- ✚ MR_2 are linear species. Diethyl zinc is a pyrophoric liquid. ZnR_2L and ZnR_2L_2 are known, where L is an ether or amine.
- ✚ Group 12 dialkyls and alkylhalides are useful in organometallic and organic synthesis.
- ✚ CpZnMe is a polymer in the solid, but has a monomeric gas phase structure, with $\eta^5\text{-Cp}$ (18 electrons). Cp_2Zn is $\eta^1:\eta^5$ coordinate (18 electron) or polymeric. Cp_2Hg is $\eta^1:\eta^1$ coordinate; an example of the tendency of Hg to have lower coordination numbers than Zn.

Group 13 Organometallics

- ✚ Gallium, Indium and Thallium all form monomeric trialkyls.
- ✚ R_2TIHal is cleaved by water to yield the water-soluble linear R_2TI^+ cation. R_2TIOH is a strong base.
- ✚ All Cp M^{III} compounds, such as InCp_3 , have η^1 coordination.

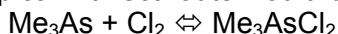
Group 14 Organometallics

- ✚ Ge, Sn and Pb all form R_4M , like the Si analogues.
- ✚ Pb^{IV} organometallic chemistry dominated by weakness and polarisability of the Pb-C bond. Et_4Pb "anti-knock" petrol additive.
- ✚ Contrast to Group 4 alkyls which are considerably less stable kinetically, despite due to stronger Ti-C bond than Sn-C. Due to role of extra valence orbitals in Ti in providing decomposition routes.
- ✚ $\text{R}_n\text{MX}_{4-n}$ are also known. R_3SnX is an important biocide, e.g. antifouling paint.
- ✚ Coordination numbers and structural diversity increase as the metal gets larger. Pb compounds, especially, are prone to high coordination, e.g. Me_2SnCl_2 loosely aggregated tetrahedral molecules, while Me_2PbCl_2 is fully octahedral.
- ✚ R_3MH are known and exhibit radical chemistry, useful in synthetic organic protocols.
- ✚ CpMR_3 (M = Si, Ge, Sn) have η^1 (σ) Cp rings (like InCp_3); they are fluxional. Compare with Group 4 Cp compounds where pentahapto structures are common. The reason is the greater number of valence orbitals available in Group

4 and consequent tendency to try to achieve an 18 electron configuration as opposed to 8 electron (though the metal usually reaches steric saturation before electronic saturation).

Group 15 Organometallics

- MR₅ are known but cannot be prepared directly from MX₅ + R⁻ because MX₅ is too oxidising. A more typical indirect route would be:



- Most are trigonal bipyramidal.
- SbPh₅ is a rare example of a square prismatic molecular species.
- MR_nX_{5-n} also known; as dimers, trigonal bipyramids, tetrahedral, octahedral compounds or polymers.
- R₃AsO can act as Lewis Bases (via the oxygen) to metals.

The N-2 Oxidation State

Introduction

Definition:

- The oxidation state of the post-transition elements in which two of the valence electrons are not ionised, or are not involved in covalent bonding. N-2 ions have the configuration [core](n-1)d¹⁰ns². Examples are Tl^I, Sn^{II}, As^{III}.
- N and N-2 are by far the commonest oxidation states for the post-transition metals (contrast transition metals where the pattern of oxidation states varies greatly from element to element).
- The tendency to form the N-2 oxidation state is often called the "inert pair effect".
- Note that a few formally N-2 compounds actually have M-M or M=M bonds (see later).

Summary

N-2 oxidation state becomes more common moving right across periods and down groups.

The lone pair may be accommodated in a stereochemically active hybrid-type orbital, or in the s-orbital, depending on the relative energies of s, p and ligand orbitals.

Oxides are amphoteric and form a range of polymerised hydrolysed species, often containing oxo and/or hydroxide bridged clusters.

Monomeric η¹ organometallics are stable only for group 15 or with bulky ligands; η⁵/η⁶ species with π-ligands are more common for groups 13 and 14.

Occurrence and Stability:

- The N-2 oxidation state is most frequent where the group oxidation state is most oxidising.
- For Group 11, N-2 corresponds to M⁻¹ and is not an important state.
- In Group 12, N-2 corresponds to M⁰ and no compounds are known.
- For all the remaining post-transition elements, at least some N-2 compounds are known.

Other General Features:

- All N-2 compounds are diamagnetic. Contrast with N-2 transition metal species such as V³⁺(aq).

- As with the group oxidation state, the stereochemistry of the compounds of the post-transition metals in oxidation state N-2 is determined by a combination of both covalency and size. There are, however, unique features in the N-2 state.

Structural Peculiarities

Observation

- Many post-transition metal N-2 compounds have irregular or unsymmetrical coordination geometries, though others do not.
- For example, $\text{SnCl}_2(\text{g})$ has a bond angle of 95° and the solid also has unsymmetrical coordination. $\text{SnO}(\text{s})$ has local C_{4v} symmetry about each Sn. AsH_3 is pyramidal.
- MX_6^{3-} [M=As,Sb,Bi] are regular octahedral.
- This is commonly attributed to the possibility of the two valence electrons which are chemically inert being stereochemically active or inert.

Rationalisation: Irregular Geometry

- A simple model is that the two unused electrons occupy a hybrid orbital.
- $\text{Ge}^{\text{II}}\text{F}_2$ has a chain of vertex-sharing GeF_3 pyramids explainable as sp^3 Ge with a "lone pair".
- Similar models can be applied to other unsymmetrically-coordinated compounds, although for some such as SnO (where the metal is 4-coordinate), a multi-centre-multi-electron bonding model must be used.

Rationalisation: Regular Geometry

Consider $\text{Te}^{\text{IV}}\text{X}_6^{2-}$ [X=Cl,Br,I], $\text{M}^{\text{III}}\text{X}_6^{3-}$ [M=As,Sb,Bi] which are regular octahedral. This is at variance with VSEPR which predicts non-octahedral geometry due to the "lone pair". In these regular geometry species it seems that the "lone pair" occupies the spherically-symmetrical s orbital and only the p orbitals are involved in bonding.

Complications:

The degree of involvement of the s orbital in bonding appears to vary from compound to compound.

- Consider MX_3 [M=As,Sb,Bi; X=Cl,Br,I,H,Me etc] – all are pyramidal. An obvious explanation is that both s and p orbitals are involved in the bonding and that "lone pair" occupies a sp^3 hybrid type orbital.
- Bond angles (90 - 100°) seem to support this model (VSEPR would predict $<109^\circ$).
- Observed Lewis Basicity seems to be consistent, e.g. organoarsines.

But ...

- The heavier MH_3 are weaker bases than NH_3 .
- Bond angles in MH_3 are 107.8° , 93.8° , 91.8° , 91.3° for N through Sb respectively (though VSEPR predictions are not obvious due to size and electronegativity changes down the group).
- Data are suggestive that bonding from P onwards may be thought of as involving p orbitals only, with an s lone pair.

Is it possible to predict if a compound will be symmetrically or unsymmetrically coordinated?

Generally, it seems that structures with and without “stereochemical lone pair activity” are very close in energy. Nevertheless, a number of generalisations are possible:

- Low (2-3) coordination number molecular species will always have irregular geometries, since non-linear or non-planar geometry is expected regardless of the degree of s orbital participation in bonding.
- High coordination number compounds are likely to have suppressed stereochemical lone pair activity, e.g. TeX_6^{2-} , MX_6^{3-} [M = As, Sb, Bi] – regular octahedron.
- Regular geometry is more common in the heaviest elements. Compare PbS (NaCl structure) with SnS (SnO structure) and TlCl (CsCl structure) with InCl (TlI structure).
- The lone pair is less likely to be stereochemically active with the heavier halogens (or other partner elements). As one descends the halogen group, the halogen valence orbital energies increase and are too high to effectively overlap with the metal s orbital; the lone pair thus becomes s-based and the bonding p-only.

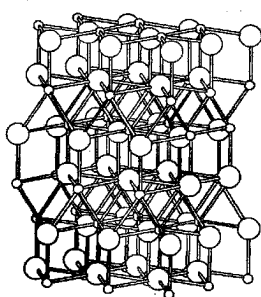
Examples: GeI_2 (octahedral), GeF_2 (chains inked pyramidal units), PbS (NaCl), PbO (SnO).

Examples of Compounds

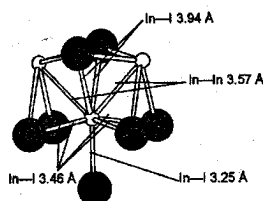
N-2 Oxidation State Halides

Monohalides of Group 13

- Known for most combinations of elements, though GaF and InF are only unstable gas phase species.
- TlCl and TlBr have the CsCl structure, thus having 8-coordination, appropriate to the large cation.
- InX and yellow-TlI have a curious structure with 1+4+2 coordination (slipped version of NaCl). This odd coordination may be due to a stereochemically active lone pair, though it is a less obvious distortion than, for example, SnO.



Showing relationship to a “slipped” NaCl structure



Showing the 1+4+2 In coordination by I and In-In approaches

InCl, InBr and yellow-TlI have similar structures

- Note that TlI_3 is also a Tl^I compound, with a triiodide anion.

Dihalides of Group 14

- The dihalides are Lewis Acids.
- They hydrolyse in aqueous solution to give a variety of hydroxide and oxo species (depending on the pH).
- Generally bent in the gas phase (though some, e.g. GeF_2 , are oligomeric), with varying degrees of lone pair influence in the solid state.

- In terms of stability $\text{PbX}_2 \gg \text{SnX}_2 > \text{GeX}_2 \gg \text{SiX}_2 < \text{CX}_2$; GeX_2 in solution is oxidised in air to give Ge^{IV} species. Aqueous solutions of Sn^{II} species are somewhat more slowly oxidised by air (SnX_2 useful as a selective reducing agent in organic chemistry).
- Pb^{II} halides stable wrt air oxidation. No lone pair stereochemical activity: high T form of PbF_2 has the fluorite structure; PbI_2 has the Cadmium Iodide structure; low T PbF_2 , PbCl_2 and PbBr_2 have the so-called PbCl_2 structure (9-coordinate lead, though not all the ions are equidistant – this is typical of large cations and is not representative of a “stereochemically active” lone pair structure).

Trihalides of Group 15

- All of the group 15 trihalides are known. Many are volatile pyramidal species, all are hydrolysed by water, and are good Lewis Acids.

N-2 Oxidation State Oxides and Chalcogenides

M^I Oxides and Chalcogenides of Group 13

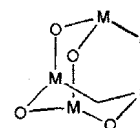
- Several examples are known, though structures are not known in every case.
- Tl_2S has a distorted anti- CdI_2 structure, trigonal pyramidal coordination (consistent with stereochemically active lone pairs).

M^{II} Oxides and Chalcogenides of Group 14

- GeO , SnO and PbO are all known. The first two disproportionate at high T.
- Several polymorphs of the Sn and Pb compounds exist; all are layered with stereochemically active lone pairs.
- SnO is amphoteric, dissolves in acid to give Sn^{2+} (or complexes of) and in alkali to give $\text{Sn}(\text{OH})_3^-$ (pyramidal). Contrast to the dioxide which is more acidic and only dissolves in fused hydroxides.
- PbO is also amphoteric.

M^{III} Oxides and Chalcogenides of Group 15

- All M_2O_3 known; for $\text{M}=\text{As}$ and Sb , these are both molecular and extended solid polymorphs. Bi_2O_3 has more complex structural chemistry.
- As^{III} and Sb^{III} oxides are acidic (soluble in base or with coordinating anions), whilst the Bi analogue is more basic (soluble in acids). Complex chemistry of the various aqueous oxo and hydroxyl species.
- All M_2E_3 ($\text{E} = \text{S}, \text{Se}, \text{Te}$) are known.



N-2 Species in Aqueous Solution

- The aquo cations of Tl^+ (class b, soft), Sn^{2+} (class a, borderline hard/soft), Pb^{2+} (class b, borderline hard/soft) and Bi^{3+} (borderline a-b, borderline hard/soft) are all known.
- Several aquoanions are known, e.g. $[\text{Sn}(\text{OH})_3]^-$ and $[\text{AsO}(\text{OH})_2]^-$.
- A number of polymerised oxo species are formed over certain pH ranges, e.g. $[\text{Sn}_3(\text{OH})_4]^{2+}$ and $[\text{Bi}_6(\text{OH})_{12}]^{6+}$.
- Ga^{I} , In^{I} and Ge^{II} are all unstable wrt disproportionation in aqueous solution.

N-2 Hydrides

- Not known for Group 13.

- Simple monomeric MH_2 not known for Group 14.
- MH_3 exist for all Group 15; are extremely poisonous, thermally unstable (instability increases down the group). The gases are composed of pyramidal molecules. They are much less basic than ammonia but can be protonated by superacids.

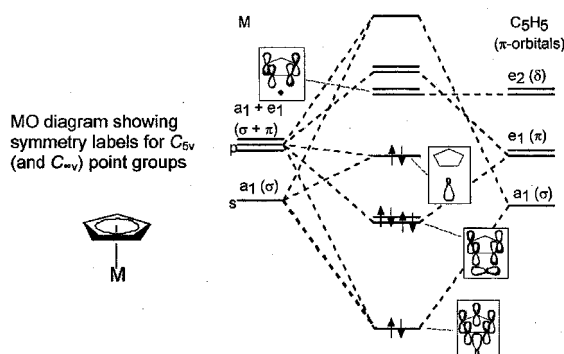
N-2 Organometallics

General Facts:

- Examples exist from group 13,14,15.
- π -complexes much more common in the N-2 oxidation state than in the group oxidation state; e.g. compare $InCp_3$ ($\eta^1:\eta^1:\eta^1$) with $InCp$ (η^5).
- σ -complexes much scarcer than in the group oxidation state.

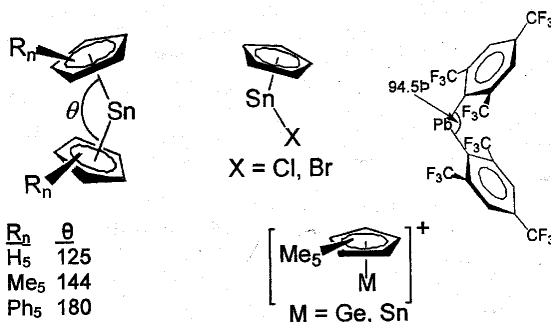
Group 13 N-2 Organometallics

- σ -complexes essentially unknown. MCp [$M=In,Tl$] have monomeric gas phase structures (polymeric in solid state).



Group 14 N-2 Organometallics

- MR_2 σ -complexes are only stable when the organic groups are large, e.g. $Ge(CH_2(SiMe_3)_2)_2$.
 - Generally made from $MCl_2 + R^-$
 - Less stable species (less bulky R) tend to dimerise (to $M=M$ bonds) or oligomerise.
 - More reactive – polarity of $Sn-C$ bond + valence shell expansion.
 - Similarity to hydrocarbon analogues in that commonly colourless, volatile liquids.



- $[MR_3]^+$ are formally M^{II} σ organometallics and are more stable than MR_2 ; pyramidal. Generated in reactions such as $R_3SnX + Na$, or $R_3Ge-GeR_3 + Na$.

- N-2 π -complexes are more stable, e.g. MCp_2 .
 - Mostly have a “bent” ring tilted structure with considerable variation in (ring)-M-(ring) angle.
 - Reason for this is variation in angle is a balance between electronic and steric factors. σ -donation overlaps with p and lone pair in s.
- Comparison with Group 4:
 - Ti^{II} organometallics often have higher coordination numbers in attempts to satisfy the 18e rule.
 - Many have π -acceptor ligands, e.g. $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2 - 18\text{e}$.
- Simple metallocenes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}$ (14e) unknown.

Group 15 N-2 Organometallics

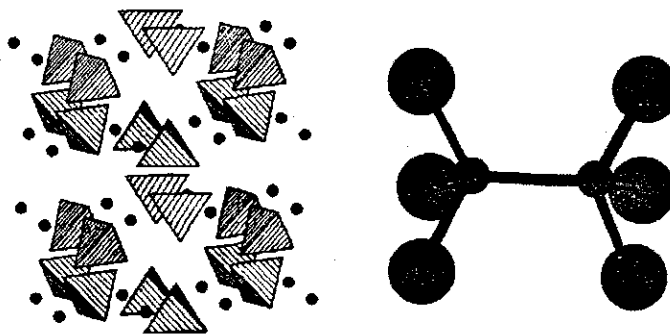
- Pyramidal MR_3 are known for all the elements.
 - Readily oxidised to M^{V} organometallics, e.g. R_3MX_2 .
 - Soft Lewis Bases; can act as ligands to transition metal complexes.
- Usually molecular, but Ph_2SbF has Sb-F-Sb bridges and a 4 coordinate Sb.
- Cp compounds are also known.
 - σ -complexes in cases where the 8e rule may be satisfied without π -bonding (as with group 14 in the group oxidation state), e.g. $\text{Me}_2(\eta^1\text{-Cp})\text{M}$, $(\eta^1\text{-Cp}_3)\text{M}$.
- heterocyclic analogues.

Odd Oxidation States, Clusters, etc.

N-1 Compounds

Genuine examples of isolated N-1 oxidation state post-transition metal species are rare.

- ❖ Most apparent N-1 compounds actually have M-M bonds or are mixed valence N/N-2.
- ❖ A monomeric N-1 compound has 1 unpaired electron, i.e. paramagnetic.
- ❖ A few group 14 species with bulky substituents can be kinetically stable, e.g. $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_3$, $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_3$.
- ❖ Examples of “real” and apparent N-1 compounds: GaCl_2 (left) and LiGaCl_2 (right):



Oxidation States Lower than N-2

Rare as isolated cases. Plenty of formally low oxidation state examples in clusters, M-M bonded compounds, etc.

- ❖ Isolated N-4 compounds occur for elements at the bottom right of the post-transition metals, e.g. $\text{Bi}_{10}\text{Hf}_3\text{Cl}_{18}$ is $\text{Bi}^+\text{Bi}_9^{5+}(\text{HfCl}_6^{2-})_3$, i.e. contains isolated Bi^{I} (N-4) and a Bi cluster.

- ❖ As we move further right, N-4 becomes increasingly important.

Many post-transition metal apparent N-1 compounds are, in fact, mixed valence N-2 and N.

- ❖ The two different oxidation states usually have strikingly different coordination geometries.

Group 13 Examples

- ❖ Group 13 “dihalides” (Cl, Br, I for Ga and In, Cl and Br for Tl) are, in fact, $[M^I]^+ [M^{III}X_4]^-$.
- ❖ Other mixed valence group 13 halides are known, the stoichiometries varying with M^I and M^{III} ratio, e.g. In_4Br_7 .

Group 14 Examples

- ❖ Ge_5F_{12} is a II/IV mixed-valence compound.
- ❖ Pb_3O_4 is $Pb^{II}_2Pb^{IV}O_4$. Chains of edge sharing $Pb^{IV}O_6$ octahedra bridged by 3-coordinate pyramidal Pb^{II} .

Group 15 Examples

- ❖ SbO_2 is $Sb^{III}Sb^{V}O_4$. Layers of $Sb^{V}O_6$ octahedra are bridged by 4-coordinate pyramidal Sb^{III} .
- ❖ $BaBiO_3$ is $Ba_2Bi^{III}Bi^{V}O_6$.
- ❖ $(NH_4)_2SbBr_6$ is $(NH_4)^+_4[Sb^{V}Br_6][Sb^{III}Br_6]^{3-}$ containing two types of regular octahedral anions (s-type lone pair on Sb^{III} species).

N-1 Compounds with M-M Bonds

Generally,

- ❖ These are “genuine” N-1 compounds insofar as the formal oxidation state of the metal is N-1 (as opposed to mixed valence apparent N-1 compounds).
- ❖ M-M bond allows compounds to be diamagnetic.
- ❖ Relatively rare (compared to N and N-2 compounds), but a few important examples.

Examples:

- ❖ M_2^{2+} ions have been observed for Zn and Cd, but are generally unimportant.
- ❖ Hg_2^{2+} much more important; compounds such as Hg_2Cl_2 found in aqueous solution.
- ❖ $M_2X_6^{2-}$ (M=Ga, In) are ethane-like and may be staggered or eclipsed; these ions also feature in a few mixed valence compounds; $InBr_3$ is $[In^I]_2[In^{III}_2Br_6]^{2+}$.
- ❖ GaS, GaSe, GaTe, red-InS and red-InSe are isostructural and have layered structures with M-M bonds.
- ❖ M_2R_6 organometallics in group 14.
 - Can be made from $R_3MX + Na$
 - Can be cleaved in various ways, e.g. with Na to give R_3M^- or hv to give R_3M^+ .

Other M-M bonded Compounds

Linear Chain Catenates

- ❖ Hg forms a range of linear chain catenates, e.g. $2\text{Hg} + \text{HgCl}_2 + 2\text{AlCl}_3 \rightleftharpoons \text{Hg}_3^{2+}(\text{AlCl}_4^-)_2$.
- ❖ This contains linear [Hg-Hg-Hg] ; can understand in terms of 2c2e bonding by imagining 2Hg atoms coordinating to a Hg^{2+} ion, or by recognising that 3 Hg's have 6 valence electrons, so in Hg_3^{2+} there are 4 valence electrons – sufficient to form 2x 2c2e bonds.
- ❖ Also $\text{Hg}_{2.82}\text{AsF}_6$. This consists of 2 interpenetrating perpendicular sets of infinite Hg atom chains with fractional oxidation states.
- ❖ A few similar indium species are known, e.g. $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ has In_5^{7+} and In_6^{8+} chains.

Catenated formally N-2 Organometallics of Group 14

- ❖ Some MR_2 are monomeric but often polymeric or cyclic.

Formally N-3 Compounds of Group 15

- ❖ As_2I_4 and Sb_2I_4 are known and can be regarded as having a single M-M bond and a lone pair; i.e. 8e configurations.
- ❖ M_2R_4 known for As and Sb; M=As, R=Me – the compound is called dicacodyl and was made in 1760, thus making it one of the first organometallics.

Catenated formally N-4 Organometallics of Group 15

- ❖ MR in group 15 is often cyclic or polymeric, e.g. $\text{cyclo-As}_6\text{Me}_6$, poly-(MeAs) , $\text{cyclo-Sb}_4^t\text{Bu}_4$.

M-M multiple Bonds

- ❖ These are rare in the post-transition metals.
- ❖ Ge and Sn form $\text{R}_2\text{M}=\text{MR}_2$.
 - R must be a bulky group to be more stable than oligomers, cyclics, etc, with 2 M-M bonds in place of M=M.
 - Compounds are non-planar; due to weakness of double bond and bulk of substituents.
 - Bonding has been described in terms of dimerisation of two sp^2 MR_2 species.
 - Typical Synthesis: $\text{R}_2\text{SnCl}_2 + [\text{Na}^+][\text{naph}]^- \rightarrow \text{cyclo-(R}_2\text{M)}_3 + \text{hv} \rightarrow \text{R}_2\text{M}=\text{MR}_2$.
 - Formally regarded as N-2 compounds.
 - Also $\text{RAs}=\text{AsR}$ (R = 2,4,6- $\text{Me}_3\text{C}_6\text{H}$; less bulky R gives cyclics).
 - Recent example: $\text{RBi}=\text{BiR}$ with R = 2,4,6-tris[di(trimethylsilyl)methylphenyl] ligands.

Clusters

- ❖ In later post-transition metals, and in group 16, there are a variety of cluster compounds known.
- ❖ Zintl salts contain alkali metal cations and post-transition metal in liquid NH_3 in the presence of alkali metal. The salts can be stabilised in solution by cryptands or ethylenediamine to complex to the alkali metal.
- ❖ M_5^{2-} (M = Sn,Pb) are trigonal bipyramidal and can be rationalised using 2c2e bonding.
- ❖ M_9^{4-} (M = Ge,Sn,Pb) are capped square antiprisms; bonding cannot be rationalised using a 2c2e model. Wades Rules can be applied in explanation / prediction of many of these cluster structures.

- ❖ Closely related cationic Bi examples, many of which are components of low-valent halides.
 - Bi_5^{3+} isoelectronic with Sn_5^{2-} and trigonal bipyramid.
 - Bi_9^{5+} tricapped trigonal prism – at variance with Wades Rules.
 - Bi_6^{2+} square antiprism.
 - Bi_4^{2-} isoelectronic with Se_4^{2+} .
- ❖ Reduction of Group 15 elements by alkali metals leads to M_7^{3-} (M = P, As, Sb).

Compounds with Metals

- ❖ Some of these also contain extensive M-M bonding.
- ❖ MM' [M = alkali metal, M' = Group 15 metal] have spiral chains of the post-transition metal, similar to structures of elemental Se. Some are metallic.
- ❖ $\text{M}_3\text{M}'$ [M=Li,Na,K; M'=As,Sb,Bi]. Often metallic.
- ❖ CoAs_3 (also MSb_3 for M = Co, Rh, Ir) contains As_4 units.
- ❖ GaAs can be regarded as a Ga^{III} compound or as an intermetallic compound with substantial M-M' bonding.