

COURSE CODE: SC202(CHEMISTRY)
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Coordinate Chemistry

The term **complex** means a central metal atom or ion surrounded by a set of ligands.

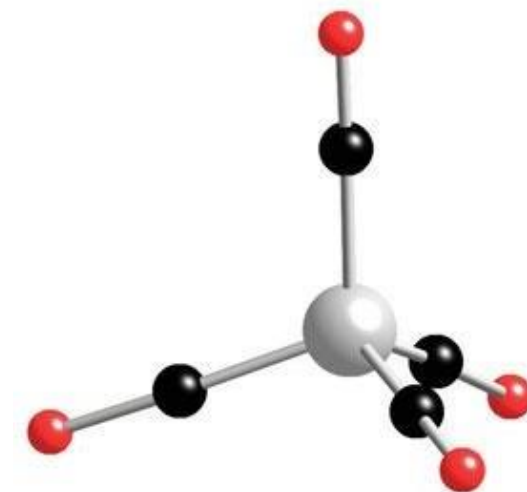
A **ligand** is an ion or molecule that can have an independent existence. Two examples of complexes are $[\text{Co}(\text{NH}_3)_6]^{3+}$, in which the Co^{3+} ion is surrounded by six NH_3 ligands, and $[\text{Na}(\text{OH}_2)_6]^+$, in which the Na^+ ion is surrounded by six H_2O ligands.

Coordination compound means a neutral complex or an ionic compound in which at least one of the ions is a complex.

Thus, $\text{Ni}(\text{CO})_4$ (**1**) and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (**2**) are both coordination compounds.

A complex is a combination of a Lewis acid (the central metal atom) with a number of Lewis bases (the ligands). The atom in the Lewis base ligand that forms the bond to the central atom is called the

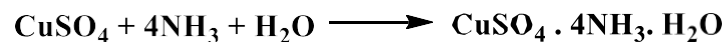
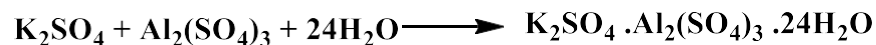
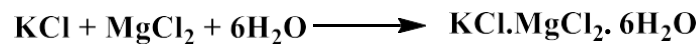
donor atom because it donates the electrons used in bond formation. Thus, N is the donor atom when NH_3 acts as a ligand, and O is the donor atom when H_2O acts as a ligand. The metal atom or ion, the Lewis acid in the complex, is the **acceptor atom**.



(1) $\text{Ni}(\text{CO})_4$

DOUBLE SALTS AND COORDINATION COMPOUNDS

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. For example:



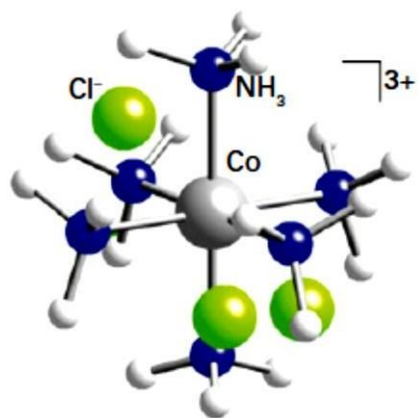
Addition compounds are of two types:

- I. Those which lose their identity in solution (double salts)
 2. Those which retain their identity in solution (complexes)
- When crystals of carnallite are dissolved in water, the solution shows the properties of K^+ , Mg^{2+} and Cl^- ions. In a similar way, a solution of potassium alum shows the properties of L^+ , Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state.
 - When the other two examples of coordination compounds dissolve they do not form simple ions – Cu^{2+} or Fe^{2+} and CN^- – but instead their complex ions remain intact. Thus the cuproammonium ion $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ and the ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ exist as distinct entities both in the solid and in solution.
 - Complex ions are shown by the use of square brackets. Compounds containing these ions are called coordination compounds.

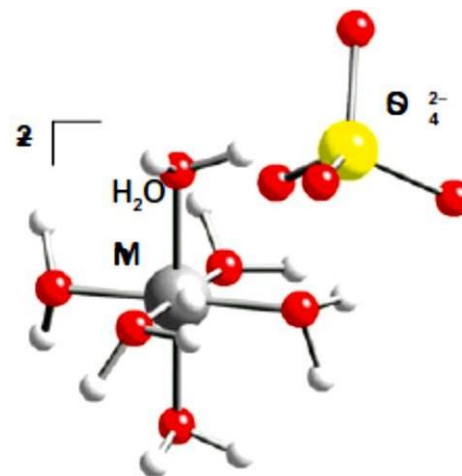
In an inner-sphere complex, the ligands are attached directly to a central metal ion; outer sphere complexes occur where cation and anion associate in solution.

In **inner-sphere complex**, the ligands are attached directly to the central metal atom or ion. These ligands form the **primary coordination sphere** of the complex and their number is called the **coordination number** of the central metal atom. eg. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (2)

Complex cations can associate electrostatically with anionic ligands (and, by other weak interactions, with solvent molecules) without displacement of the ligands that are already present. The product of this association is called an **outer-sphere complex**. With $[\text{Mn}(\text{OH}_2)_6]^{2+}$ and SO_4^{2-} ions, for instance, the equilibrium concentration of the outer-sphere complex eg. $\{[\text{Mn}(\text{OH}_2)_6]_2\text{SO}_4\}^{-2}$ (3)



(2) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



(3) $\{[\text{Mn}(\text{OH}_2)_6]_2\text{SO}_4\}^{-2}$

Werners Work

Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency:

1. *Primary valencies.* These are non-directional. The complex commonly exists as a positive ion.

The primary valency is the number of charges on the complex ion. In compounds, this charge is matched by the same number of charges from negative ions. Primary valency applies equally well to simple salts and to complexes. Thus in CoCl_2 ($\text{Co}^{2+} + 2\text{Cl}^-$) there are two primary valencies. i.e. two ionic bonds. The complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ actually exists as $[\text{Co}(\text{NH}_3)_6]^{3+}$ and 3Cl^- . Thus the primary valency is 3.

2. *Secondary valencies.* These are directional. The number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is now called the coordination number. Each metal has a characteristic number of secondary valencies. Thus in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ the 3Cl^- are held by primary valencies. The six NH_3 groups are held by secondary valencies.

[Werner's coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. This theory was put forward before the electron had been discovered by J .J, Thompson in 1896, and before the electronic theory of valency. This theory won Alfred Werner the Nobel Prize for Chemistry in 1913.]

EFFECTIVE ATOMIC NUMBERS

Sidgwick, with his effective atomic number rule, suggested that electron pairs from ligands were added until the central metal was surrounded by the same number of electrons as the next noble gas. Consider potassium hexacyanoferrate(II) $K_4[Fe(CN)_6]$.

An iron atom has 26 electrons, and so the central metal ion Fe^{2+} has 24 electrons. The next noble gas Kr has 36 electrons. Thus the addition of six electron pairs from six CN^- ligands adds 12 electrons, thus raising the effective atomic number (EAN) of Fe^{2+} in the complex $[Fe(CN)_6]^{4-}$ to 36.

$[Fe(CO)_5]$	Fe(Atomic number)-26	Electrons gained by coordination-10	EAN-36
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$Cr(CO)_6$	Cr-24	Electrons gained by coordination-12	EAN-36
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$[Co(NH_3)_6]^{3+}$	Co-27	Electrons gained by coordination-12 ,	Electrons lost in ion formation-3	EAN-36
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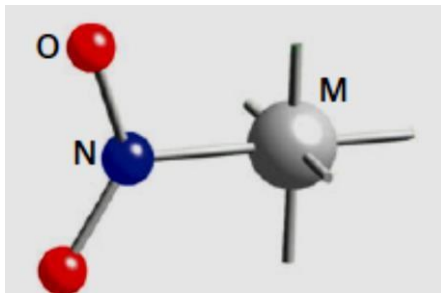
$[Cu(NH_3)_4]^{2+}$	Cu-29	Electrons gained by coordination-12,	EAN -35
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Denticity refers to the number of donor groups in a single ligand that bind to a central atom in a coordination complex. Some of these ligands have only a single donor pair of electrons and will have only one point of attachment to the metal: such ligands are classified as **monodentate** (from the Latin meaning ‘one-toothed’).

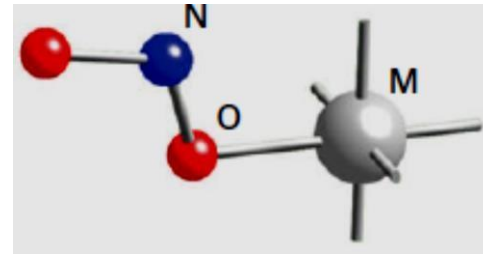
Ligands that have more than one point of attachment are classified as **polydentate**.

Ligands that specifically have two points of attachment are known as **bidentate**, those with three, **tridentate**, and so on.

Ambidentate ligands have more than one different potential donor atom. An example is the thiocyanate ion (NCS^-), which can attach to a metal atom either by the N atom, to give thiocyanato- κN complexes, or by the S atom, to give thiocyanato- κS complexes. Another example of an ambidentate ligand is NO_2^- : as MNO_2 (**4**) the ligand is nitrito- κN and as MONO^- (**5**) it is nitrito- κO .

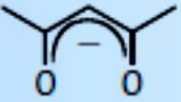
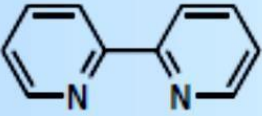
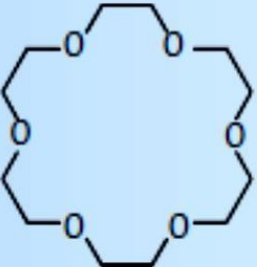


(4) Nitrito- κN ligand



(5) Nitrito- κO ligand

Typical ligands and their names

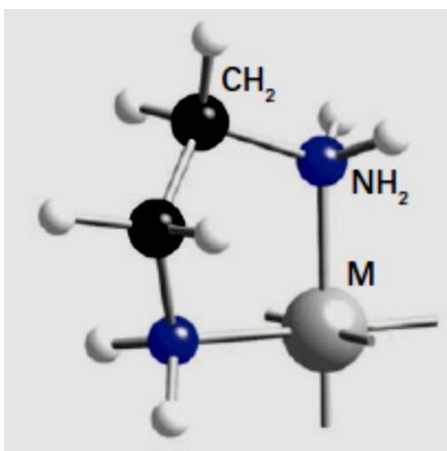
Name	Formula	Abbreviation	Donor atoms	Number of donors
Acetylacetonato		acac ⁻	O	2
Ammine	NH ₃		N	1
Aqua	H ₂ O		O	1
2,2-Bipyridine		bpy	N	2
Bromido	Br ⁻		Br	1
Carbanato	CO ₃ ²⁻		O	1 or 2
Carbonyl	CO		C	1
Chlorido	Cl ⁻		Cl	1
1,4,7,10,13,16-Hexaoxa-cyclooctadecane		18-crown-6	O	6

Prefixes used for naming complexes

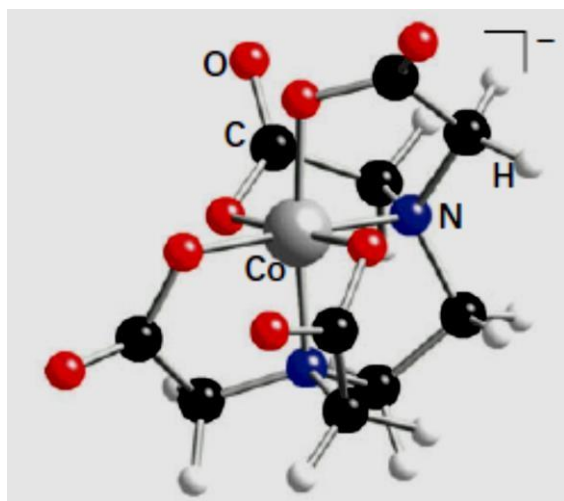
Prefix	Meaning
mono-	1
di-, bis-	2
tri-, tris-	3
tetra-, tetrakis-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

Polydentate ligands can produce a **chelate** (from the Greek for ‘claw’), a complex in which a ligand forms a ring that includes the metal atom (**6**). An example is the bidentate ligand ethylenediamine (1,2-diaminoethane, en, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), which forms a five-membered ring when both N atoms attach to the same metal atom.

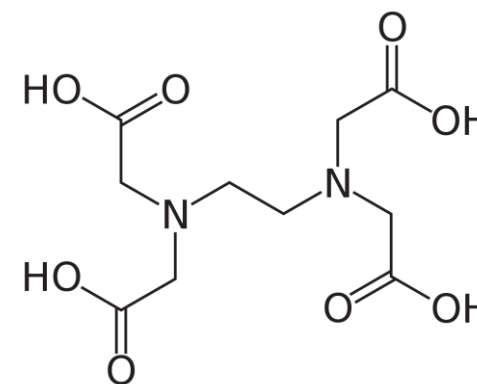
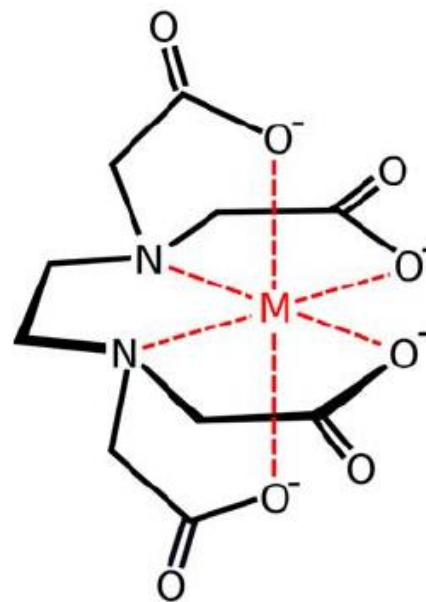
The hexadentate ligand ethylene-diaminetetraacetic acid, as its anion (edta^{4-}), can attach at six points (at two N atoms and four O atoms) and can form an complex with five five-membered rings (**7**). This ligand is used to trap metal ions, such as Ca^{2+} ions, in ‘hard’ water. Complexes of chelating ligands often have additional stability over those of non-chelating ligands—the origin of this so called **chelate effect**.



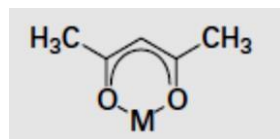
6 Ethylenediamine ligand (en)



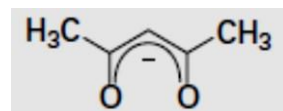
7 $[\text{Co}(\text{edta})]^-$



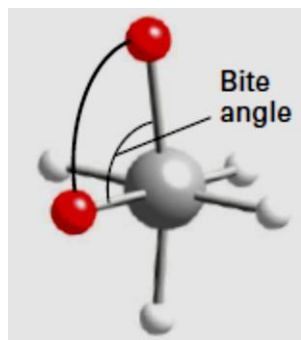
In a chelate formed from a saturated organic ligand, such as ethylenediamine, a five membered ring can fold into a conformation that preserves the tetrahedral angles within the ligand and yet still achieve an L-M-L angle of 90° , the angle typical of octahedral complexes. The bidentate β -diketones, for example, coordinate as the anions of their enols in six-membered ring structures (**8**). An important example is the acetylacetonato anion (acac-, **9**). The degree of strain in a chelating ligand is often expressed in terms of the **bite angle**, the L-M-L angle in the chelate ring(**10**).



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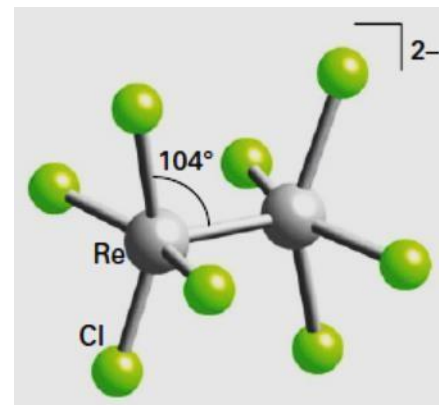
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Nomenclature

- For compounds that consist of one or more ions, the cation is named first followed by the anion.
- Complex ions are named with their ligands in alphabetical order (ignoring any numerical prefixes).
- The ligand names are followed by the name of the metal with either its oxidation number in parentheses, as in hexaamminecobalt(III) for $[\text{Co}(\text{NH}_3)_6]^{3+}$, or with the overall charge on the complex specified in parentheses, as in hexaamminecobalt(3).
- The suffix -ate is added to the name of the metal if the complex is an anion, as in the name hexacyanoferrate(II) for $[\text{Fe}(\text{CN})_6]^{4-}$.
- The number of a particular type of ligand in a complex is indicated by the prefixes mono-, di-, tri-, and tetra-. The same prefixes are used to state the number of metal atoms if more than one is present in a complex, as in octachloridodirhenate(III), $[\text{Re}_2\text{Cl}_8]^{2-}$ (**11**).



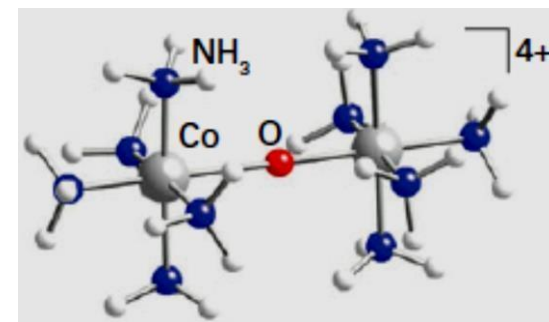
11 $[\text{Re}_2\text{Cl}_8]^{2-}$

- Where the name already includes a prefix, as with ethylenediamine, the alternative prefixes bis-, tris-, and tetrakis are used, with the ligand name in parentheses. For example, dichlorido- is unambiguous but tris(ethylenediamine) shows more clearly that there are three ethylenediamine ligands, as in tris(ethylenediamine)cobalt(II), $[\text{Co}(\text{en})_3]^{2+}$.
- Ligands that bridge two metal centres are denoted by a prefix μ (mu) added to the name of the relevant ligand, as in μ -oxido-bis(pentamminecobalt(III))(**12**). If the number of centres bridged is greater than two, a subscript is used to indicate the number; for instance a hydride ligand bridging three metal atoms is denoted $\mu_3\text{-H}$.

$\text{Ni}(\text{CO})_4$ - tetracarbonylnickel(0)

MnO_4^- for tetraoxidomanganate(VII).

$[\text{Fe}(\text{OH}_2)_6]^{2+}$ hexaaquairon(II)



12 $[(\text{H}_3\text{N})_5\text{CoOCOC}(\text{NH}_3)_5]^{4+}$

The metal symbol is given first then the ligands in alphabetical order (the earlier rule that anionic ligands precede neutral ligands has been superseded), as in $[\text{Co}(\text{Cl})_2(\text{NH}_3)_4]^+$ for tetraamminedichloridocobalt(III).

The donor atom of an ambidentate ligand is sometimes indicated by underlining it, for example $[\text{Fe}(\text{OH}_2)_5(\underline{\text{NCS}})]^{2+}$.

Problem 1: Name the complexes (a) $[\text{Pt}(\text{Cl})_2(\text{NH}_3)_4]^{2+}$; (b) $[\text{Ni}(\text{CO})_3(\text{py})]$; (c) $[\text{Cr}(\text{edta})]^-$; (d) $[\text{Co}(\text{Cl})_2(\text{en})_2]^+$; (e) $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

To name a complex, we start by working out the oxidation number of the central metal atom and then add the names of the ligands in alphabetical order.

(a) The complex has two anionic ligands (Cl), four neutral ligands (NH_3) and an overall charge of +2; hence the oxidation number of platinum must be 4. The name of the complex is tetraamminedichloridoplatinum(IV). ($x - 2 + 0 = 2$)

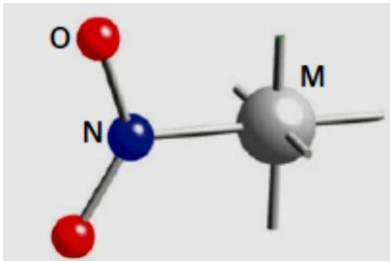
(b) The ligands CO and py (pyridine) are neutral, so the oxidation number of nickel must be 0. So, the name of the complex is tricarbonylpyridinenickel(0). ($x + 0 + 0 = 0$)

(c) This complex contains the hexadentate edta^{4-} ion as the sole ligand. The four negative charges of the ligand result in a complex with a single negative charge if the central metal ion is Cr^{3+} . The complex is therefore ethylenediaminetetraacetatochromate(III). $\{x + (-4) = -1\}$

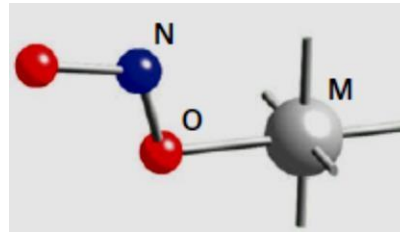
(d) This complex contains two anionic chloride ligands and two neutral en ligands. The overall charge of 1 must be the result of the cobalt having oxidation number 3. The complex is therefore dichloridobis(ethylenediamine)cobalt(III). (e) This complex contains two anionic I (iodido) ligands and two neutral CO ligands. The overall charge of 1 must be the result of the rhodium having oxidation number 1. The complex is therefore dicarbonyldiiodidorhodate(I).

Isomerism

Ambidentate ligands give rise to the possibility of **linkage isomerism**, in which the same ligand may link through different atoms. This type of isomerism accounts for the red and yellow isomers of the formula $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$. The red compound has a nitrito- κO Co-O link; the yellow isomer, which forms from the unstable red form over time, has a nitro nitrito- κN Co-N link.



Nitrito- κN ligand



Nitrito- κO ligand

Ionization isomerism occurs when a ligand and a counterion in one compound exchange places. An example is $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$. If the compounds are soluble, the two isomers exist as different ionic species in solution (in this example, with free Br^- and Cl^- ions, respectively).

Hydrate isomerism, arises when one of the ligands is water, for example there are three differently coloured hydration isomers of a compound with molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$: the violet $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$, the pale green $[\text{CrCl}(\text{OH}_2)_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and the dark green $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Coordination isomerism arises when there are different complex ions that can form from the same molecular formula, as in $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.

Geometric isomerism:

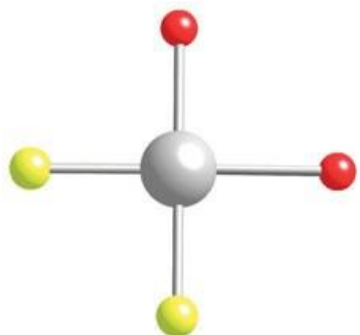
Problem 2: What types of isomerism are possible for complexes with the following molecular formulas: (a) $[\text{Pt}(\text{PEt}_3)_3\text{SCN}]^+$, (b) $\text{CoBr}(\text{NH}_3)_5\text{SO}_4$, (c) $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$?

Answer (a) The complex contains the ambidentate thiocyanate ligand, SCN^- , which can bind through either the S or the N atom to give rise to two linkage isomers: $[\text{Pt}(\underline{\text{S}}\text{CN})(\text{PEt}_3)_3]^+$ and $[\text{Pt}(\underline{\text{N}}\text{CS})(\text{PEt}_3)_3]^+$. (b) With an octahedral geometry and five coordinated ammonia ligands, it is possible to have two ionization isomers: $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$. (c) Hydrate isomerism occurs as complexes of formula $[\text{Fe}(\text{OH}_2)_6]\text{Cl}_2$, $[\text{FeCl}(\text{OH}_2)_5]\text{Cl} \cdot \text{H}_2\text{O}$, and $[\text{FeCl}_2(\text{OH}_2)_4] \cdot 2\text{H}_2\text{O}$ are possible.

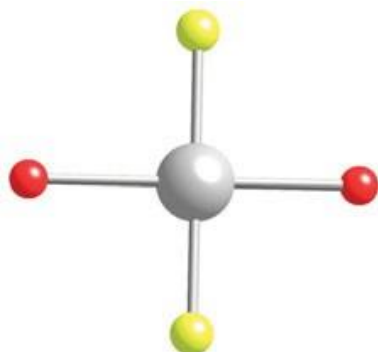
Problem 3: Two types of isomerism are possible for the six-coordinate complex $\text{Cr}(\text{NO}_2)_2 \cdot 6\text{H}_2\text{O}$. Identify all isomers.

Square-planar complexes

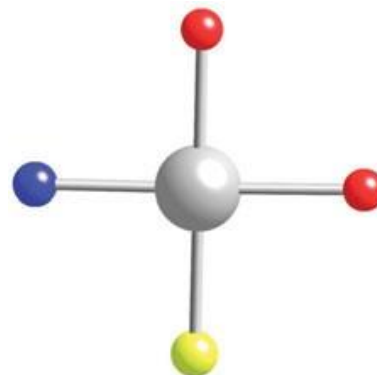
- In the simple case of two sets of two different monodentate ligands, as in $[\text{MA}_2\text{B}_2]$, there is only the case of *cis/trans* isomerism to consider, (13) and (14).
- With three different ligands, as in $[\text{MA}_2\text{BC}]$, the locations of the two A ligands also allow us to distinguish the geometric isomers as *cis* and *trans*, (15) and (16).



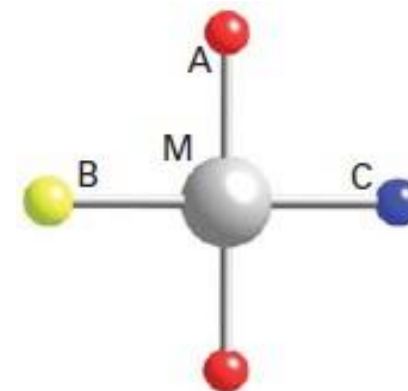
13 *cis*- $[\text{MA}_2\text{B}_2]$



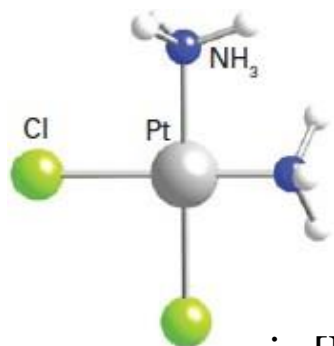
14 *trans*- $[\text{MA}_2\text{B}_2]$



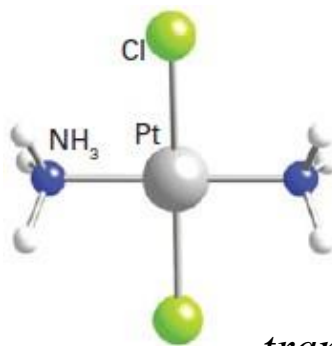
15 *cis*- $[\text{MA}_2\text{BC}]$



16 *trans*- $[\text{MA}_2\text{BC}]$

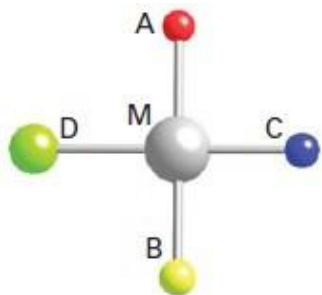


cis- $[\text{PtCl}_2(\text{NH}_3)_2]$

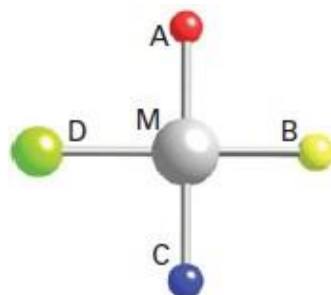


trans- $[\text{PtCl}_2(\text{NH}_3)_2]$

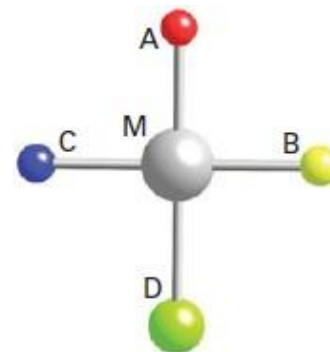
- When there are four different ligands, as in $[MABCD]$, there are three different isomers and we have to specify the geometry more explicitly, as in (17), (18), and (19).
- Bidentate ligands with different end groups, as in $[M(AB)_2]$, can also give rise to geometrical isomers that can be classified as *cis* (20) and *trans* (21).



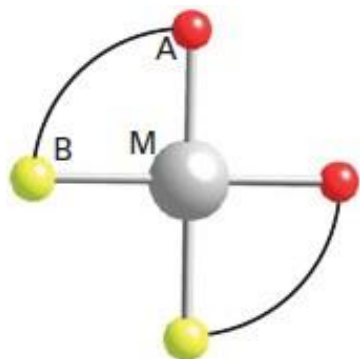
17 $[MABCD]$, A *trans* to B



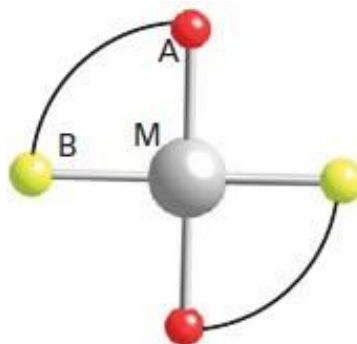
18 $[MABCD]$ A *trans* to C



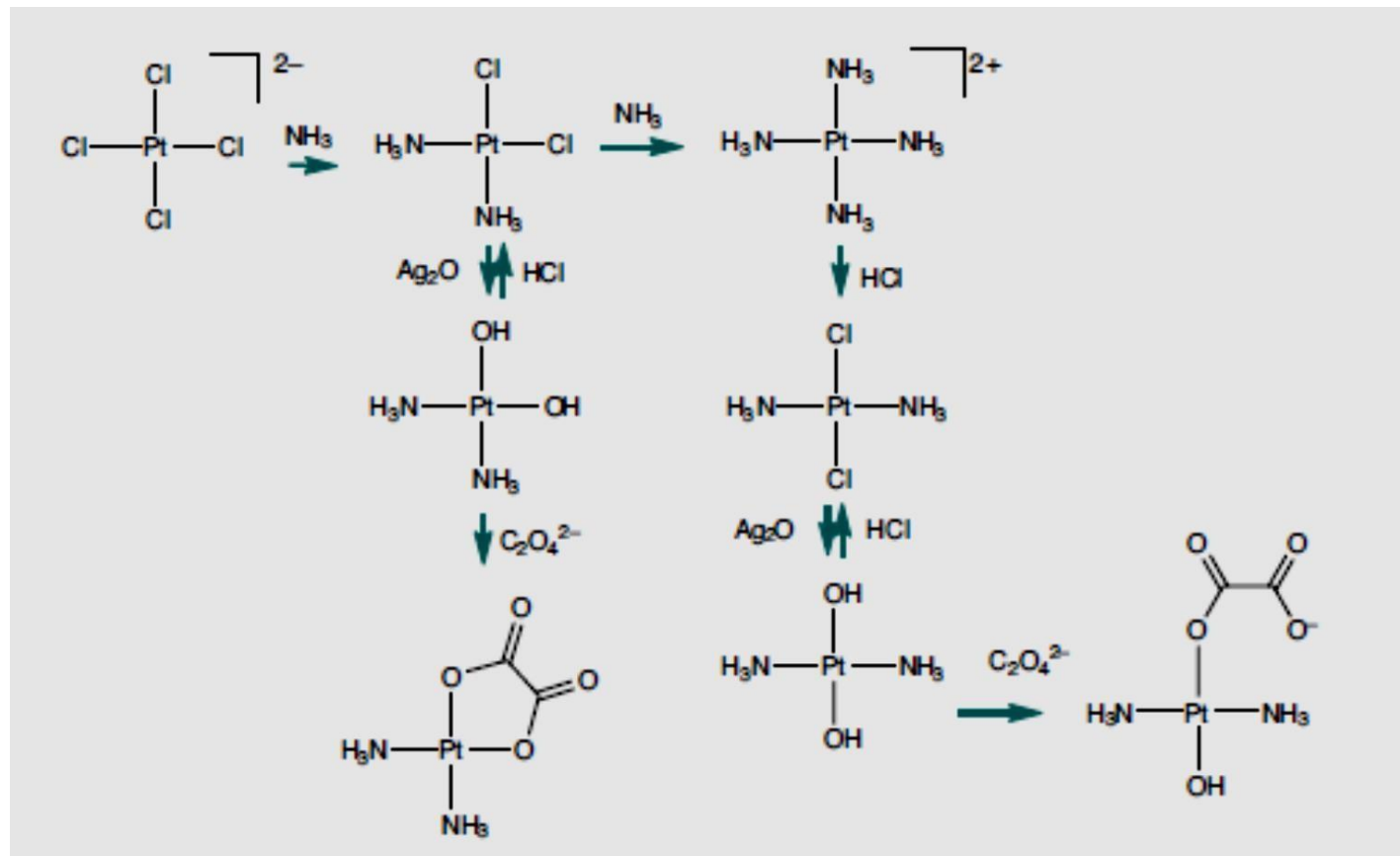
19 $[MABCD]$ A *trans* to D



20 *cis*- $[M(AB)_2]$



21 *trans*- $[M(AB)_2]$



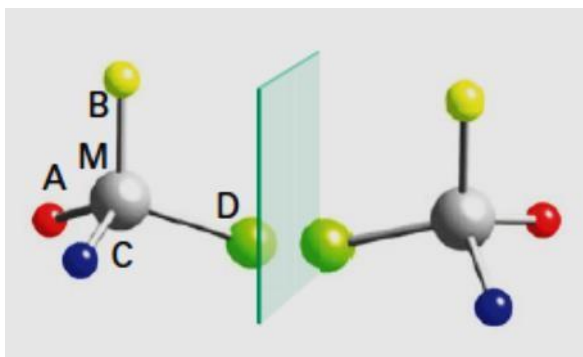
The preparation of *cis*- and *trans*-diamminedichloridoplatinum(II) and a chemical method for distinguishing the isomers.

The *cis* diamminedichlorido isomer reacts with Ag_2O to lose Cl^- , and the product adds one oxalate dianion ($\text{C}_2\text{O}_4^{2-}$) at adjacent positions. The *trans* isomer loses Cl^- , but the product cannot displace the two OH^- ligands with only one $\text{C}_2\text{O}_4^{2-}$ anion. A reasonable explanation is that the $\text{C}_2\text{O}_4^{2-}$ anion cannot reach across the square plane to bridge two *trans* positions. This conclusion is supported by X-ray crystallography.

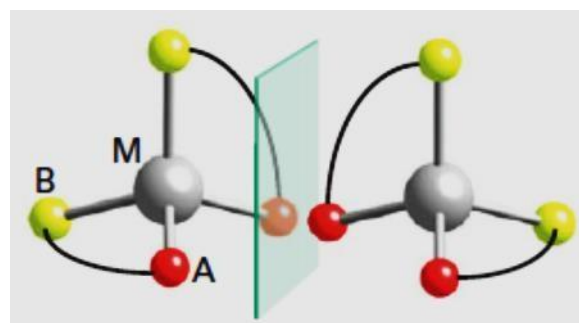
Tetrahedral complexes

In tetrahedral complexes all four ligands are different or there are two unsymmetrical bidentate chelating ligands.

In both cases, (22) and (23), the molecules are **chiral**, not superimposable on their mirror image. Two mirror-image isomers jointly make up an **enantiomeric pair**.



22[MABCD] enantiomers



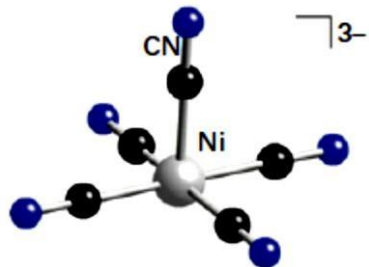
23[M(AB)₂] enantiomers

The existence of a pair of chiral complexes that are each other's mirror image (like a right hand and a left hand), and that have lifetimes that are long enough for them to be separable, is called **optical isomerism**. Optical isomers are so-called because they are **optically active**, in the sense that one enantiomer rotates the plane of polarized light in one direction and the other rotates it through an equal angle in the opposite direction.

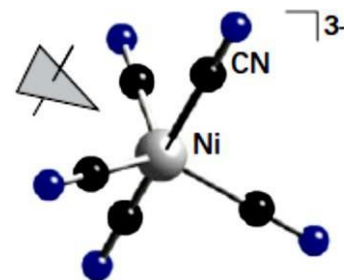
The only simple isomers of tetrahedral complexes are optical isomers.

Trigonal-bipyramidal and square-pyramidal complexes

- The energies of the various geometries of five-coordinate complexes differ little from one another.
- $[\text{Ni}(\text{CN})_5]^{3-}$ can exist as both square-pyramidal (**24**) and trigonal-bipyramidal (**25**) conformations in the same crystal.

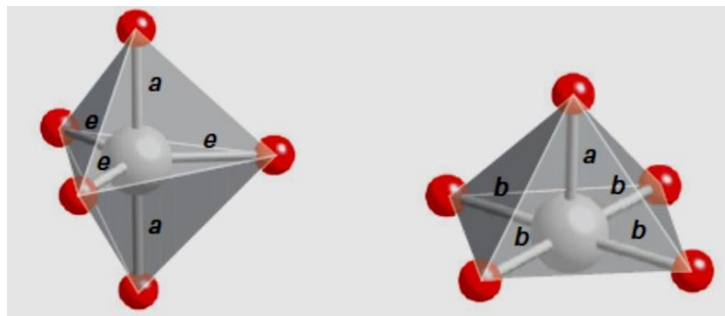


24 $[\text{Ni}(\text{CN})_5]^{3-}$, square pyramidal (C_{4v})



25 $[\text{Ni}(\text{CN})_5]^{3-}$, trigonal bipyramidal (D_{3h})

- Both trigonal bipyramidal and square-pyramidal complexes have two chemically distinct sites: axial (a) and equatorial (e) for the trigonal bipyramid (**26**) and axial (a) and basal (b) for the square pyramid (**27**).



26 Trigonal bipyramid

27 Square-pyramidal

- In solution, trigonal-bipyramidal complexes with monodentate ligands are often highly fluxional (that is, able to twist into different shapes), so a ligand that is axial at one moment becomes equatorial at the next moment: the conversion from one stereochemistry to another may occur by a **Berry pseudorotation** (Fig.1).

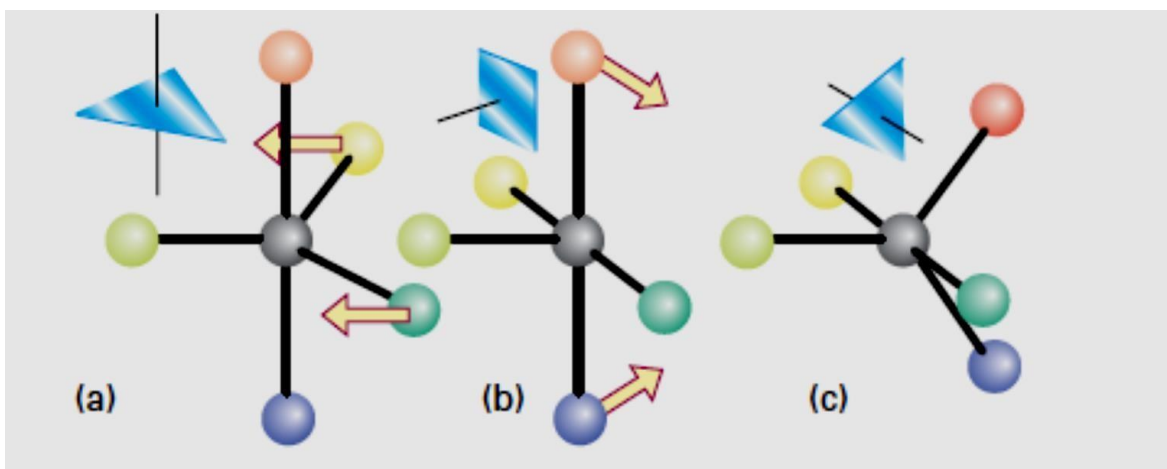
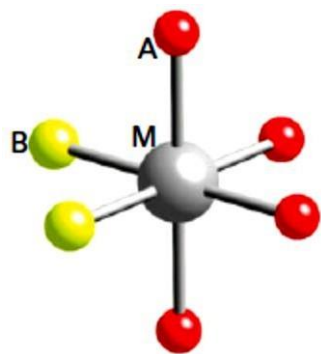


Fig 1: A Berry pseudorotation in which (a) a trigonal-bipyramidal $\text{Fe}(\text{CO})_5$ complex distorts into (b) a square-pyramidal isomer and then (c) becomes trigonal bipyramidal again, but with the two initially axial ligands now equatorial

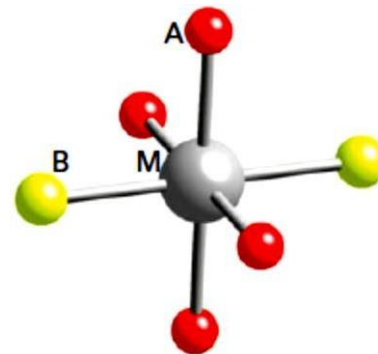
Octahedral complexes

(a) Geometrical isomerism

Whereas there is only one way of arranging the ligands in octahedral complexes of general formula $[MA_6]$ or $[MA_5B]$, the two B ligands of an $[MA_4B_2]$ complex may be placed on adjacent octahedral positions to give a *cis* isomer (**28**) or on diametrically opposite positions to give a *trans* isomer (**29**). Provided we treat the ligands as structureless points, the *trans* isomer has D_{4h} symmetry and the *cis* isomer has C_{2v} symmetry

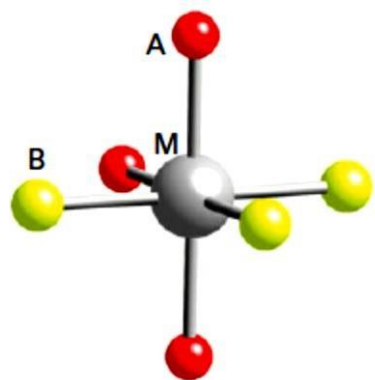


28 *cis*- $[MA_4B_2]$

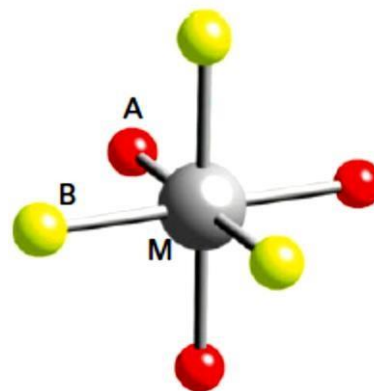


29 *trans*- $[MA_4B_2]$

There are two ways of arranging the ligands in $[\text{MA}_3\text{B}_3]$ complexes. In one isomer, three A ligands lie in one plane and three B ligands lie in a perpendicular plane (**30**). This complex is designated the *mer* isomer (for meridional) because each set of ligands can be regarded as lying on a meridian of a sphere. In the second isomer, all three A (and B) ligands are adjacent and occupy the corners of one triangular face of the octahedron (**31**); this complex is designated the *fac* isomer (for facial). If we treat the ligands as structureless points, the *mer* isomer has C_{2v} symmetry and the *fac* isomer has C_{3v} symmetry.



30 *mer*- $[\text{MA}_3\text{B}_3]$



31 *fac*- $[\text{MA}_3\text{B}_3]$

Write the formulas of the following complexes: (a) diaquadichlorido-platinum(II);
(b) diamminetetra(thiocyanato-*N*)chromate(III); (c) tris(ethylenediamine)rhodium(III);
(d) bromidopentacarbonylmanganese(I); (e) chloridotris(triphenylphosphine)rhodium(I).

Give the IUPAC name of following complexes

- | | |
|---|------------------------------------|
| (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ | Hexaamminecobalt(III) chloride |
| (b) $[\text{CoSO}_4(\text{NH}_3)_4]\text{NO}_3$ | |
| (c) $[\text{Zn}(\text{NCS})_4]^{2+}$ | Tetrathiocyanato-N-zinc(II) |
| (d) $\text{Li}[\text{AlH}_4]$ | Lithium tetrahydridoaluminate(III) |
| (e) $\text{Na}_2[\text{ZnCl}_4]$ | |
| (f) $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$ | |
| (g) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ | |

Valence bond theory

- Valence bond theory considers the interaction of atomic orbitals on separate atoms as they are brought together to form a molecule.
- The two-electron wavefunction for two widely separated H atoms is $\psi = \chi_A(1)\chi_B(2)$, where χ_A and χ_B are H1s orbitals on atoms A and B.
- When the atoms are close, it is not possible to know whether it is electron 1 that is on A or electron 2. Therefore $\psi = \chi_A(2)\chi_B(1)$, in which electron 2 is on A and electron 1 is on B.

$$\psi = \chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1) \longrightarrow (1)$$

This function is the (unnormalized) VB wavefunction for an H-H bond.

VB wavefunction is formed by **spin pairing** of the electrons in the two contributing atomic orbitals. The electron distribution described by the wavefunction in eqn 1 is called a **σ bond**.



Fig. 1. The formation of a bond from (a) s orbital overlap, (b) p orbital overlap. A bond has cylindrical symmetry around the internuclear axis.

- The **molecular potential energy curve** for H_2 , a graph showing the variation of the energy of the molecule with internuclear separation, is calculated by changing the internuclear separation R and evaluating the energy at each selected separation (Fig. 2).
- The energy is found to fall below that of two separated H atoms as the two atoms are brought within bonding distance.
- The energy begins to rise as R becomes small due to the coulombic (electrostatic) repulsion between the two positively charged nuclei.
- Consequently, the total potential energy curve passes through a minimum and then climbs to a strongly positive value at small internuclear separations.
- The depth of the minimum of the curve is denoted D_e . The deeper the minimum, the more strongly the atoms are bonded together.
- The steepness of the curve, an indication of the *stiffness* of the bond, therefore governs the vibrational frequency of the molecule

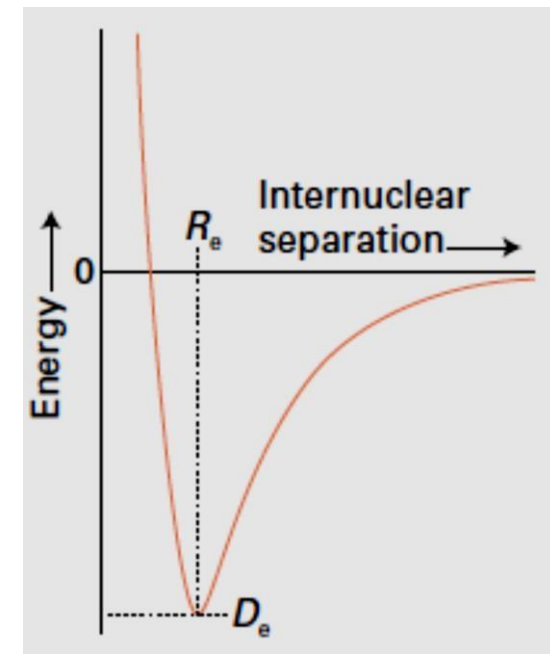


Fig. 2 A molecular potential energy Curve showing how the total energy of a molecule varies as the internuclear separation is changed.

Homonuclear diatomic molecules

Homonuclear diatomic molecules, diatomic molecules in which both atoms belong to the same element eg. N_2 .

- The valence electron configuration of each atom is $2s^2 2p_z^1 2p_y^1 2p_x^1$. Considering the z -axis to be the internuclear axis, we have $2p_z$ orbital pointing towards a $2p_z$ orbital on the other atom, with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis.
- A σ bond is then formed by spin pairing between the two electrons in the opposing $2p_z$ orbitals. Its spatial wavefunction is still given by eqn 1, but now χ_A and χ_B stand for the two $2p_z$ orbitals.
- A simple way of identifying a σ bond is to envisage rotation of the bond around the internuclear axis: if the wavefunction remains unchanged, the bond is classified as σ .

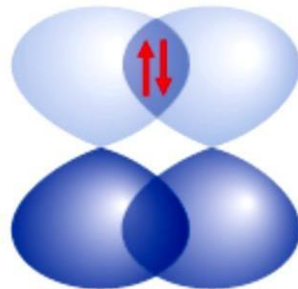
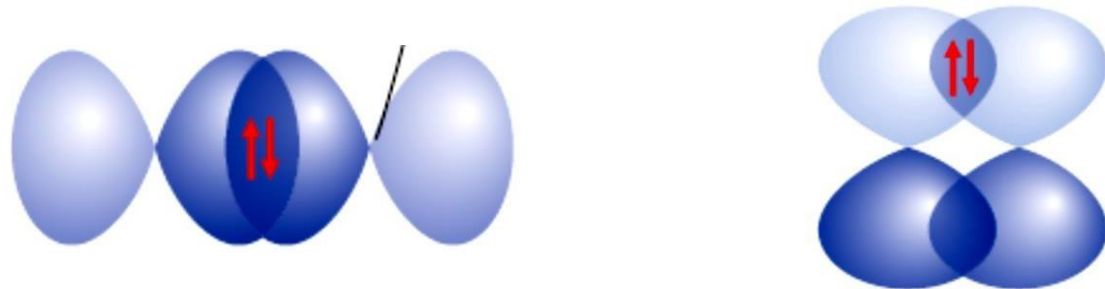


Fig 3. The VB description of N_2 . Two electrons form a bond and another two pairs form two bonds

- The remaining $2p$ orbitals merge to form two π **bonds**.

- A π bond arises from the spin pairing of electrons in two p orbitals that approach side by side (Fig. 3).
- A simple way of identifying a bond is to envisage rotation of the bond through 180° around the internuclear axis. If the signs (as indicated by the shading) of the lobes of the orbital are interchanged, then the bond is classified as π .
- There are two π bonds in N_2 , one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals.
- The overall bonding pattern in N_2 is therefore a σ bond plus two π bonds, which is consistent with the structure $\text{N}\equiv\text{N}$

Polyatomic molecules

VB description of H_2O .

The valence electron configuration of a hydrogen atom is $1s^1$ and that of an O atom is $2s^2 2p_z^2 2p_y^1 2p_x^1$

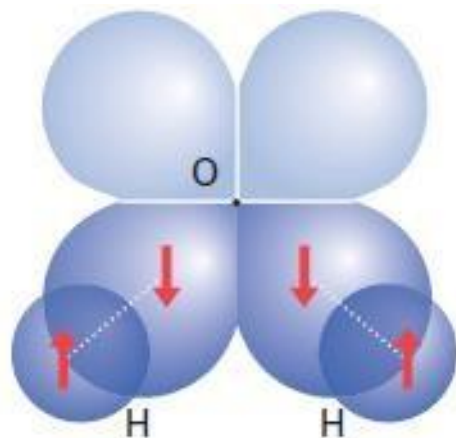


Fig. 4 The VB description of H_2O . There are two bonds formed by pairing electrons in O $2p$ and H $1s$ orbitals. This model predicts a bond angle of 90° .

- The two unpaired electrons in the O2p orbitals can each pair with an electron in an H1s orbital, and each combination results in the formation of a σ bond.
- Because the $2p_y$ and $2p_z$ orbitals lie at 90° to each other, the two bonds also lie at 90° to each other (Fig. 4). Therefore, H_2O should be an angular molecule.
- However, the theory predicts a bond angle of 90° , whereas the actual bond angle is 104.5° .
- Similarly VBT theory cannot account for the trigonal pyramidal of NH_3 molecule.
- Another deficiency of the VB theory presented so far is its inability to account for the tetravalence of carbon, its ability to form four bonds. The ground-state configuration of C is $2s^2 2p_z^1 2p_y^1$ which suggests that a C atom should be capable of forming only two bonds, not four.

These two deficiencies—the failure to account for bond angles and the valence of carbon—are overcome by introducing two new features, promotion and hybridization.

Promotion

- **Promotion** is the excitation of an electron to an orbital of higher energy in the course of bond formation.
- In carbon, for example, the promotion of a 2s electron to a 2p orbital leads to the configuration $2s^1 2p_z^1 2p_y^1 2p_x^1$, with four unpaired electrons in separate orbitals.
- These electrons may pair with four electrons in orbitals provided by four other atoms, such as four H1s orbitals if the molecule is CH₄, and hence form four σ bonds.
- Promotion of electrons may occur if the outcome is to achieve more or stronger bonds and a lower overall energy.

Hybridization

- Hybrid orbitals are formed when atomic orbitals on the same atom interfere or mix together.

The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{aligned} h_1 &= s + p_x + p_y + p_z & h_2 &= s - p_x - p_y + p_z \\ h_3 &= s - p_x + p_y - p_z & h_4 &= s + p_x - p_y - p_z \end{aligned}$$

- As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the direction of one corner of a regular tetrahedron and a smaller lobe pointing in the opposite direction (Fig.5).
- The angle between the axes of the hybrid orbitals is the tetrahedral angle, 109.47° . Because each hybrid is built from one s orbital and three p orbitals, it is called an **sp^3 hybrid orbital**.

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, pd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	$sp^2d^2, sd^4, pd^4, p^3d^2$
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

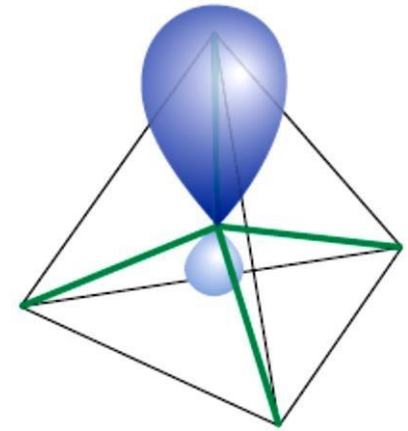
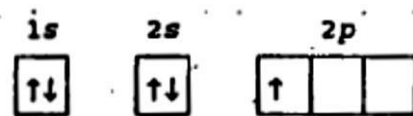


Fig. 5 One of the four equivalent sp^3 hybrid orbitals. Each one points towards a different vertex of a regular tetrahedron.



Boron atom - ground state



Boron atom - excited state



BF₃ molecule having gained a share in three electrons by bonding to three F atoms



sp^2 hybridization of the three orbitals
in outer shell, hence structure is a planar triangle

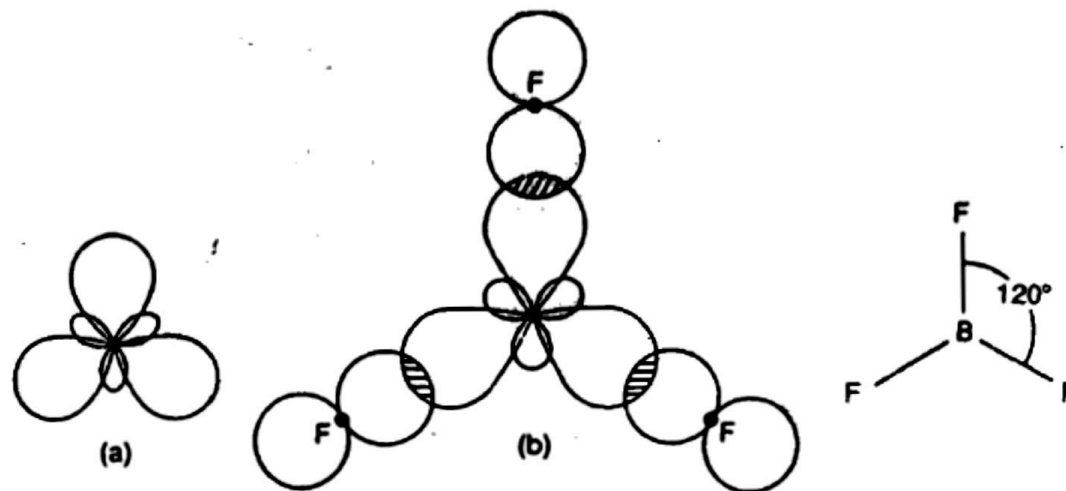
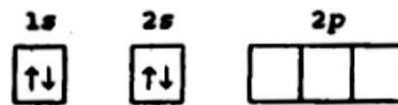


Fig (a) sp^2 hybrid orbitals and (b) the BF_3 molecule.

BeF₂

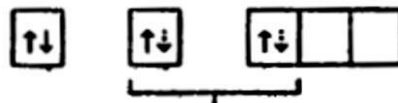
Beryllium atom - ground state



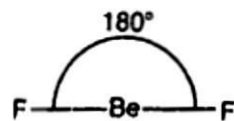
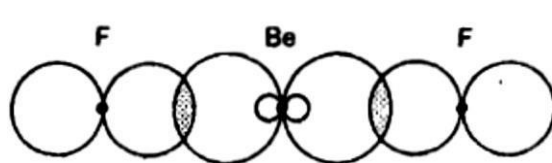
Beryllium atom - excited state



BeF₂ molecule having gained a share in two electrons by bonding to two F atoms



sp hybridization of the two orbitals in the outer shell, hence structure is linear



Problem 2: Deduce the hybridization of NO₃⁻, H₂O, PCl₅ and SF₆ molecules.

Crystal-field theory

In **crystal-field theory**, a ligand lone pair is modelled as a point negative charge (or as the partial negative charge of an electric dipole) that repels electrons in the d orbitals of the central metal ion.

(a) Octahedral complexes

- In the model of an octahedral complex used in crystal-field theory, six point negative charges representing the ligands are placed in an octahedral array around the central metal ion.
- These charges ('ligands') interact strongly with the central metal ion, and the stability of the complex stems in large part from this attractive interaction between opposite charges.
- Electrons in d_{z^2} and $d_{x^2-y^2}$ orbitals (symmetry type e_g in O_h) are concentrated close to the ligands, along the axes, whereas electrons in d_{xy} , d_{yz} , and d_{zx} orbitals (which are of symmetry type t_{2g}) are concentrated between the ligands (Fig. 1).
- As a result, the former are repelled more strongly by the negative charge on the ligands than the latter and lie at a higher energy.

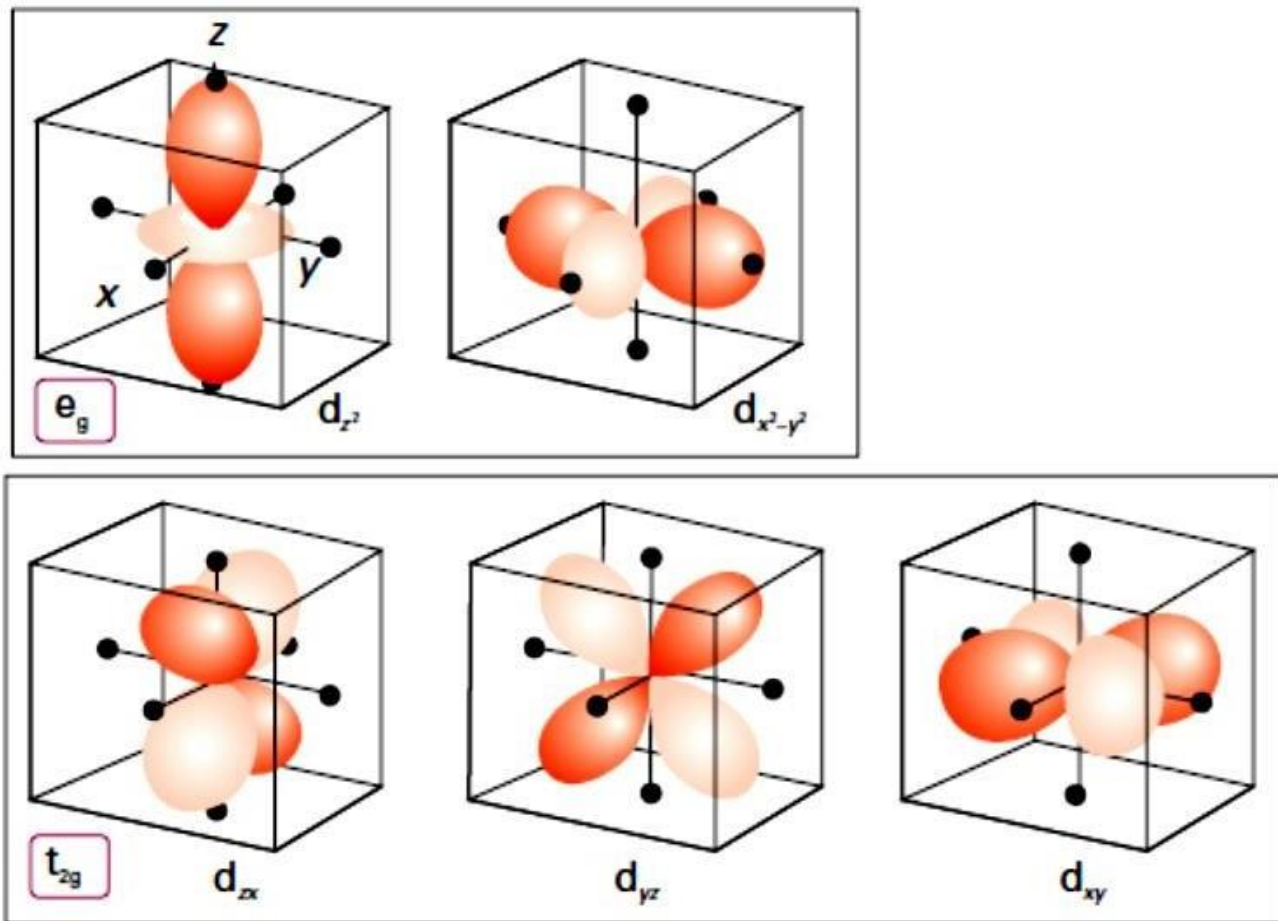


Fig. 6 The orientation of the five d orbitals with respect to the ligands of an octahedral complex: the degenerate (a) e_g and (b) t_{2g} orbitals.

- Two e_g orbitals have the same energy and the three t_{2g} orbitals also have the same energy.
- The three degenerate t_{2g} orbitals lie below the two degenerate e_g orbitals (Fig. 2). The separation of the two sets of orbitals is called the **ligand-field splitting parameter**, Δ_o (where the subscript O signifies an octahedral crystal field).

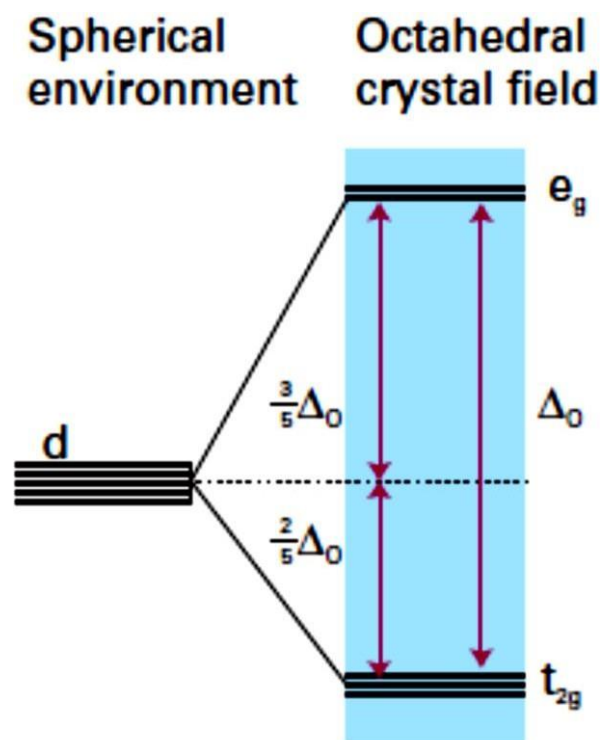
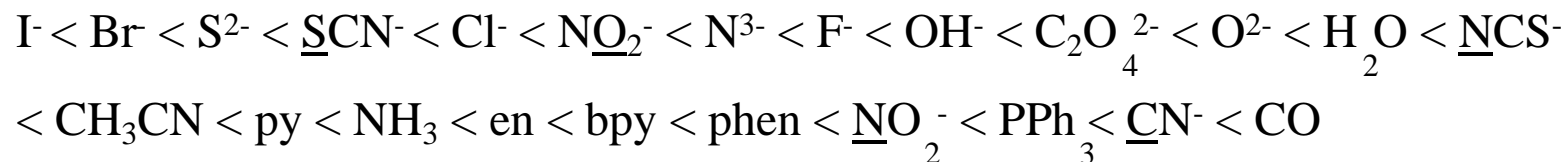


Fig. 7 The energies of the d orbitals in an octahedral crystal field. The mean energy remains unchanged relative to the energy of the d orbitals in a spherically symmetrical environment (such as in a free atom).

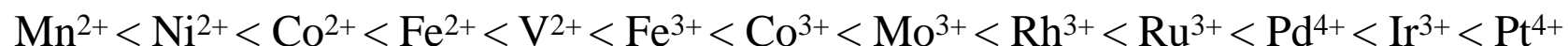
- The ligand-field splitting parameter, Δ_O , varies systematically with the identity of the ligand.
- Thus ligands can be arranged in a **spectrochemical series**, in which the members are arranged in order of increasing energy of transitions that occur when they are present in a complex:



(The donor atom in an ambidentate ligand is underlined.) Thus, for the same metal, the optical absorption of the cyano complex will occur at higher energy than that of the corresponding chlorido complex.

- A ligand that gives rise to a high energy transition (such as CO) is referred to as a **strong-field ligand**, whereas one that gives rise to a low-energy transition (such as Br) is referred to as a **weak-field ligand**.

The ligand-field strength also depends on the identity of the central metal ion, the order being approximately:



- The value of Δ_O increases with increasing oxidation state of the central metal and also increases down a group.
- The variation with oxidation state reflects the smaller size of more highly charged ions and the consequently shorter metal ligand distances and stronger interaction energies.
- The increase down a group reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands.

Selection rules and intensities

The strength of an electronic transition is determined by the transition dipole moment.

The **transition dipole moment**, which is defined as the integral

$$\mu = \int \psi_f^* \mu \psi_i d\tau$$

where μ is the electric dipole moment operator, a transition from a state with wavefunction ψ_i to one with wavefunction ψ_f .

A spectroscopic **selection rule** is a statement about which transitions are allowed and which are forbidden. An **allowed transition** is a transition with a nonzero transition dipole moment, and hence nonzero intensity. A **forbidden transition** is a transition for which the transition dipole moment is calculated as zero.

(a) Spin selection rules

- Electronic transitions with a change of multiplicity are forbidden. (multiplicity is $2S+1$, where S is the total spin angular momentum)
- For example, an initially antiparallel pair of electrons cannot be converted to a parallel pair, so a singlet ($S = 0$) cannot undergo a transition to a triplet ($S=1$). This restriction is summarized by the rule $\Delta S = 0$ for **spin allowed transitions**, Fig..
- The coupling of spin and orbital angular momenta can relax the spin selection rule, but such **Spin-forbidden**, $\Delta S \neq 0$, transitions are generally much weaker than spin-allowed transitions and can occur.
- Intensities of spin-forbidden transitions are greater for 4d- or 5d-series metal complexes than for comparable 3d-series complexes. The breakdown of the spin selection rule by spin-orbit coupling is called the **heavy-atom effect**.
- $d^5 \text{Mn}^{2+}$ ion, have no spin-allowed transitions, and hence are only weakly coloured.

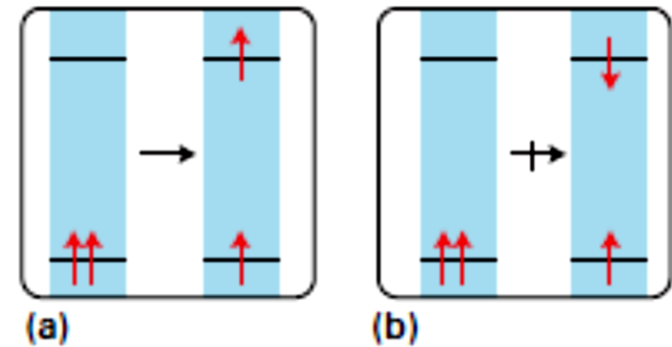


Fig. 8 (a) A spin-allowed transition does not change the multiplicity. (b) A spin-forbidden transition results in a change in the multiplicity.

(b) The Laporte selection rule

The **Laporte selection rule** states that *in a centrosymmetric molecule or ion, the only allowed transitions are those accompanied by a change in parity*. That is, transitions between g and u terms are permitted, but a g term cannot undergo a transition to another g term and a u term cannot undergo a transition to another u term:

$$g \leftrightarrow u \quad g \nleftrightarrow g \quad u \nleftrightarrow u$$

- Thus, s-s, p-p, d-d, and f-f transitions are forbidden. Since s and d orbitals are g, whereas p and f orbitals are u it follows that s-p, p-d, and d-f transitions are allowed whereas s-d and p-f transitions are forbidden.
- In a centrosymmetric complex, d-d ligand-field transitions are $g \leftrightarrow g$ and are therefore forbidden.
- Asymmetric vibrations relax this restriction.

Band type	$\epsilon_{\text{max}} /$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)
Spin-forbidden	< 1
Laporte-forbidden d-d	20–100
Laporte-allowed d-d	c. 250
Symmetry-allowed (e.g. CT)	1000–50 000

Intensities of spectroscopic
bands in 3d complexes

Concept of Gerade and Ungerade orbitals

- For homonuclear diatomics, it is convenient to signify the symmetry of the molecular orbitals with respect to their behavior under inversion through the centre of the molecule.
- The operation of **inversion** consists of starting at an arbitrary point in the molecule, travelling in a straight line to the centre of the molecule, and then continuing an equal distance out on the other side of the centre.
- The orbital is designated g (for *gerade*, even) if it is identical under inversion, and u (for *ungerade*, odd) if it changes sign. Thus, a bonding orbital is g and an antibonding orbital is u (Fig.9).

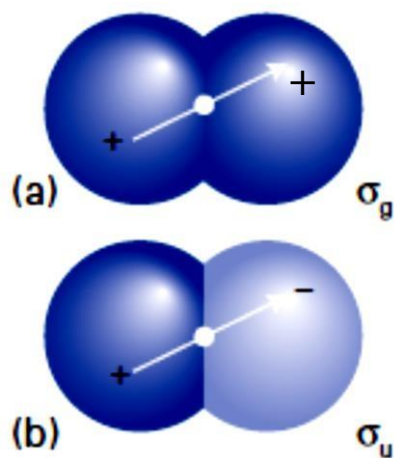
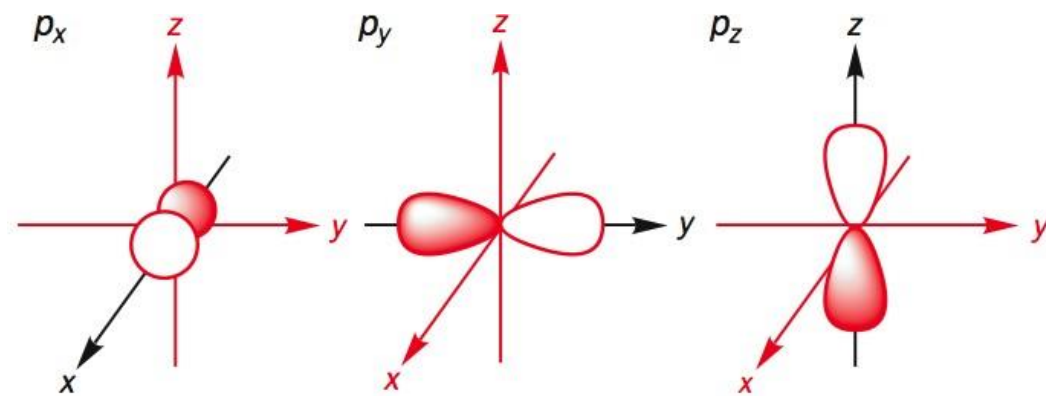
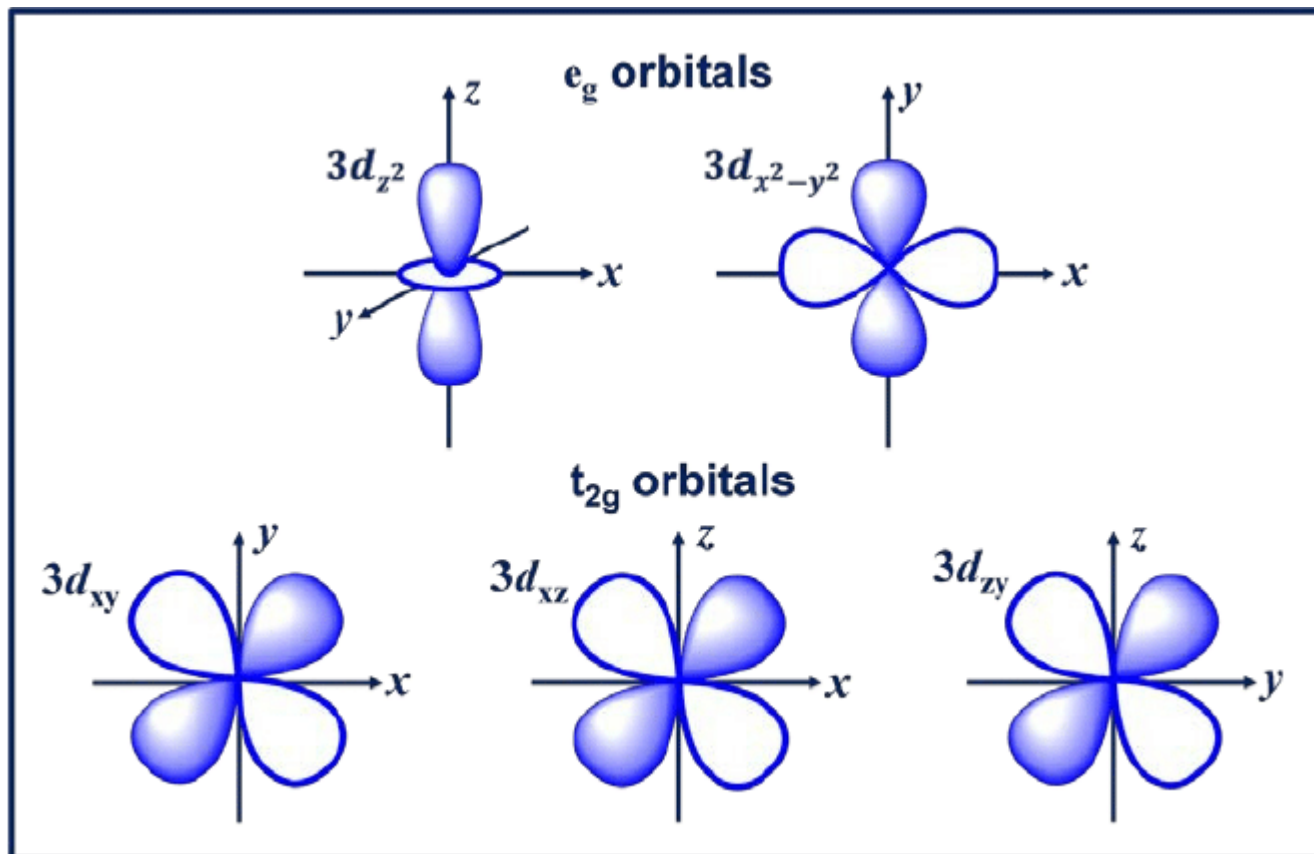


Fig 9. (a) Bonding and (b) antibonding interactions with the arrow indicating the inversion.

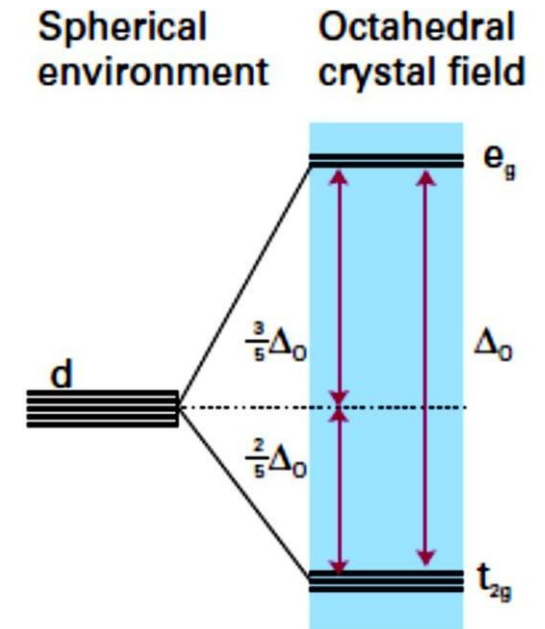
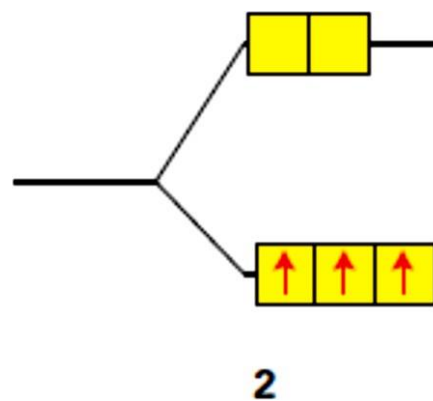
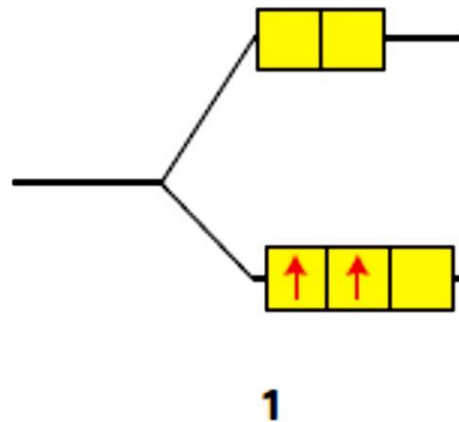


the three degenerate p orbitals are aligned along perpendicular axes

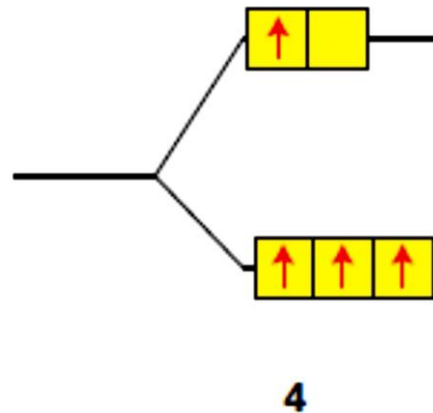
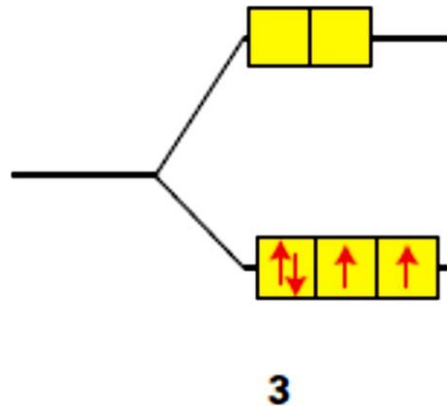
Ligand-field stabilization energies(LFSE/CFSE)

In an octahedral complex, the first three d electrons of a $3d^n$ complex occupy separate t_{2g} nonbonding orbitals, and do so with parallel spins.

For example, the ions Ti^{2+} and V^{2+} have electron configurations $3d^2$ and $3d^3$, respectively. The d electrons occupy the lower t_{2g} orbitals as shown in (1) and (2), respectively. The energy of a t_{2g} orbital relative to the barycentre of an octahedral ion is $-0.4\Delta_O$ and the complexes are stabilized by $2 \times (0.4\Delta_O) = 0.8\Delta_O$ (for Ti^{2+}) and $3 \times (0.4\Delta_O) = 1.2\Delta_O$ (for V^{2+}). This additional stability, relative to the barycentre is called the **ligand-field stabilization energy** (LFSE).



- The next electron needed for the $3d^4$ ion Cr^{2+} may enter one of the t_{2g} orbitals and pair with the electron already there (3). However, if it does so, it experiences a strong Coulombic repulsion, which is called the **pairing energy**, P . Here the net **LFSE of $1.6\Delta_O - P$** .
- Alternatively, the electron may occupy one of the e_g orbitals (4). In this case ($t_{2g}^3 e_g^1$) the **LFSE is $3 \times (0.4\Delta_O) - 0.6\Delta_O = 0.6\Delta_O$** , as there is no pairing energy to consider.
- Which configuration is adopted depends on which of $1.60\Delta_O - P$ and $0.60\Delta_O$ is the larger



- The term *crystal-field stabilization energy* (CFSE) is widely used in place of LFSE.

If $\Delta_O < P$, which is called the **weak-field case**, a lower energy is achieved when the upper orbital is occupied to give the configuration $t_{2g}^3 e_g^1$.

If $\Delta_O > P$, which is called the **strong-field case**, a lower energy is achieved by occupying only the lower orbitals despite the cost of the pairing energy. The resulting configuration is now t_{2g}^4 . For example, $[\text{Cr}(\text{OH}_2)_6]^{3+}$ has the ground-state configuration $t_{2g}^3 e_g^2$ whereas $[\text{Cr}(\text{CN})_6]^{4-}$, with relatively strong-field ligands, has the configuration t_{2g}^4 . In the weak-field case all the electrons occupy different orbitals and have parallel spins.

	Weak-field ligands		Strong-field ligands	
	Configuration	Unpaired electrons	Configuration	Unpaired electrons
$3d^4$	$t_{2g}^3 e_g^1$	4	t_{2g}^4	2
$3d^5$	$t_{2g}^3 e_g^2$	5	t_{2g}^5	1
$3d^6$	$t_{2g}^4 e_g^2$	4	t_{2g}^6	0
$3d^7$	$t_{2g}^5 e_g^2$	3	$t_{2g}^6 e_g^1$	1

The species with the smaller number of parallel electron spins is called a **low-spin complex**, and the species with the greater number of parallel electron spins is called a **high-spin complex**.

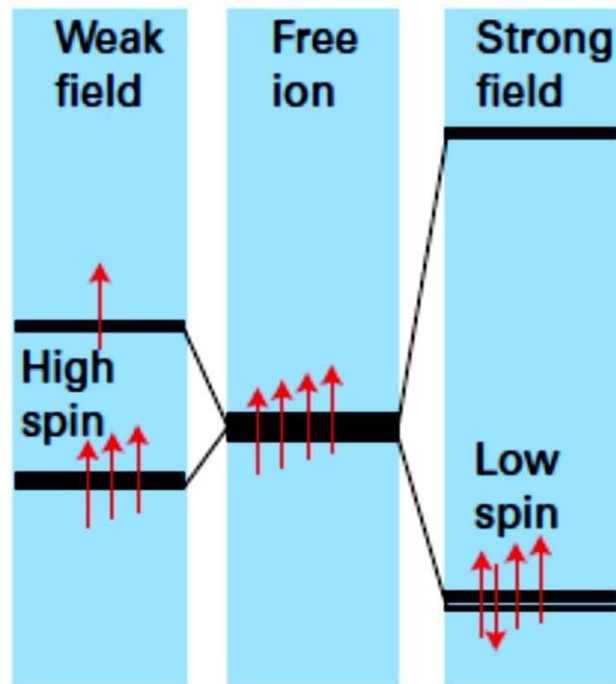


Fig 10. The effect of weak and strong ligand fields on the occupation of electrons for a d^4 complex. The former results in a high-spin configuration and the latter in a low-spin configuration.

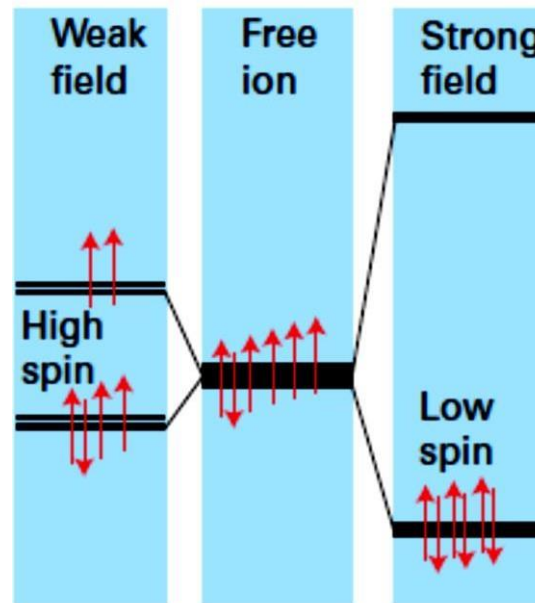


Fig. 11 The effect of weak and strong ligand fields on the occupation of electrons for a d^6 complex. The former results in a high-spin configuration and the latter in a low-spin configuration.

- In general, the net energy of a $t_{2g}^x e_g^y$ configuration relative to the barycentre, without taking the pairing energy into account, is $(0.4x - 0.6y)\Delta_O$.

- The values of Δ_O for complexes of 4d- and 5d-series metals are typically higher than for the 3d-series metals.
- Pairing energies for the 4d- and 5d-series metals tend to be lower than for the 3d-series metals because the orbitals are less compact and electron-electron repulsions correspondingly weaker.
- Consequently, complexes of these metals generally have electron configurations that are characteristic of strong crystal fields and typically have low spin. An example is the 4d⁴ complex $[\text{RuCl}_6]^{2-}$, which has a t_{2g}^4 configuration, which is typical of a strong crystal field despite Cl^- being low in the spectrochemical series. Likewise, $[\text{Ru}(\text{ox})_3]^{3-}$ has the low-spin configuration t_{2g}^5 whereas $[\text{Fe}(\text{ox})_3]^{3-}$ has the high-spin configuration $t_{2g}^3 e_g^2$.

Problem 1 : Determine the LFSE for the following octahedral ions : (a) d³, (b) high-spin d⁵, (c) high-spin d⁶, (d) low-spin d⁶, (e) d⁹.

(a) A d³ ion has configuration t_{2g}^3 (no pairing of electrons) and therefore $\text{LFSE} = 3 \times (0.4\Delta_O) = 1.2\Delta_O$.

(b) A high spin d⁵ ion has configuration $t_{2g}^3 e_g^2$ (no pairing of electrons) therefore $\text{LFSE} = 3 \times (0.4\Delta_O) - 2 \times (0.6\Delta_O) = 0$.

(d) A low-spin d⁶ ion has configuration t_{2g}^6 with the pairing of three pairs of electrons. However, since one pair of electrons would be paired in a spherical field the additional pairing energy is $2P$. Therefore $\text{LFSE} = 6 \times (0.4\Delta_O) - 3P = 2.4\Delta_O - 3P$.

Problem 2: What is the LFSE for both high- and low-spin d^7 configurations?

Ligand-field stabilization energies for octahedral complexes

d^n	Example	N (high spin)	LFSE/ Δ_0	N (low spin)	LFSE/ Δ_0
d^0		0	0		
d^1	Ti^{3+}	1	0.4		
d^2	V^{3+}	2	0.8		
d^3	Cr^{3+}, V^{2+}	3	1.2		
d^4	Cr^{2+}, Mn^{3+}	4	0.6	2	$1.6 - P$
d^5	Mn^{2+}, Fe^{3+}	5	0	1	$2.0 - 2P$
d^6	Fe^{2+}, Co^{3+}	4	0.4	0	$2.4 - 2P$
d^7	Co^{2+}	3	0.8	1	$1.8 - P$
d^8	Ni^{2+}	2	1.2		
d^9	Cu^{2+}	1	0.6		
d^{10}	Cu^+, Zn^{2+}	0	0		

Magnetic measurements

Compounds are classified as **diamagnetic** if they are repelled by a magnetic field and **paramagnetic** if they are attracted by a magnetic field.

The spin-only magnetic moment, μ , of a complex with total spin quantum number S is

$$\mu = 2\{S(S + 1)\}^{1/2}\mu_{\text{B}}$$

where μ_{B} is the **Bohr magneton**, $\mu_{\text{B}} = eh/2m_{\text{e}}$ with the value $9.274 \times 10^{-24} \text{ J T}^{-1}$. Because $S = \left(\frac{1}{2}\right)N$, where N is the number of unpaired electrons, each with spin $s = 1/2$,

$$\mu = \{N(N + 2)\}^{1/2}\mu_{\text{B}}$$

For example, magnetic measurements on a d^6 complex easily distinguish between a high-spin $t_{2g}^4 e_g^2$ ($N = 4$, $S = 2$, $\mu = 4.90\mu_{\text{B}}$) configuration and a low-spin t_{2g}^6 ($N = 0$, $S = 0$, $\mu = 0$) configuration.

For instance, $[\text{Fe}(\text{OH}_2)_6]^{3+}$ is paramagnetic with a magnetic moment of $5.9\mu_{\text{B}}$. this value is consistent with there being five unpaired electrons ($N = 5$ and $S = 5/2$), which implies a high-spin $t_{2g}^3 e_g^2$ configuration.

Problem 3 : Calculate the spin only magnetic moments of the (a) Ti^{3+} (b) V^{3+} (c) Cr^{3+} (d) Mn^{3+} (e) Fe^{3+}

(a) Ti^{3+} t_{2g}^1 $S = 1/2$, $\mu = 1.73 \mu_B$

(b) V^{3+} t_{2g}^2 $S =$, μ

(c) Cr^{3+} t_{2g}^3 $S = 3/2$, $\mu = 3.87 \mu_B$

(d) Mn^{3+}

(e) Fe^{3+}

Problem 4 : The magnetic moment of a certain octahedral Co(II) complex is $4.0 \mu_B$. What is its d-electron configuration?

Answer. A Co(II) complex is d^7 . The two possible configurations are $t_{2g}^5 e_g^2$ (high spin, $N = 3$, $S = 3/2$) with three unpaired electrons or $t_{2g}^6 e_g^1$ (low spin, $N = 1$, $S = 1/2$) with one unpaired electron. The spin-only magnetic moments are $3.87 \mu_B$ and $1.73 \mu_B$, respectively. Therefore, the only consistent assignment is the high-spin configuration $t_{2g}^5 e_g^2$.

Problem 5: The magnetic moment of the complex $[\text{Mn(NCS)}_6]^{4-}$ is $6.06 \mu_B$. What is its electron configuration?

Tetrahedral complexes

A tetrahedral crystal field splits d orbitals into two sets but with the two e orbitals (the $d_{x^2-y^2}$ and the d_{z^2}) lower in energy than the three t_2 orbitals (the d_{xy} , the d_{yz} and the d_{zx}) (Fig.12).1

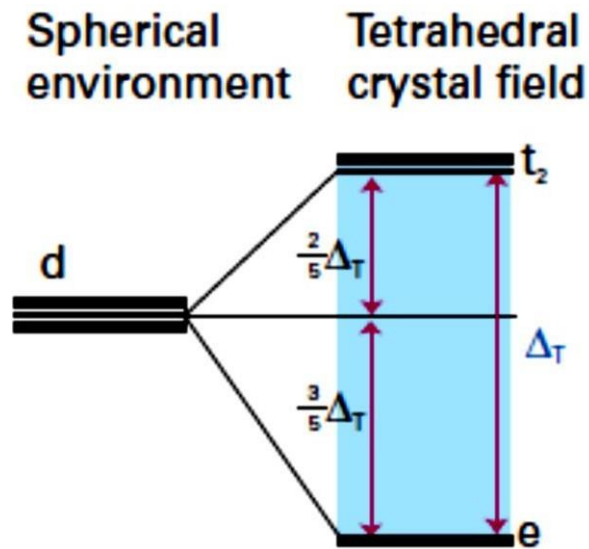
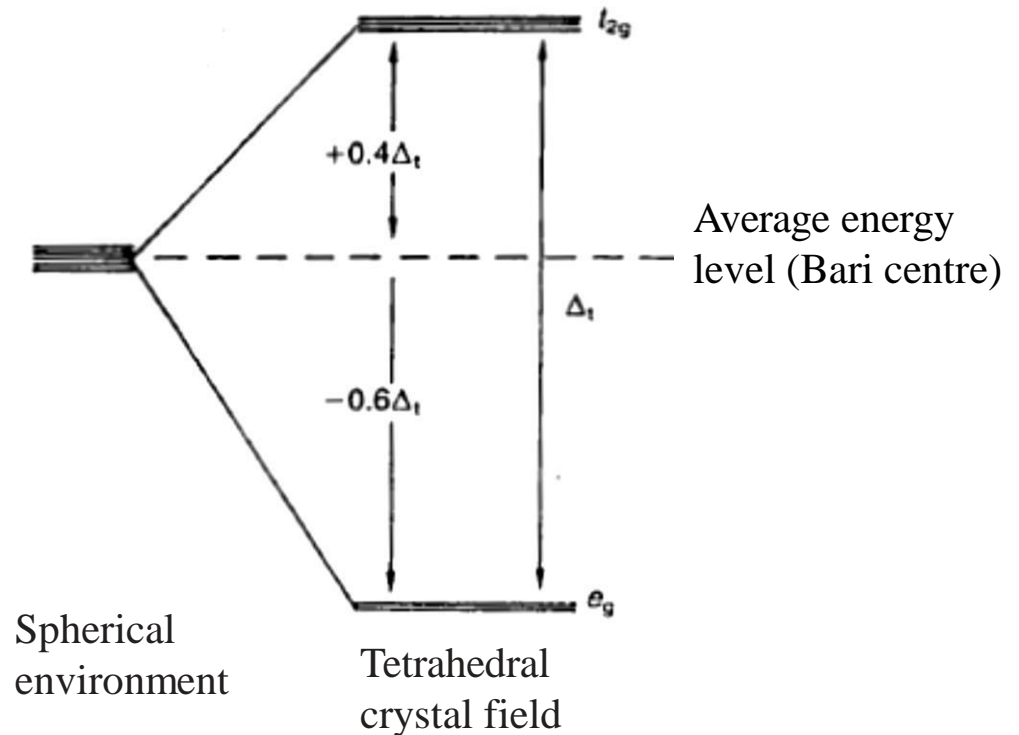


Fig 12. The orbital energy level diagram used in the application of the building-up principle in a crystal-field analysis of a tetrahedral complex



- The e orbitals point between the positions of the ligands and their partial negative charges whereas the t_2 orbitals point more directly towards the ligands (Fig. 13).
- A second difference is that the ligand-field splitting parameter in a tetrahedral complex, Δ_T , is less than Δ_O , as there are fewer ligands, none of which is oriented directly at the d orbitals (in fact, $\Delta_T \approx 4/9 \Delta_O$).

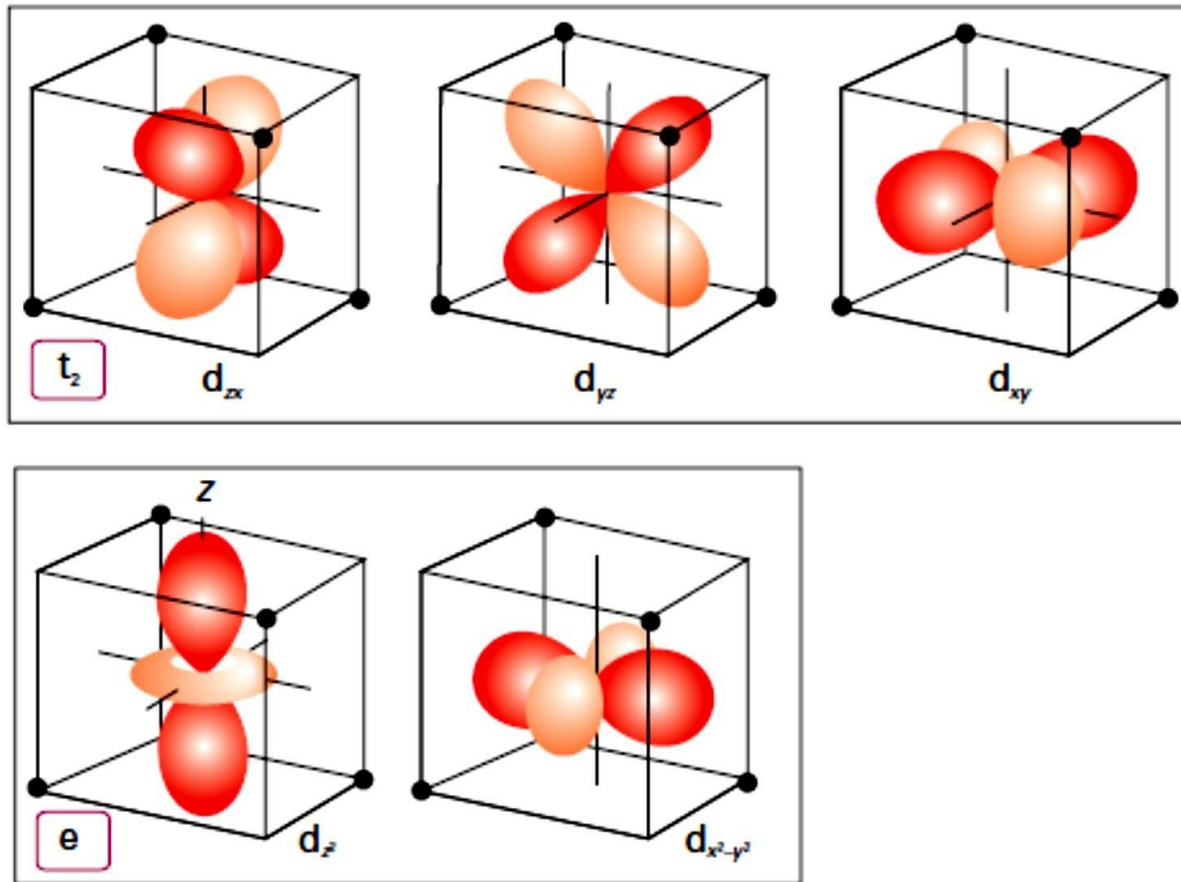


Fig. 13 The effect of a tetrahedral crystal field on a set of d orbitals is to split them into two sets; the e pair (which point less directly at the ligands) lie lower in energy than the t_2 triplet.

The magnitude of Δ_o depends on three factors:

1. The nature of the ligands.
2. The charge on the metal ion.
3. Whether the metal is in the first, second or third row of transition elements.

Crystal field splitting for hexa-aqua complexes of M^{1+} and M^{3+}

Oxidation state		Ti	V	Cr	Mn	Fe	Co
(+II)	Electronic configuration	d^2	d^3	d^4	d^5	d^6	d^7
	Δ_o in cm^{-1}	–	12 600	13 900	7 800	10 400	9 300
	Δ_o in kJ mol^{-1}	–	151	(166)	93	124	111
(+III)	Electronic configuration	d^1	d^2	d^3	d^4	d^5	d^6
	Δ_o in cm^{-1}	20 300	18 900	17 830	21 000	13 700	18 600
	Δ_o in kJ mol^{-1}	243	226	213	(251)	164	222

Δ_o crystal field splittings in one group

	cm^{-1}	kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34 000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41 000	490

Tetragonally distorted complexes: the JahnTeller effect

Jahn–Teller effect: If the ground electronic configuration of a nonlinear complex is orbitally degenerate, and asymmetrically filled, then the complex distorts so as to remove the degeneracy and achieve a lower energy.

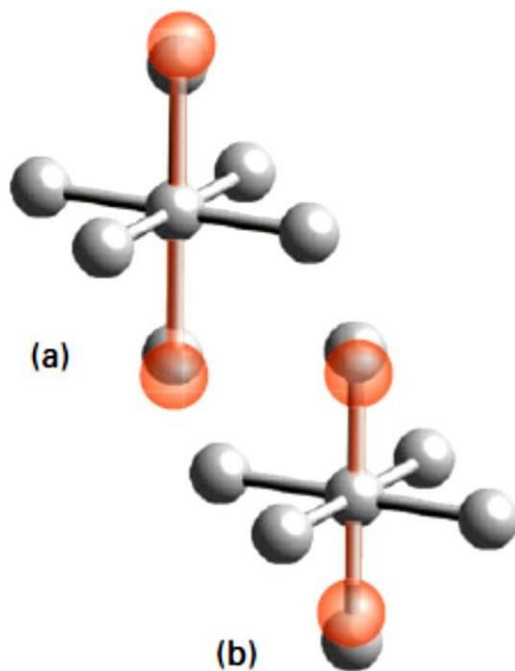


Fig.14 (a) A tetragonally distorted complex where two of the ligands have moved further away from the central ion.

(b) A tetragonally distorted complex where two of the ligands have moved closer towards the central ion.

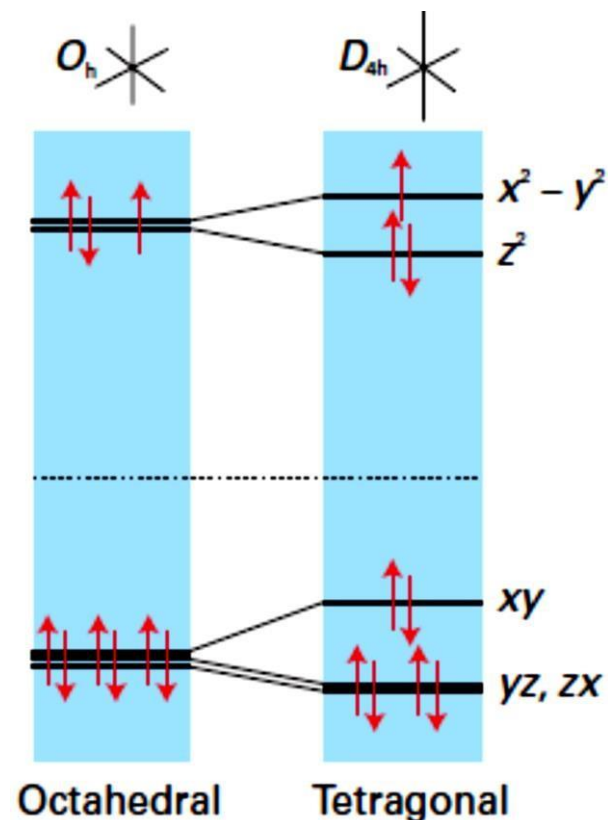
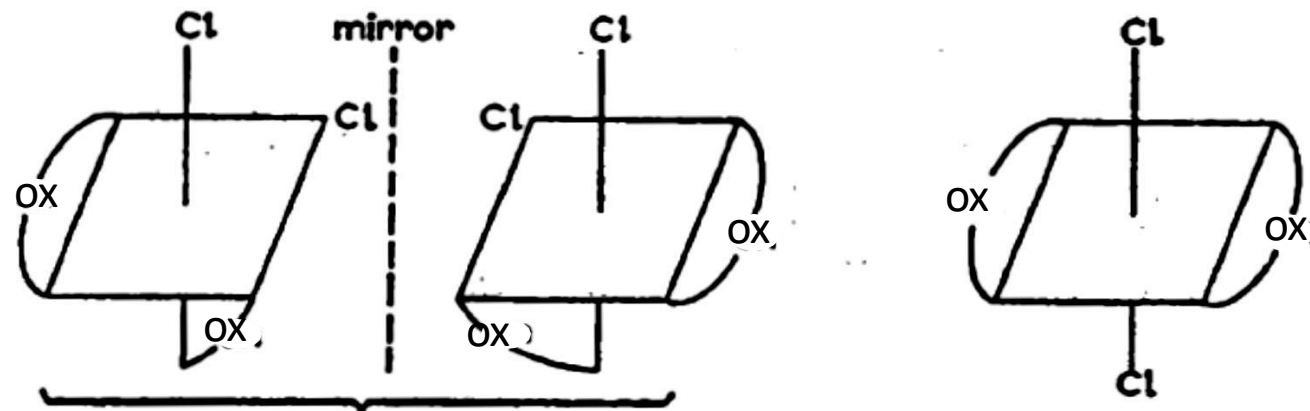


Fig.15 The effect of tetragonal distortions (compression along x and y and extension along z) on the energies of d orbitals. The electron occupation is for a d^9 complex.

- A tetragonal distortion of a regular octahedron, corresponding to extension along the z -axis and compression on the x - and y -axes, lowers the energy of the $e_g(d_{z^2})$ orbital and increases the energy of the $e_g(d_{x^2-y^2})$ orbital (Fig.).
- Therefore, if one or three electrons occupy the e_g orbitals (as in high-spin d^4 , low-spin d^7 , and d^9 complexes) a tetragonal distortion may be energetically advantageous.
- For example, in a d^9 complex (with configuration that would be $t_{2g}^6 e_g^3$ in Oh), such a distortion leaves two electrons in the d_{z^2} orbital with a lower energy and one in the $d_{x^2-y^2}$ orbital with a higher energy. Similar distortions can occur with tetrahedral complexes.

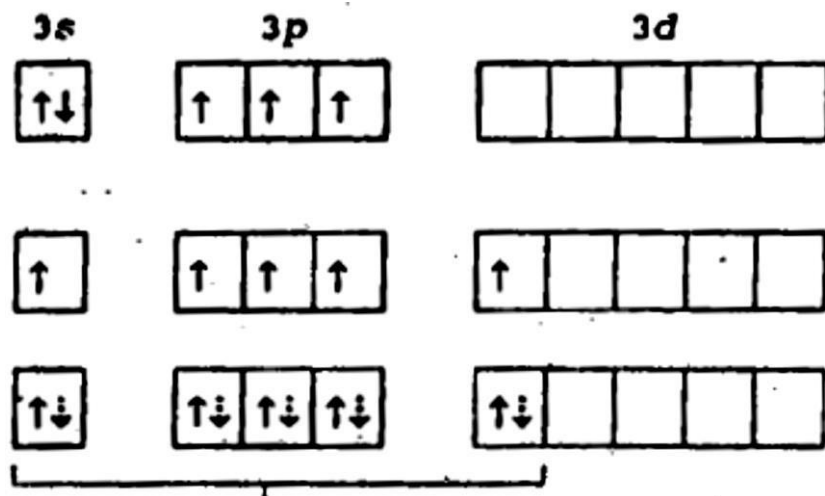
Which of the complexes (a) $cis-[Cr(Cl)_2(ox)_2]^{3-}$, (b) $trans-[Cr(Cl)_2(ox)_2]^{3-}$, (c) $cis-[RhH(CO)(PR_3)_2]$ are chiral?

Ans: a is chiral, b and c are achiral



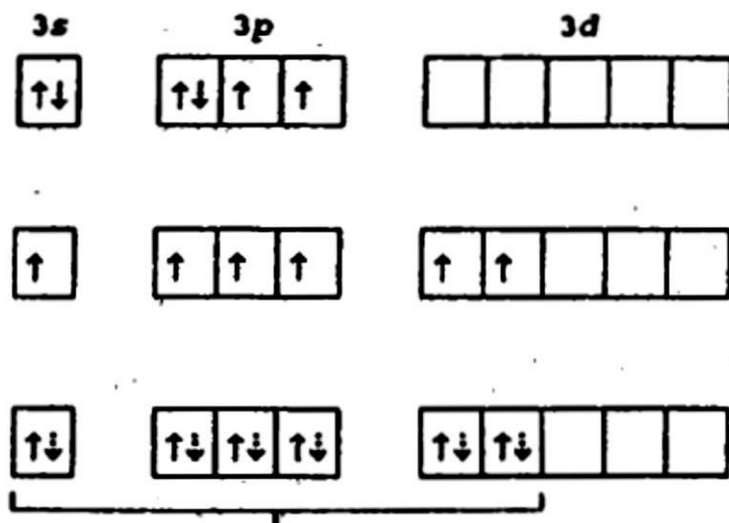
Deduce the hybridization of NO_3^- , H_2O , PCl_5 and SF_6 molecules.

PCl_5



sp^3d hybridization, trigonal bipyramid

SF_6



sp^3d^2 hybridization, octahedral structure

$$\text{Hybridization} = \frac{1}{2}(V+M-C+A)$$

V- No. of valence electrons of central atom

M- No. of monovalent atom

C- Total cation charge

A- Total anion charge

Electronic Configuration of 3d series of transition elements. The electronic configuration of these elements is $(n-1) d^{1-10} ns^{1-2}$.

Atomic number	Symbol	Electronic configuration
21	Sc	$[Ar]3d^1 4s^2$
22	Ti	$[Ar]3d^2 4s^2$
23	V	$[Ar]3d^3 4s^2$
24	Cr	$[Ar]3d^5 4s^1$
25	Mn	$[Ar]3d^5 4s^2$
26	Fe	$[Ar]3d^6 4s^2$
27	Co	$[Ar]3d^7 4s^2$
28	Ni	$[Ar]3d^8 4s^2$
29	Cu	$[Ar]3d^{10} 4s^1$
30	Zn	$[Ar]3d^{10} 4s^2$