

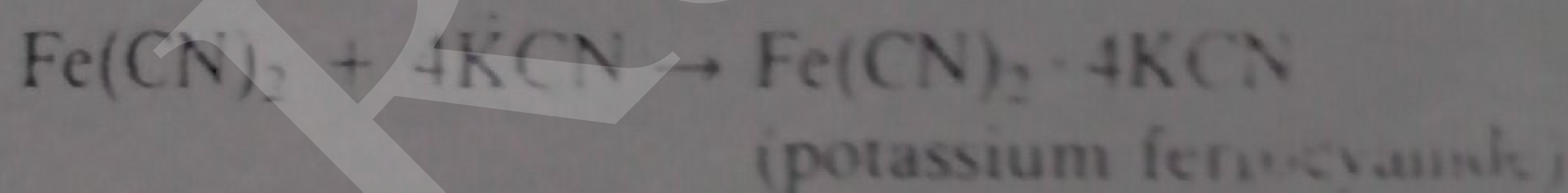
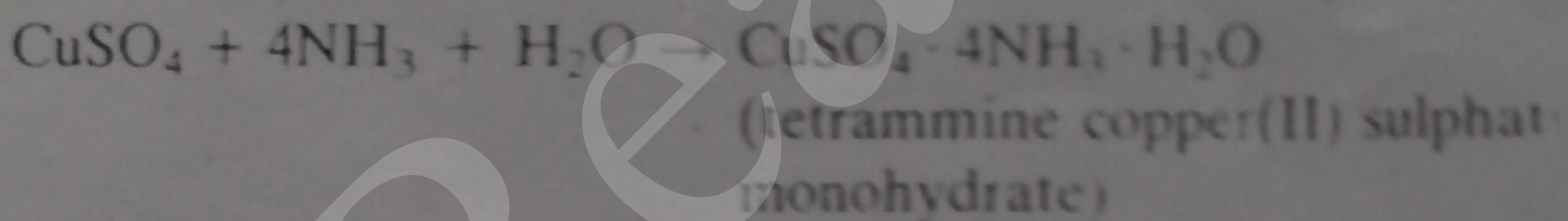
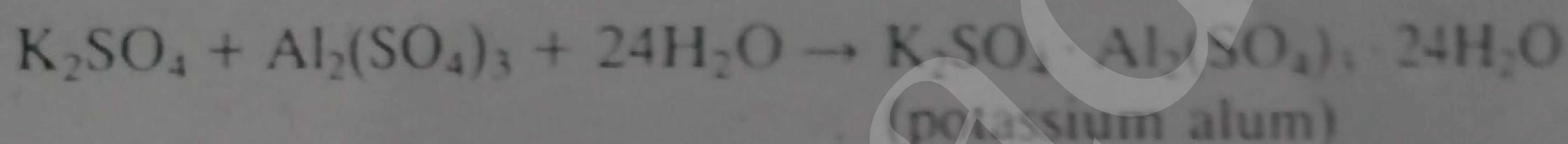
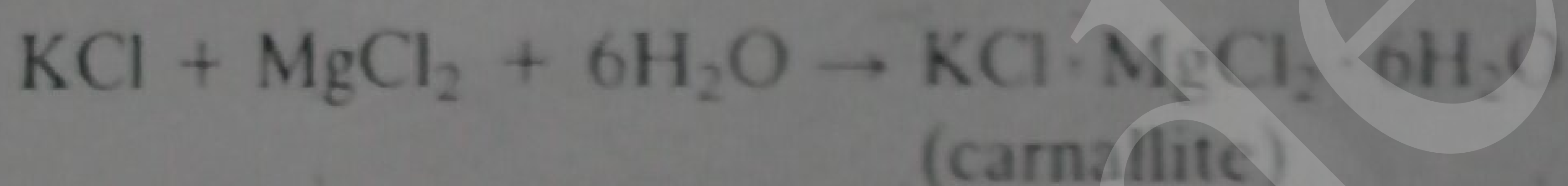
UMA SHANU
#J.D-Lee
28
25

7

NEW
Coordination compounds

DOUBLE SALTS AND COORDINATION COMPOUNDS

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

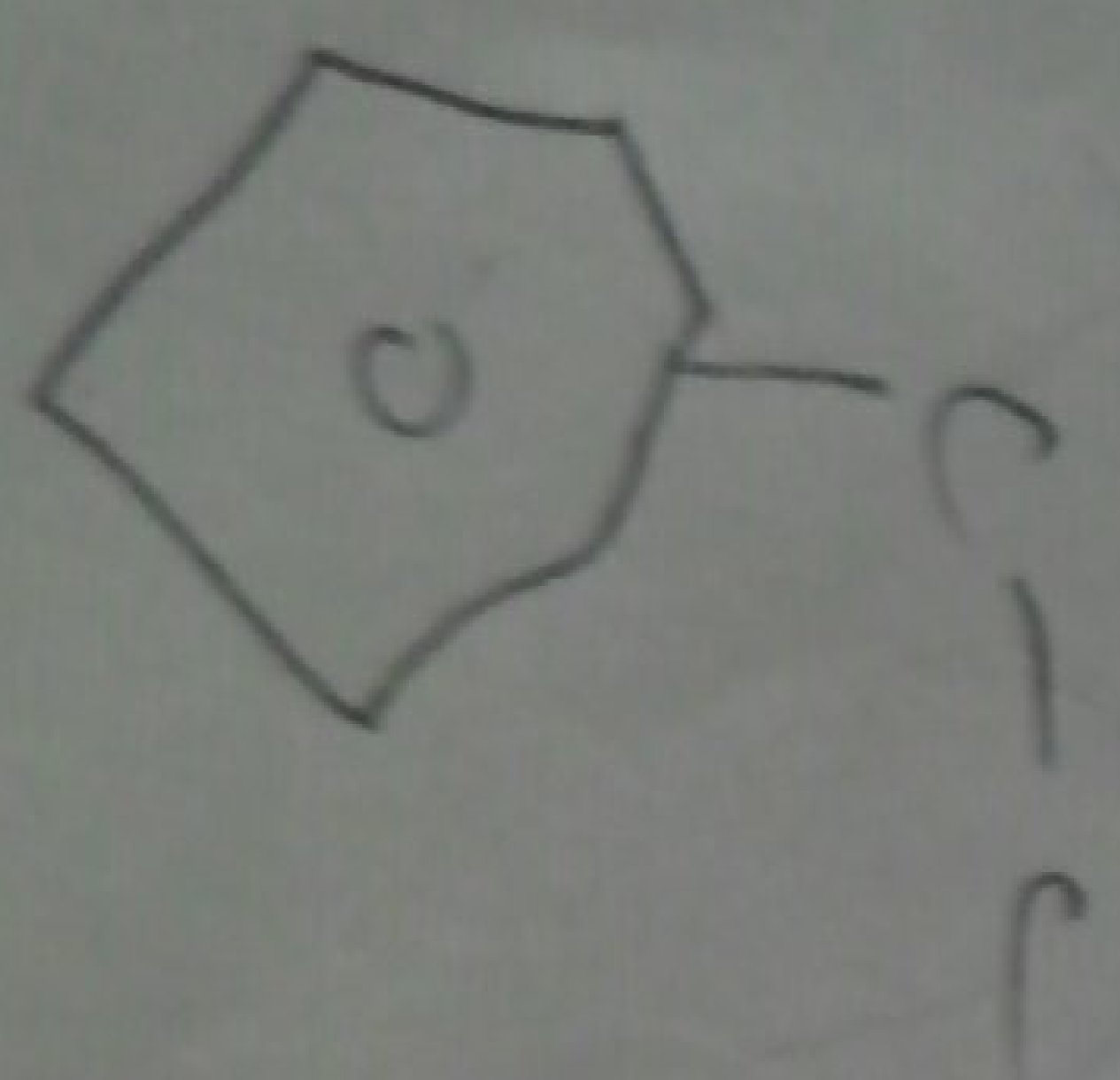


Addition compounds are of two types:

1. 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 K^+ , Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state.

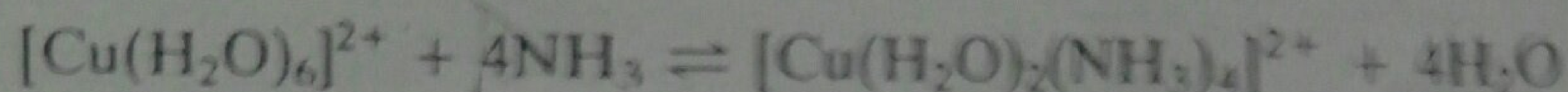
When the other two examples of coordination compounds dissolve they do not form simple ions - Cu^{2+} , or Fe^{2+} and CN^- - but instead their complex ions remain intact. Thus the cuproammonium ion $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ and the ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ 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. *The chemistry of metal ions in solution is essentially the chemistry of their complexes. Transition metal ions, in particular, form many stable complexes.* In solution 'free' metal ions are coordinated either to water or to other ligands. Thus Cu^{2+} exists as the pale blue complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution (and also in hydrated



Handwritten notes: K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, H_2O

Handwritten note: $[\text{Cu}]$

crystalline salts). If aqueous ammonia is added to this solution, the familiar deep blue cuproammonium ion is formed:



Note that this reaction is a substitution reaction, and the NH_3 replaces water in the complex ion.

WERNER'S WORK

Werner's coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. It must be remembered that this imaginative 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 and his painstaking work over the next 20 years won Alfred Werner the Nobel Prize for Chemistry in 1913.

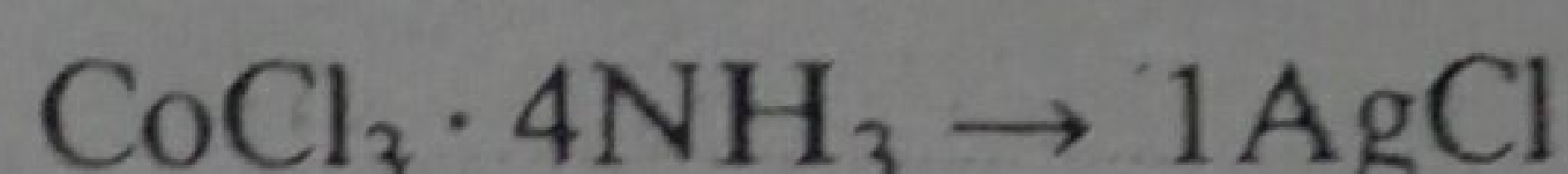
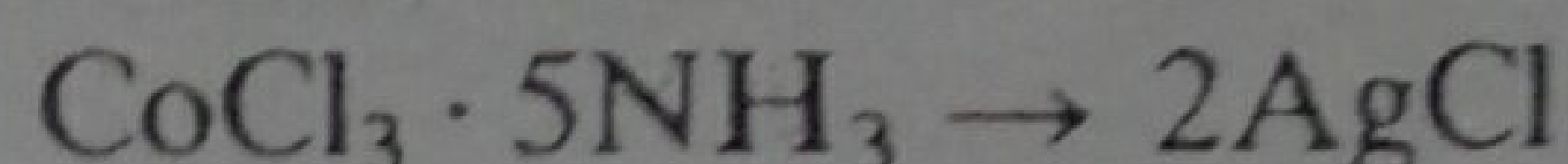
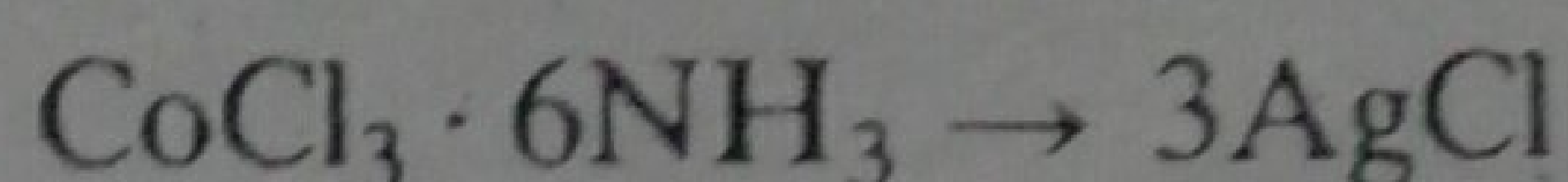
Complexes must have been a complete mystery without any knowledge of bonding or structure. For example, why does a stable salt like CoCl_2 react with a varying number of stable molecules of a compound such as NH_3 to give several new compounds: $\text{CoCl}_2 \cdot 6\text{NH}_3$, $\text{CoCl}_2 \cdot 5\text{NH}_3$ and $\text{CoCl}_2 \cdot 4\text{NH}_3$? What are their structures? At that time X-ray diffraction, which is the most powerful method of determining the structures of crystals, had yet to be discovered. Werner did not have at his disposal any of the modern instrumental techniques, and all his studies were made using simple reaction chemistry. *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 modern explanation would be as follows. 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, as there are three ionic bonds.
2. *Secondary valencies.* These are directional. In modern terms the number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is now called the coordination number. Ligands are commonly negative ions such as Cl^- , or neutral molecules such as NH_3 . Less commonly, ligands may be positive ions such as NO^+ . Each metal has a characteristic number of secondary valencies. Thus in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ the three Cl^- are held by primary valencies. The six NH_3 groups are held by secondary valencies.

Secondary valencies are directional, and so a complex ion has a particular shape, e.g. the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ is octahedral. Werner deduced the shapes of many complexes. He did this by preparing as many

different isomeric complexes of a system as was possible. He noted the number of isomers formed and related this number to the number of isomers predicted for different geometric shapes. The most common coordination number in transition metal complexes is 6, and the shape is usually octahedral. The coordination number 4 is also common, and this gives rise to either tetrahedral or square planar complexes.

Werner treated cold solutions of a series of coordination complexes with an excess of silver nitrate, and weighed the silver chloride precipitated. The stoichiometries of complex-AgCl formed were as follows:



Werner deduced that in $\text{CoCl}_3 \cdot 6\text{NH}_3$ the three chlorines acted as primary valencies, and the six ammonias as secondary valencies. In modern terms the complex is written $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. The three Cl^- are ionic and hence are precipitated as AgCl by AgNO_3 . The six NH_3 ligands form coordinate bonds to Co^{3+} , forming a complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Figure 7.1a).

Werner deduced that loss of one NH_3 from $\text{CoCl}_3 \cdot 6\text{NH}_3$ should give $\text{CoCl}_3 \cdot 5\text{NH}_3$, and at the same time one Cl changed from being a primary valency to a secondary valency. Thus this complex had two primary valencies and six secondary valencies. In modern terms the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ionizes to give $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and two Cl^- ions. Thus only two of the three chlorine atoms are ionic and thus only two are precipitated as AgCl with AgNO_3 . Five NH_3 and one Cl form coordinate bonds to Co^{3+} , forming a complex ion (Figure 7.1b).

Similarly in $\text{CoCl}_3 \cdot 4\text{NH}_3$ Werner deduced that one Cl formed a primary valency, and that there were six secondary valencies (two Cl and four NH_3). In modern terms the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ ionizes to give $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and Cl^- and so only one Cl^- can be precipitated as AgCl. The coordination number of Co^{3+} is 6; in this case four NH_3 and two Cl^- form coordinate bonds to Co^{3+} . The old and modern ways of writing the formulae of these complexes are shown in Table 7.1.

Thus Werner established that the number of secondary valencies (that is the coordination number) was 6 in these complexes. He then attempted to

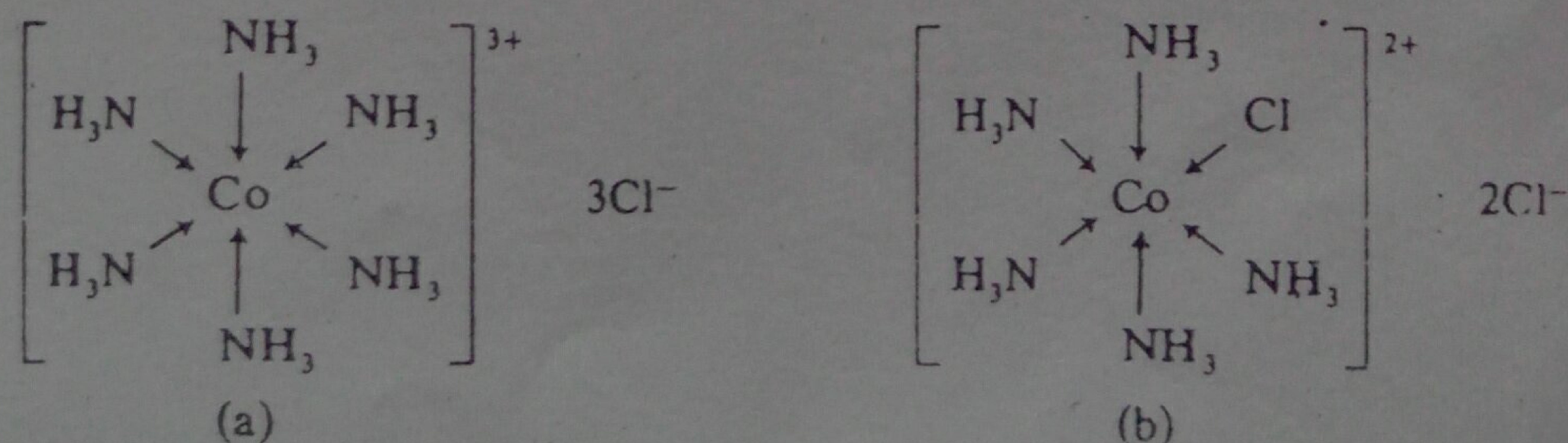


Figure 7.1 Structures of (a) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

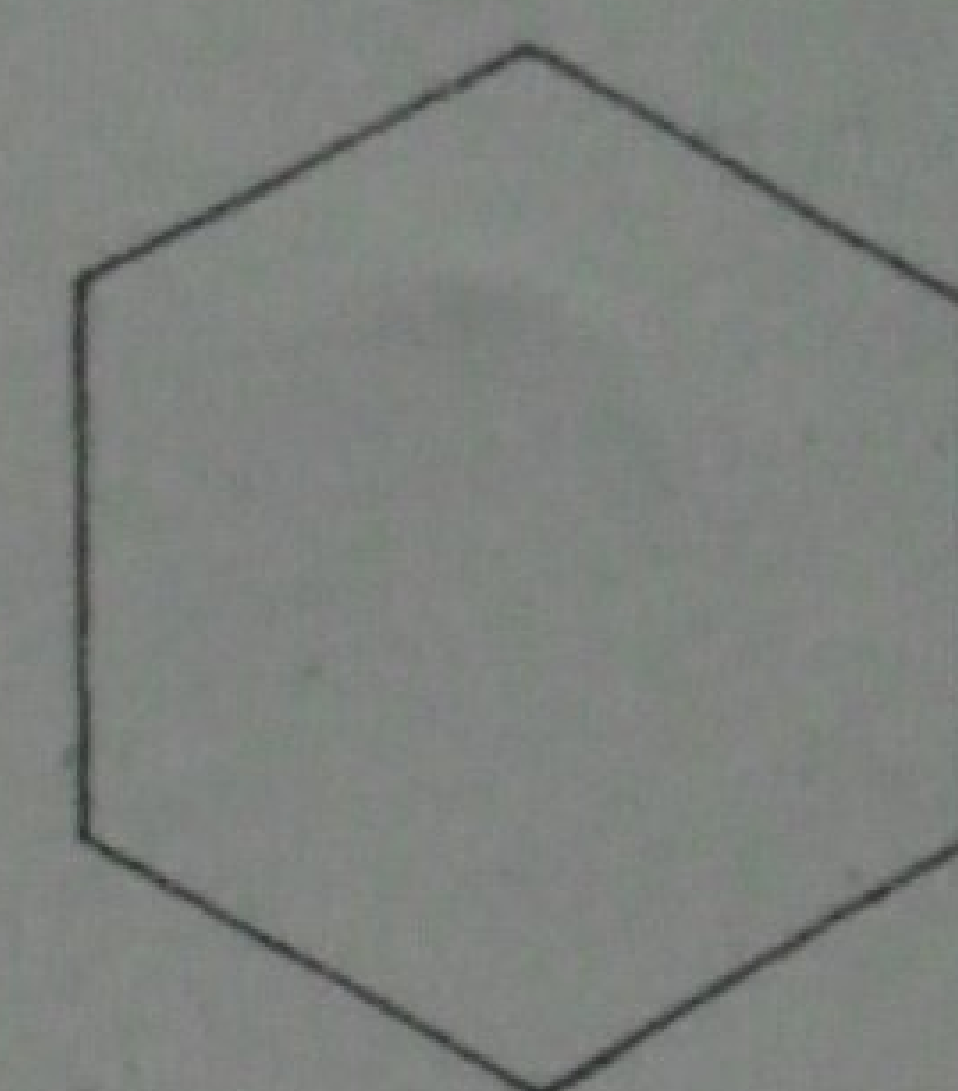
Table 7.1 Formulae of some cobalt complexes

Old	New
$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} \quad 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \quad 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \quad \text{Cl}^-$

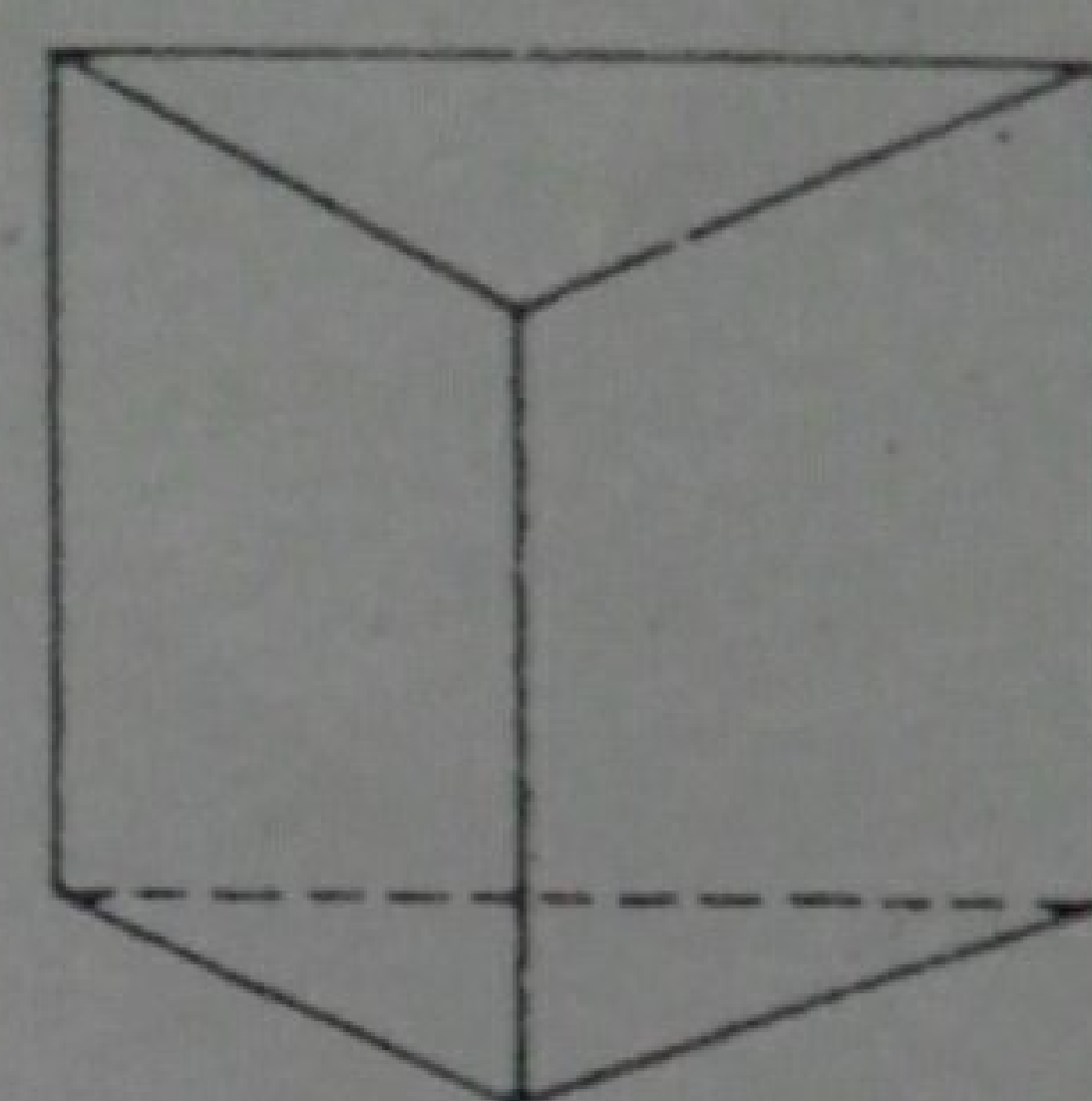
find the shapes of the complexes. The possible arrangements of six groups round one atom are a planar hexagon, a trigonal prism, and an octahedron (Figure 7.2). Werner then compared the number of isomeric forms he had obtained with the theoretical number for each of the possible shapes (Table 7.2).

Table 7.2 Number of isomers predicted and actually found

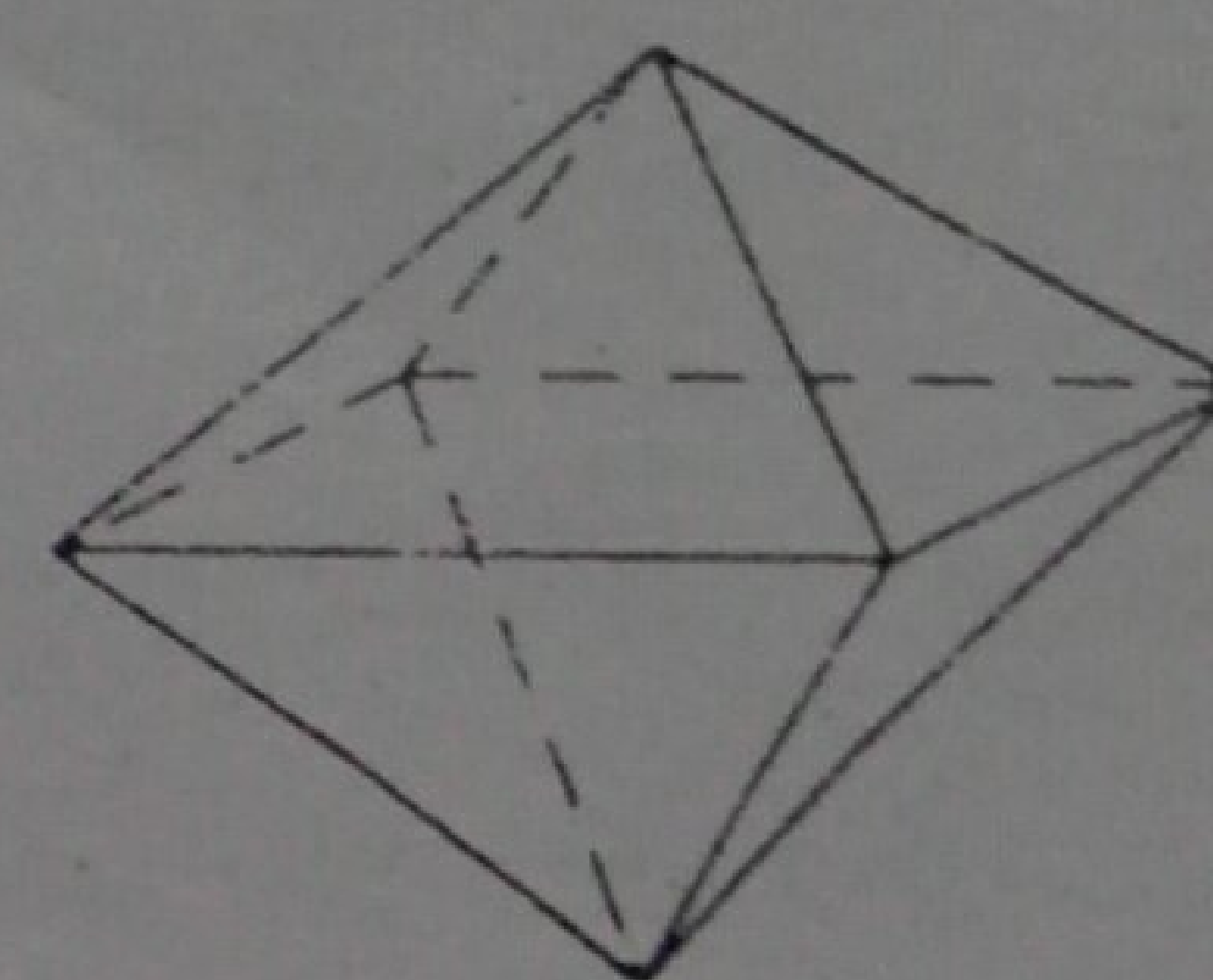
Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[\text{MX}_6]$	1	1	1	1
$[\text{MX}_5\text{Y}]$	1	1	1	1
$[\text{MX}_4\text{Y}_2]$	2	2	3	3
$[\text{MX}_3\text{Y}_3]$	2	2	3	3



Planar hexagon



Trigonal prism



Octahedron

Figure 7.2 Possible geometric shapes for six-coordination.

These results strongly suggested that these complexes have an octahedral shape. This proof was not absolute proof, as it was just possible that the correct experimental conditions had not been found for preparing all the isomers. More recently the X-ray structures have been determined, and these establish that the shape is octahedral (Figure 7.3).

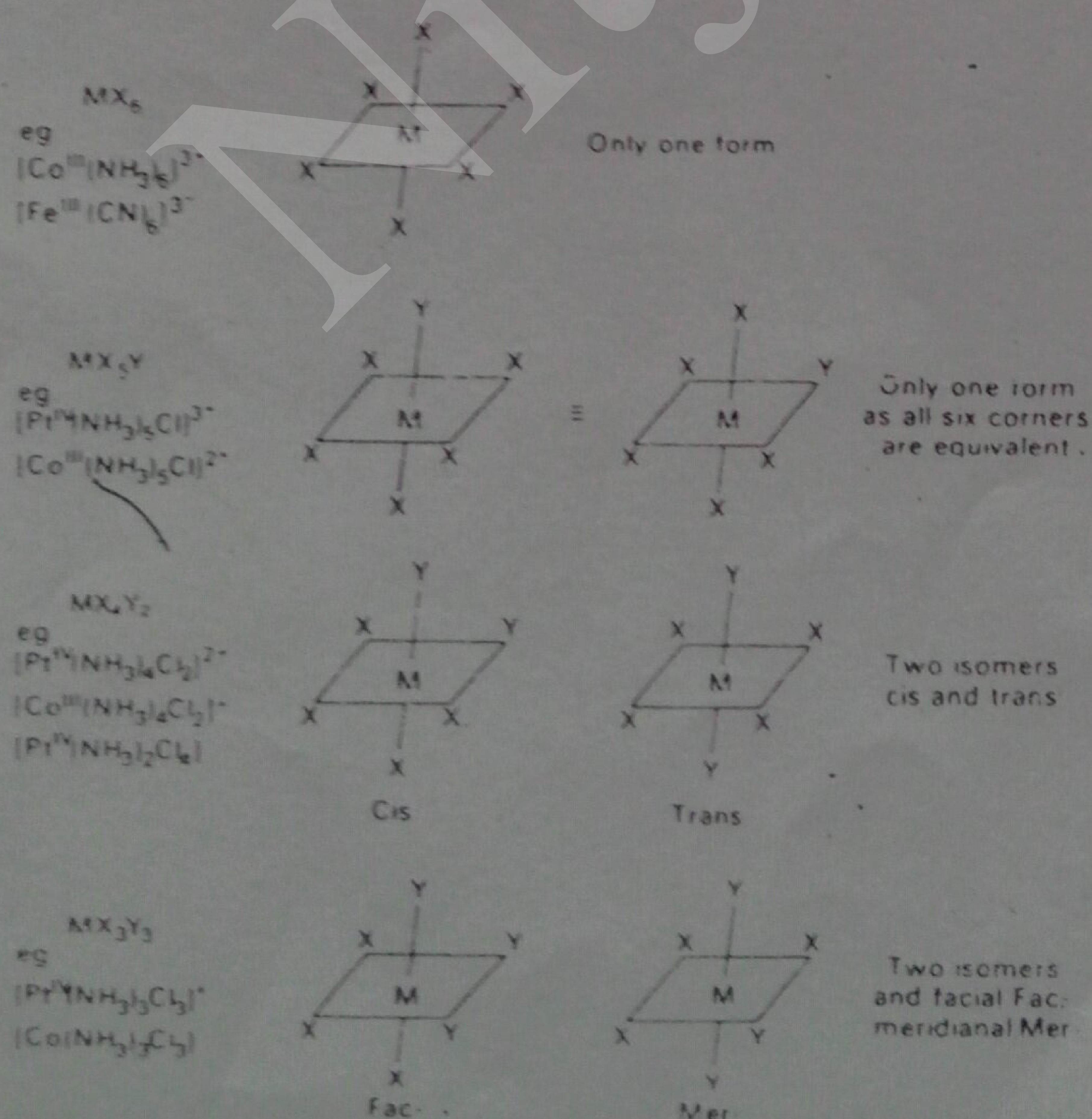


Figure 7.3 Isomers in octahedral complexes.

More recently, with a bidentate ligand such as ethylenediamine (1,2-diaminoethane), two optically active isomers have been found (Figure 7.4).

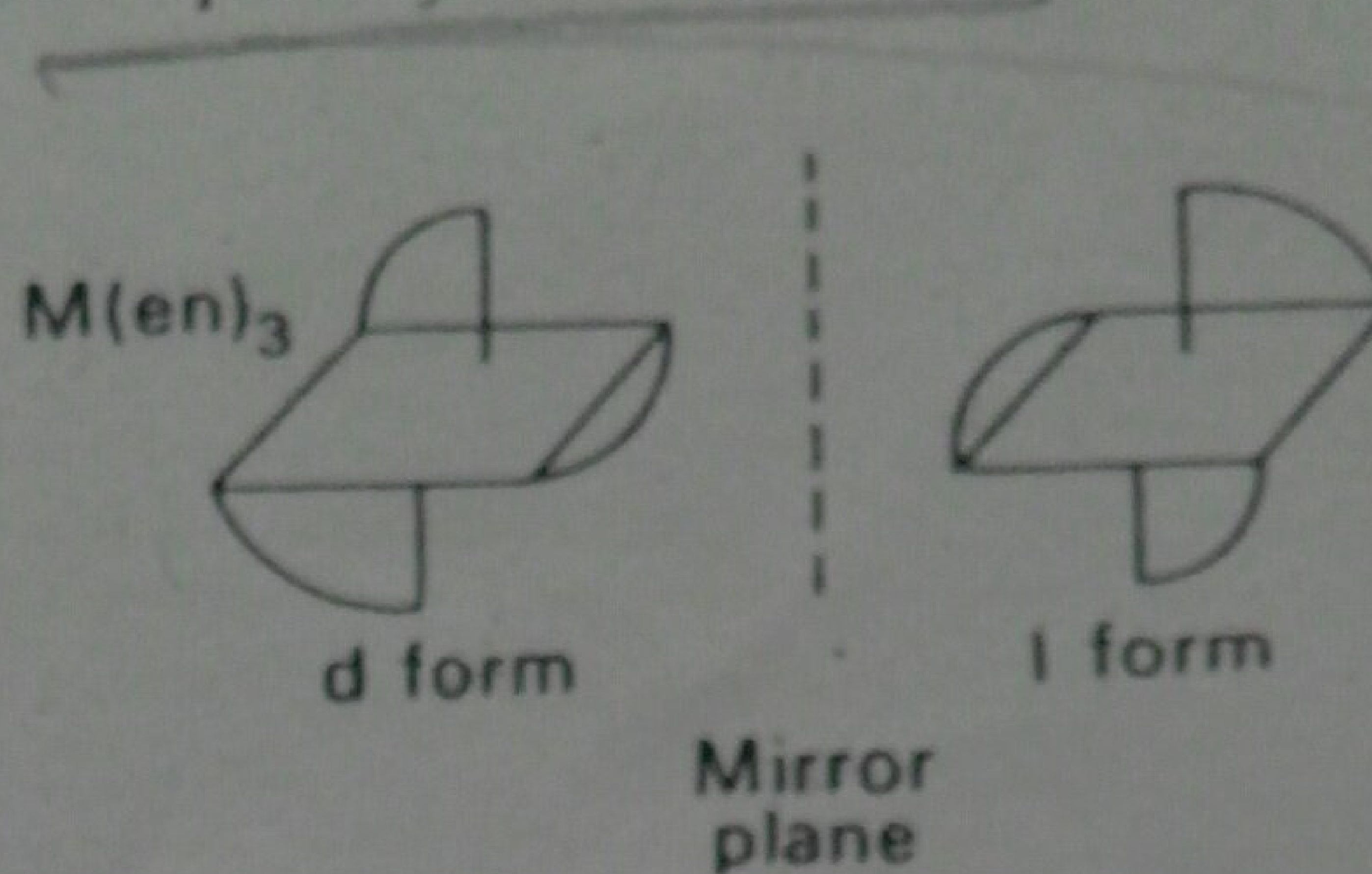


Figure 7.4 Optical isomerism in octahedral complexes.

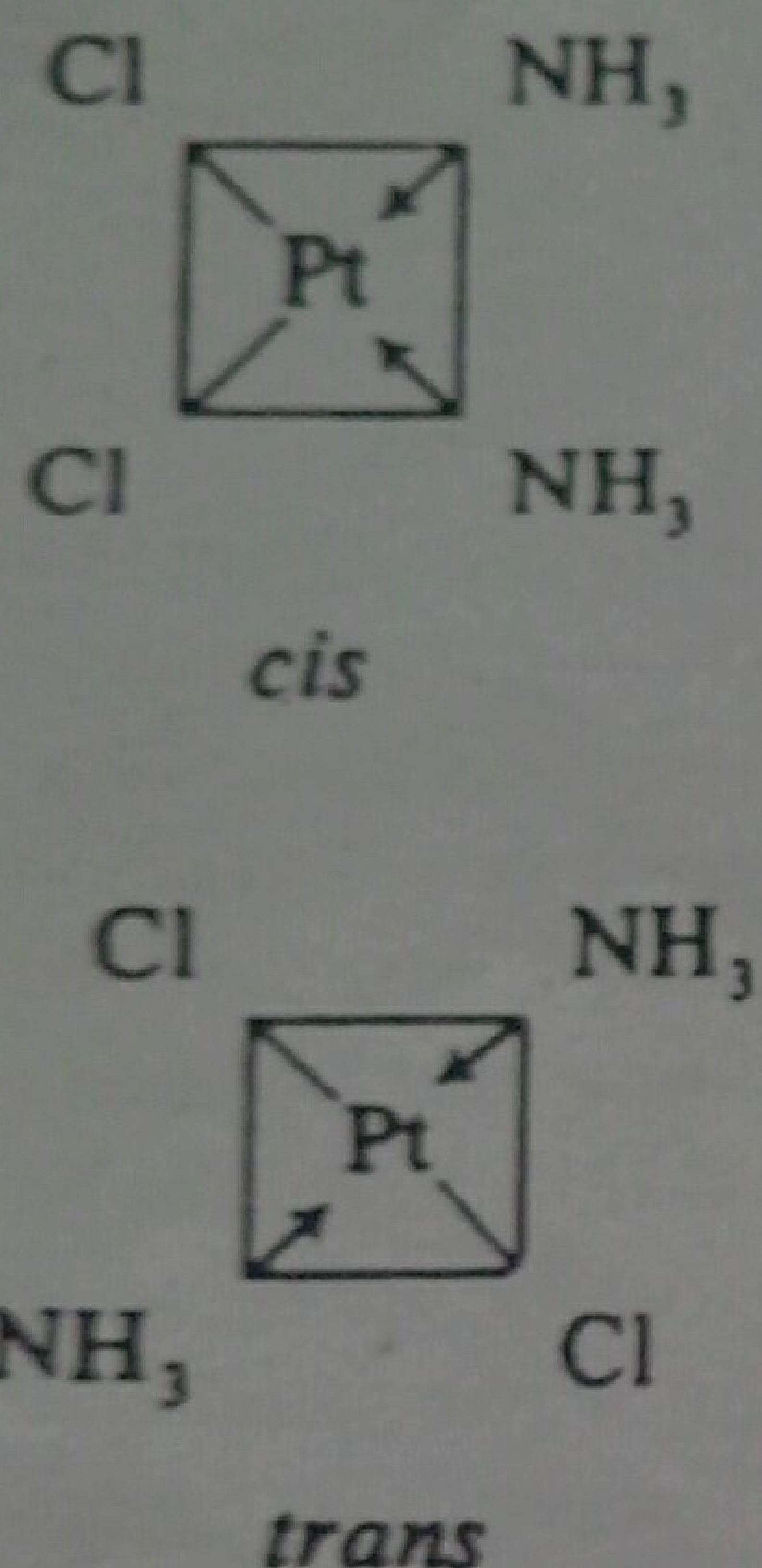


Figure 7.5 Isomerism in square planar complexes.

In a similar way, Werner studied a range of complexes which included $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$. The coordination number is 4, and the shape could be either tetrahedral or square planar. Werner was able to prepare two different isomers for these complexes. A tetrahedral complex can only exist in one form, but a square planar complex can exist in two isomeric forms. This proved these complexes are square planar rather than tetrahedral (Figure 7.5).

MORE RECENT METHODS OF STUDYING COMPLEXES

The electrical conductivity of a solution of an ionic material depends on:

1. The concentration of solute.
2. The number of charges on the species which are formed on dissolution.

Molar conductivities relate to a 1 M solution and thus the concentration factor is removed. The total number of charges on the species formed when the complex dissolves can be deduced by comparison of its molar conductivity with that of known simple ionic materials (Table 7.3). These conductivities suggest the same structures for the cobalt/ammonia/chlorine

Table 7.3 Conductivities of salts and complexes (molar conductivities measured at 0.001 M concentration)

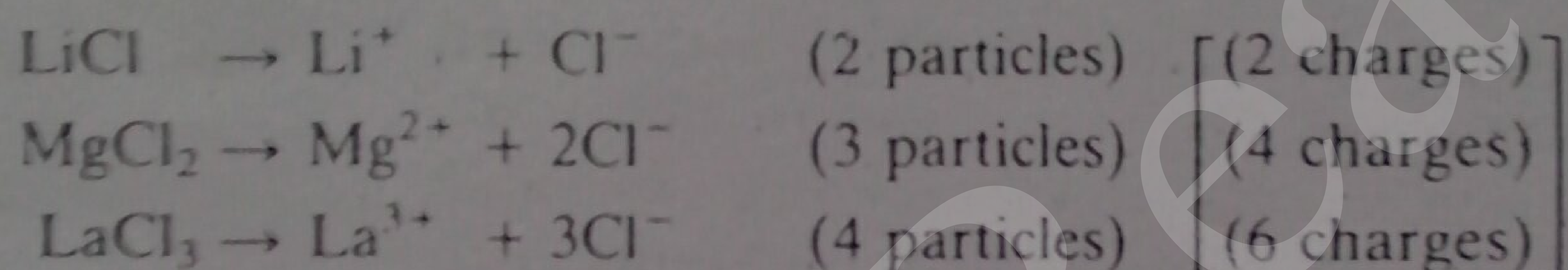
			$\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
LiCl	$\rightarrow \text{Li}^+ \text{Cl}^-$	(total of 2 charges)	112.0
CaCl_2	$\rightarrow \text{Ca}^{2+} 2\text{Cl}^-$	(total of 4 charges)	260.8
$\text{CoCl}_3 \cdot 5\text{NH}_3$			261.3
$\text{CoBr}_3 \cdot 5\text{NH}_3$			257.6
LaCl_3	$\rightarrow \text{La}^{3+} 3\text{Cl}^-$	(total of 6 charges)	393.5
$\text{CoCl}_3 \cdot 6\text{NH}_3$			431.6
$\text{CoBr}_3 \cdot 6\text{NH}_3$			426.9

Table 7.4 Number of charges related to modern and Werner structures

	Charges	Primary valency ionizable chlorines	Secondary valency
$[\text{Co}(\text{NH}_3)_6]^{3+} \quad 3\text{Cl}^-$	6	3	$6\text{NH}_3 = 6$
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \quad 2\text{Cl}^-$	4	2	$5\text{NH}_3 + 1\text{Cl}^- = 6$
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \quad \text{Cl}^-$	2	1	$4\text{NH}_3 + 2\text{Cl}^- = 6$

complexes mentioned earlier, as do the results from Werner's AgCl experiments, shown in Table 7.4.

The freezing point of a liquid is lowered when a chemical substance is dissolved in it. Cryoscopic measurements involve measuring how much the freezing point is lowered. The depression of freezing point obtained depends on the number of particles present. Cryoscopic measurements can be used to find if a molecule dissociates, and how many ions are formed. If a molecule dissociates into two ions it will give twice the expected depression for a single particle. If three ions are formed this will give three times the expected depression. Thus:



The number of particles formed from a complex molecule determines the size of the depression of freezing point. Note that the number of particles formed may be different from the total number of charges which can be obtained from conductivity measurements. The two types of information can be used together to establish the structure (Table 7.5).

The magnetic moment can be measured (see Chapter 18 - Magnetic properties). This provides information about the number of unpaired electron spins present in a complex. From this it is possible to decide how the electrons are arranged and which orbitals are occupied. Sometimes the structure of the complex can be deduced from this. For example, the compound $\text{Ni}^{II}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ might contain four ammonia mol-

Table 7.5 Establishing the structure of complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4 particles	6 charges	$[\text{Co}(\text{NH}_3)_6]^{3+} \quad 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3 particles	4 charges	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \quad 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2 particles	2 charges	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \quad \text{Cl}^-$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1 particle	0 charge	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
$\text{Co}(\text{NO}_2)_3 \cdot \text{KNO}_2 \cdot 2\text{NH}_3$	2 particles	2 charges	$\text{K}^+ \quad [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$
$\text{Co}(\text{NO}_2)_3 \cdot 2\text{KNO}_2 \cdot \text{NH}_3$	3 particles	4 charges	$2\text{K}^+ \quad [\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{2-}$
$\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$	4 particles	6 charges	$3\text{K}^+ \quad [\text{Co}(\text{NO}_2)_6]^{3-}$

ecules coordinated to Ni in a square planar $[\text{Ni}(\text{NH}_3)_4]^{2+}$ ion and two molecules of water of crystallization and have no unpaired electrons. Alternatively the water might be coordinated to the metal, giving an octahedral $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ complex with two unpaired electrons. Both these complex ions exist and their structures can be deduced from magnetic measurements.

② Dipole moments may also yield structural information but only for non-ionic complexes. For example, the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is square planar, and can exist as *cis* or *trans* forms. The dipole moments from the various metal-ligand bonds cancel out in the *trans* configuration. However, a finite dipole moment is given by the *cis* arrangement (Figure 7.5).

③ Electronic spectra (UV and visible) also provide valuable information on the energy of the orbitals, and on the shape of the complex. By this means it is possible to distinguish between tetrahedral and octahedral complexes, and whether the shape is distorted or regular.

The most powerful method, however, is the X-ray determination of the crystal structure. This provides details of the exact shape and the bond lengths and angles of the atoms in the structure.

EFFECTIVE ATOMIC NUMBERS

The number of secondary valencies in the Werner theory is now called the coordination number of the central metal in the complex. This is the number of ligand atoms bonded to the central metal ion. Each ligand donates an electron pair to the metal ion, thus forming a coordinate bond. Transition metals form coordination compounds very readily because they have vacant *d* orbitals which can accommodate these electron pairs. The electronic arrangement of the noble gases is known to be very stable. 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) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (formerly called potassium ferrocyanide). 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 $[\text{Fe}(\text{CN})_6]^{4-}$ to 36.

$$[24 + (6 \times 2) = 36]$$

Further examples are given in Table 7.6.

The EAN rule correctly predicts the number of ligands in many complexes. There are, however, a significant number of exceptions where the EAN is not quite that of a noble gas. If the original metal ion has an odd number of electrons, for example, the adding of electron pairs cannot result in a noble gas structure. The tendency to attain a noble gas configuration is a significant factor but not a necessary condition for complex formation. It is also necessary to produce a symmetrical structure (tetra-

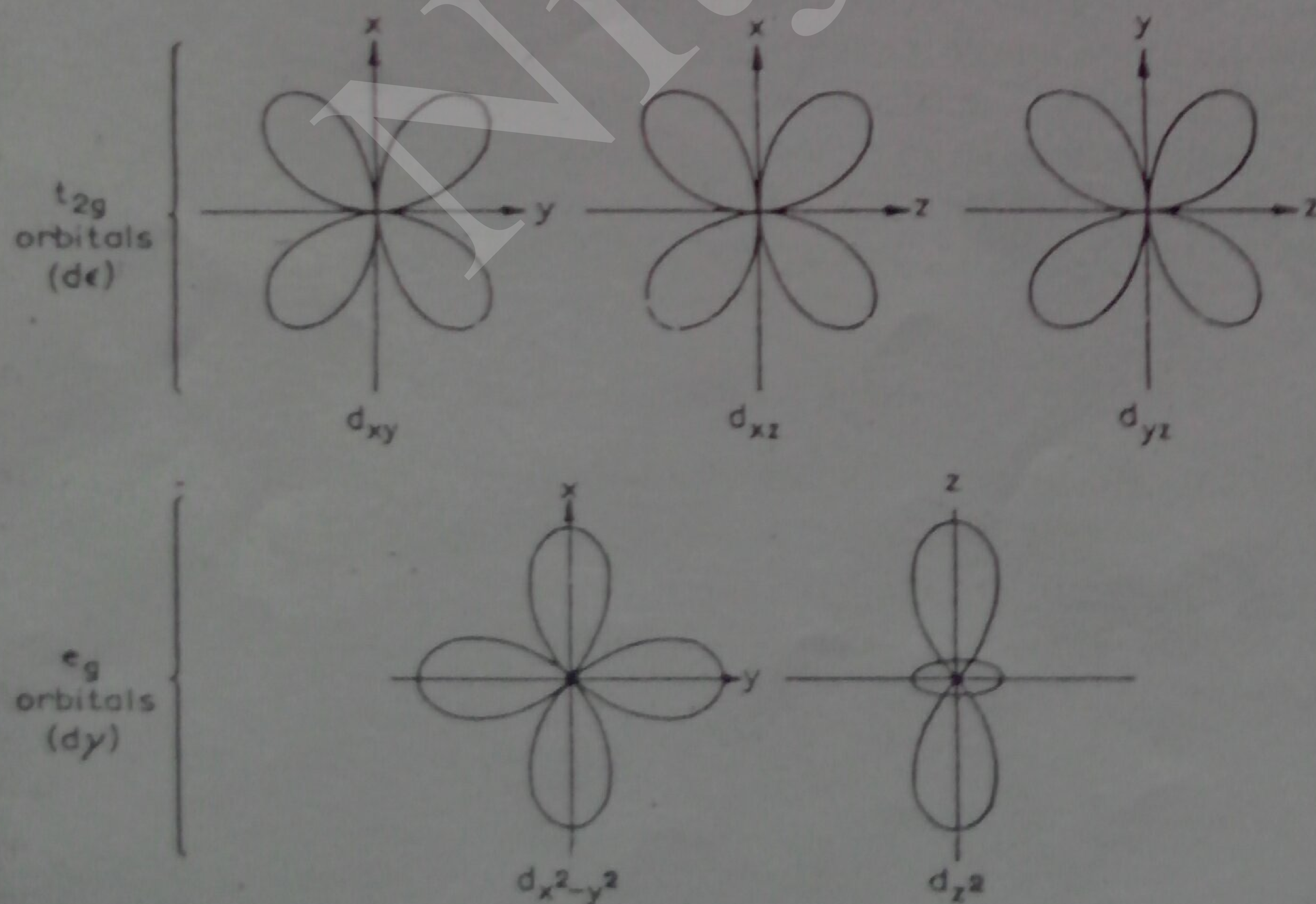
Table 7.6 Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54 (Xe)
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86 (Rn)
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84

hedral, square planar, octahedral) irrespective of the number of electrons involved.

SHAPES OF d ORBITALS

Since d orbitals are often used in coordination complexes it is important to study their shapes and distribution in space. The five d orbitals are not identical and the orbitals may be divided into two sets. The three t_{2g} orbitals have identical shape and point between the axes, x , y and z . The

Figure 7.6 Shapes of d orbitals.

two e_g orbitals have different shapes and point along the axes (Figure 7.6). Alternative names for t_{2g} and e_g are d_{xy} and d_{yz} respectively.

BONDING IN TRANSITION METAL COMPLEXES

There are three theories of metal to ligand bonding in complexes, all dating back to the 1930s.

Valence bond theory

This theory was developed by Pauling. Coordination compounds contain complex ions, in which ligands form coordinate bonds to the metal. Thus the ligand must have a lone pair of electrons, and the metal must have an empty orbital of suitable energy available for bonding. The theory considers which atomic orbitals on the metal are used for bonding. From this the shape and stability of the complex are predicted. The theory has two main limitations. Most transition metal complexes are coloured, but the theory provides no explanation for their electronic spectra. Further, the theory does not explain why the magnetic properties vary with temperature. For these reasons it has largely been superseded by the crystal field theory. However, it is of interest for study as it shows the continuity of the development of modern ideas from Werner's theory.

Crystal field theory

This theory was proposed by Bethe and van Vleck. The attraction between the central metal and ligands in the complex is considered to be purely electrostatic. Thus bonding in the complex may be ion-ion attraction (between positive and negative ions such as Co^{3+} and Cl^-). Alternatively, ion-dipole attractions may give rise to bonding (if the ligand is a neutral molecule such as NH_3 or CO). NH_3 has a dipole moment with a δ^- charge on N and δ^+ charges on H. Thus in $[\text{Co}(\text{NH}_3)_6]^{3+}$ the δ^- charge on the N atom of each NH_3 points towards the Co^{3+} . This theory is simple. It has been remarkably successful in explaining the electronic spectra and magnetism of transition metal complexes, particularly when allowance is made for the possibility of some covalent interaction between the orbitals on the metal and ligand. When some allowance is made for covalency, the theory is often renamed as the ligand field theory. Three types of interaction are possible: σ overlap of orbitals, π overlap of orbitals, or $d\pi-p\pi$ bonding (back bonding) due to π overlap of full d orbitals on the metal with empty p orbitals on the ligands.

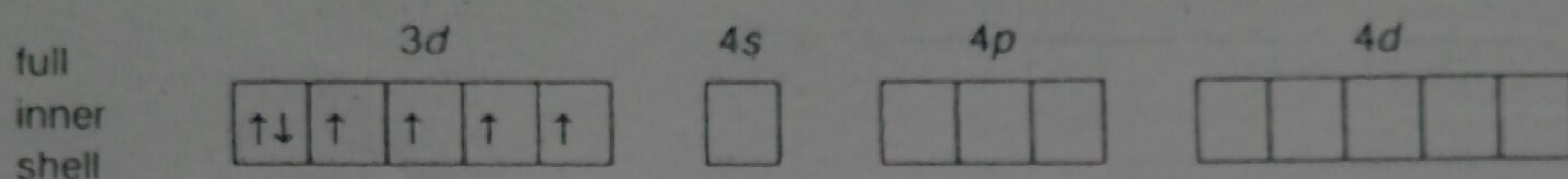
Molecular orbital theory

Both covalent and ionic contributions are fully allowed for in this theory. Though this theory is probably the most important approach to chemical bonding, it has not displaced the other theories. This is because the quantitative calculations involved are difficult and lengthy, involving the use

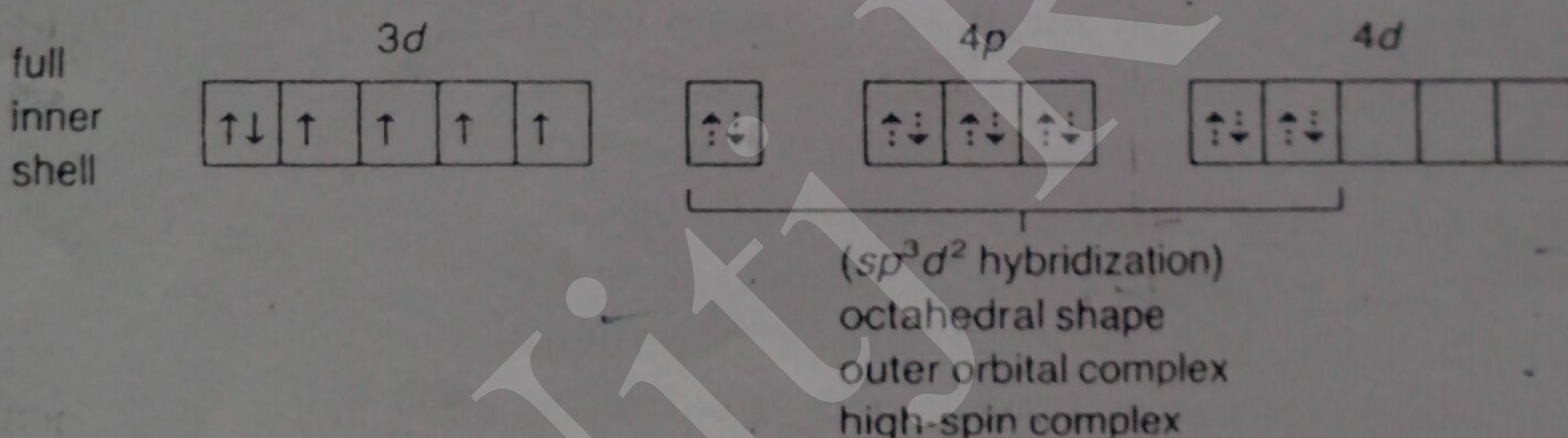
of extensive computer time. Much of the qualitative description can be obtained by other approaches using symmetry and group theory.

VALENCE BOND THEORY

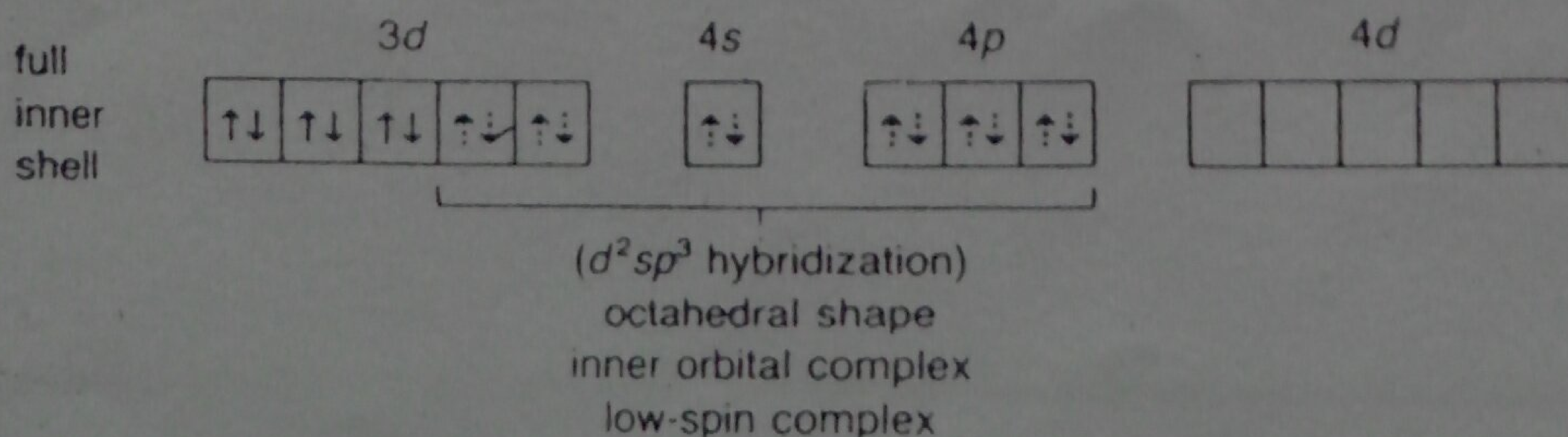
The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken, e.g. Co^{3+} . A Co atom has the outer electronic structure $3d^7 4s^2$. Thus a Co^{3+} ion will have the structure $3d^6$, and the electrons will be arranged:



If this ion forms a complex with six ligands, then six empty atomic orbitals are required on the metal ion to receive the coordinated lone pairs of electrons. The orbitals used are the $4s$, three $4p$ and two $4d$. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electrons forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The d orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. In the diagrams below, electron pairs from the ligands are shown as $\uparrow\downarrow$.

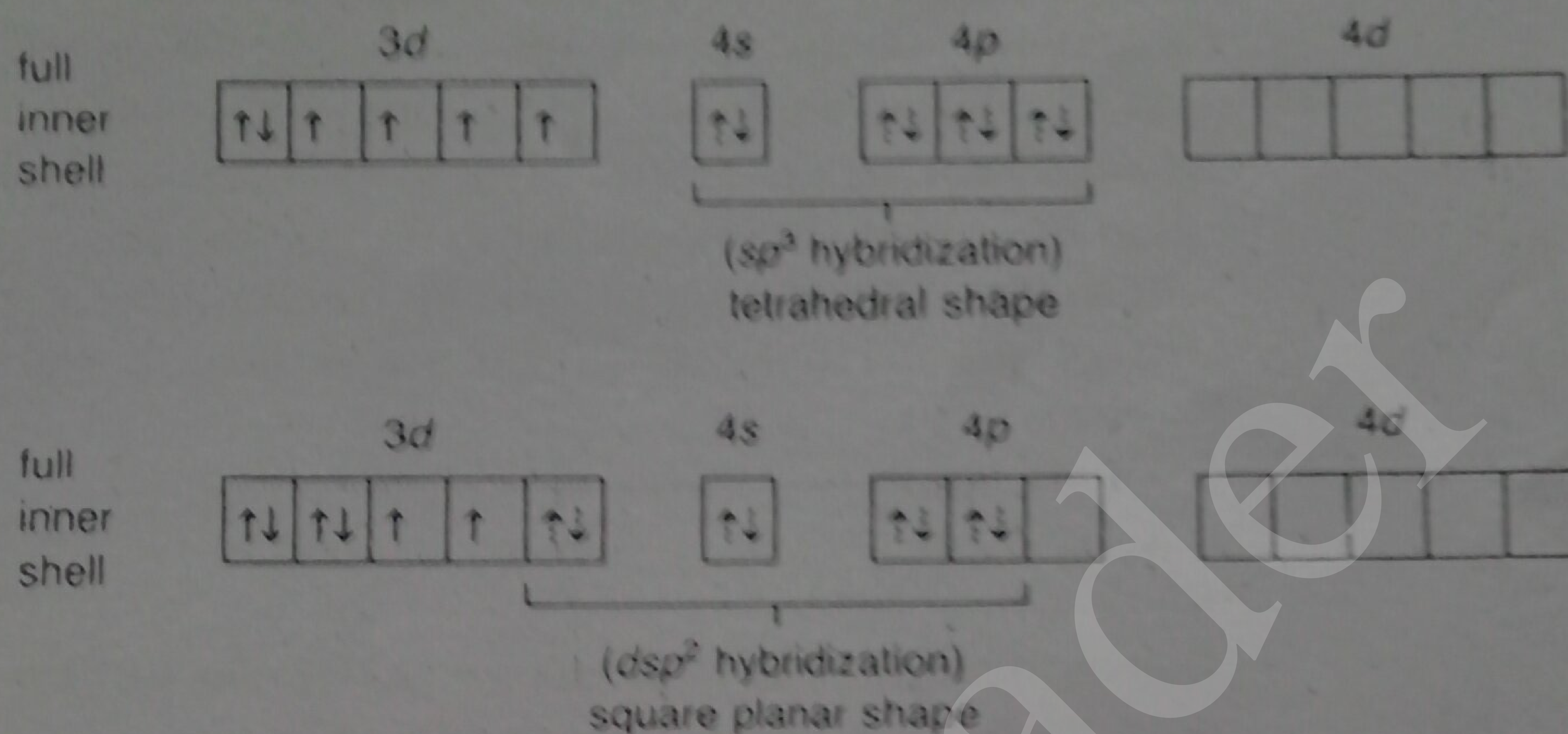


Since the outer $4d$ orbitals are used for bonding this is called an *outer orbital complex*. The energy of these orbitals is quite high, so that the complex will be reactive or labile. The magnetic moment depends on the number of unpaired electrons. The $3d$ level contains the maximum number of unpaired electrons for a d^6 arrangement, so this is sometimes called a *high-spin* or a *spin-free complex*. An alternative octahedral arrangement is possible when the electrons on the metal ion are rearranged as shown below. As before, lone pairs from the ligands are shown as $\uparrow\downarrow$.



Since low energy inner d orbitals are used this is called an *inner orbital complex*. Such complexes are more stable than the outer orbital complexes. The unpaired electrons in the metal ion have been forced to pair up, and so this is now a low-spin complex. In this particular case all the electrons are paired, so the complex will be diamagnetic.

The metal ion could also form four-coordinate complexes, and two different arrangements are possible. *It must be remembered that hybrid orbitals do not actually exist.* Hybridization is a mathematical manipulation of the wave equations for the atomic orbitals involved.



The theory does not explain the colour and spectra of complexes. The theory shows the number of unpaired electrons. From this the magnetic moment can be calculated (see Chapter 18). However, it does not explain why the magnetic moment varies with temperature.

CRYSTAL FIELD THEORY

The crystal field theory is now much more widely accepted than the valence bond theory. It assumes that the attraction between the central metal and the ligands in a complex is purely electrostatic. The transition metal which forms the central atom in the complex is regarded as a positive ion of charge equal to the oxidation state. This is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3 , the negative end of the dipole in the molecule is directed towards the metal ion. The electrons on the central metal are under repulsive forces from those on the ligands. Thus the electrons occupy the d orbitals furthest away from the direction of approach of ligands. In the crystal field theory the following assumptions are made.

1. Ligands are treated as point charges.
2. There is no interaction between metal orbitals and ligand orbitals.
3. The d orbitals on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroy the degeneracy of these orbitals, i.e. the orbitals now have

different energies. In an isolated gaseous metal ion, the five d orbitals do all have the same energy, and are termed degenerate. If a spherically symmetrical field of negative charges surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field and the electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical. Thus the d orbitals are not all affected equally by the ligand field.

Octahedral complexes

In an octahedral complex, the metal is at the centre of the octahedron, and the ligands are at the six corners. The directions x , y and z point to three adjacent corners of the octahedron as shown in Figure 7.7.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x , y and z . The lobes of the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point in between the axes. It follows that the approach of six ligands along the x , y , z , $-x$, $-y$ and $-z$ directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) much more than it increases the energy of the d_{xy} , d_{xz} and d_{yz} orbitals (which point between the axes). Thus under the influence of an octahedral ligand field the d orbitals split into two groups of different energies (Figure 7.8).

Rather than referring to the energy level of an isolated metal atom, the weighted mean of these two sets of perturbed orbitals is taken as the zero; this is sometimes called the Bari centre. The difference in energy between the two d levels is given either of the symbols Δ_o or $10 Dq$. It follows that

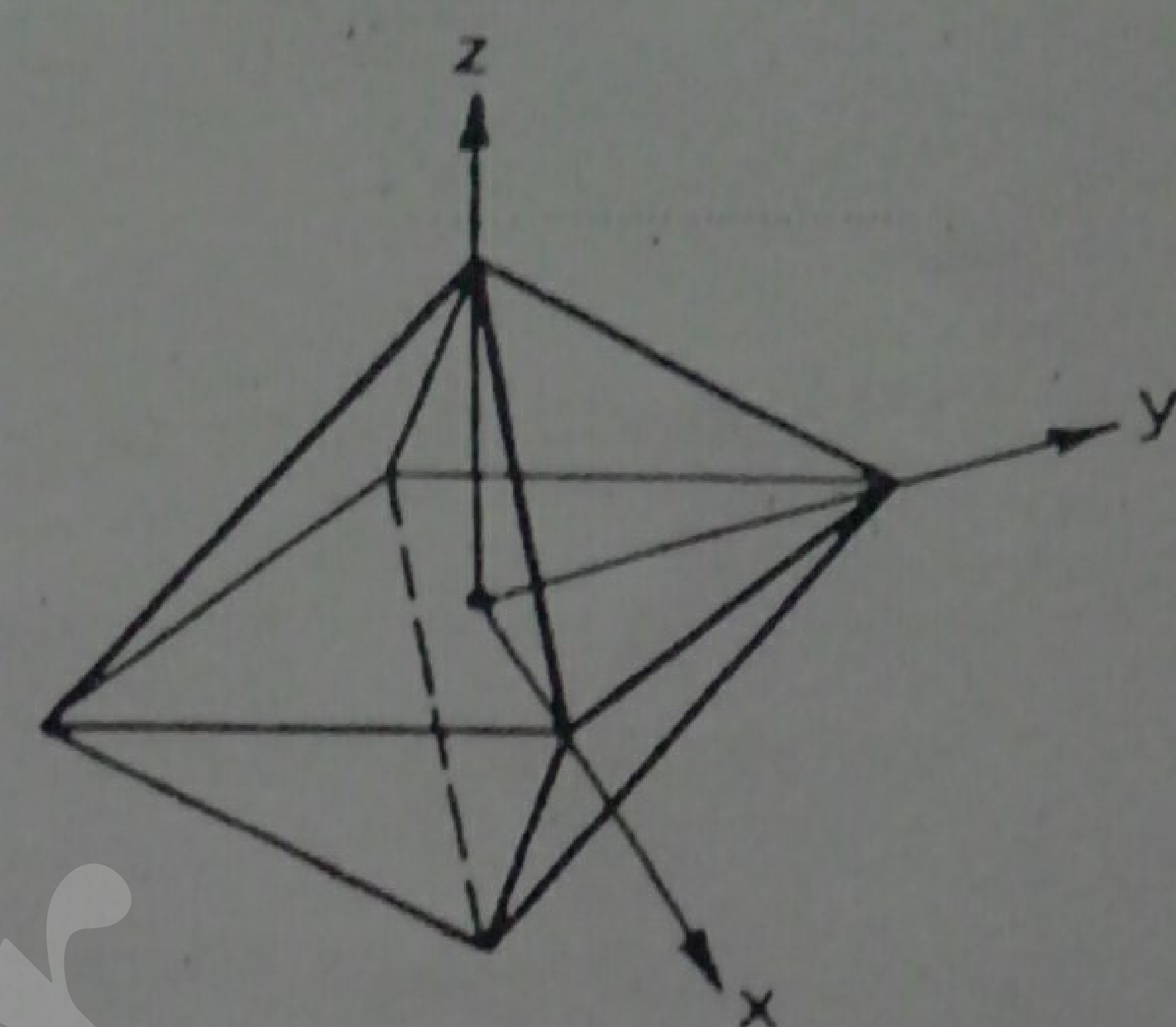


Figure 7.7 The directions in an octahedral complex.

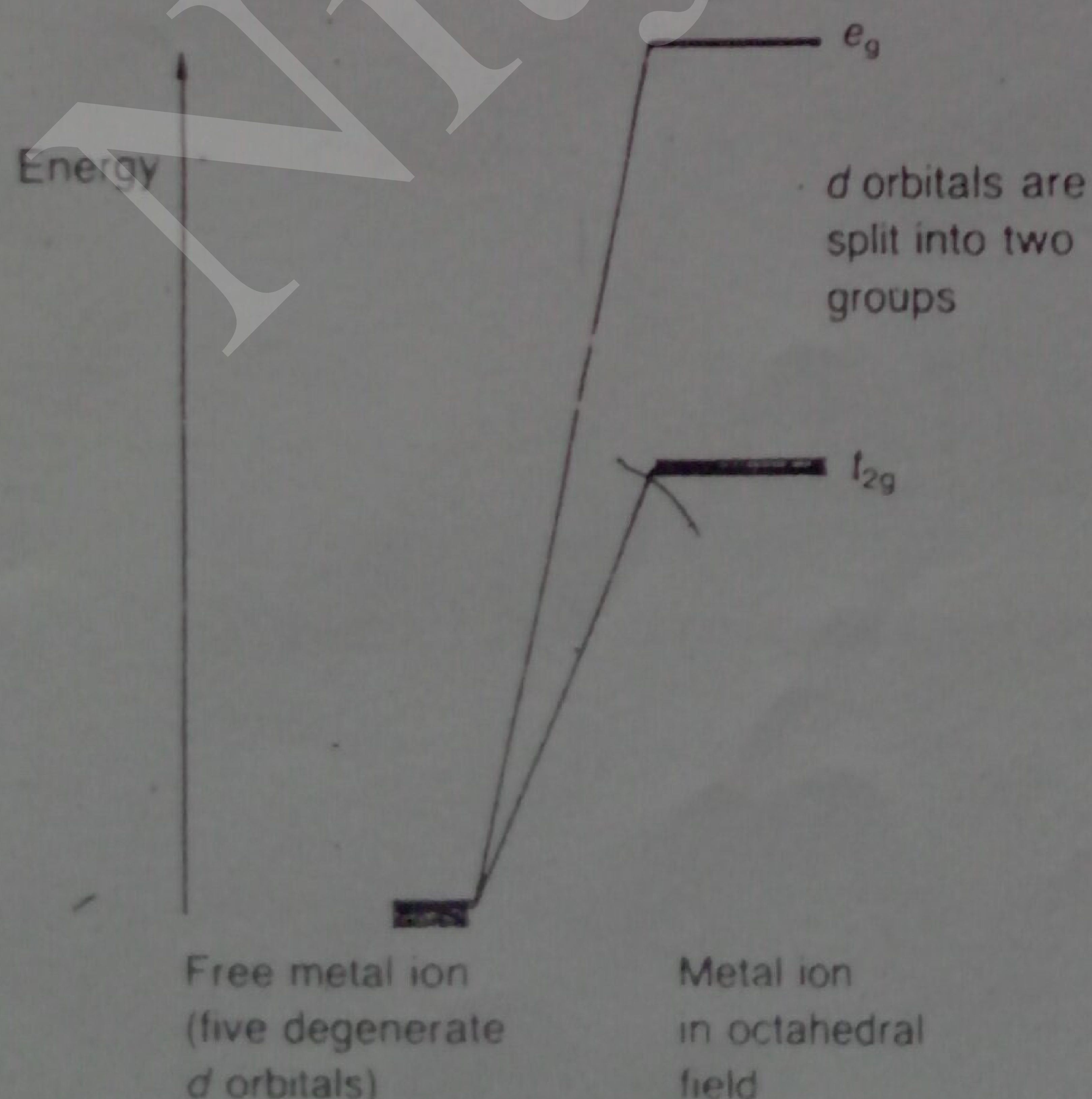


Figure 7.8 Crystal field splitting of energy levels in an octahedral field.

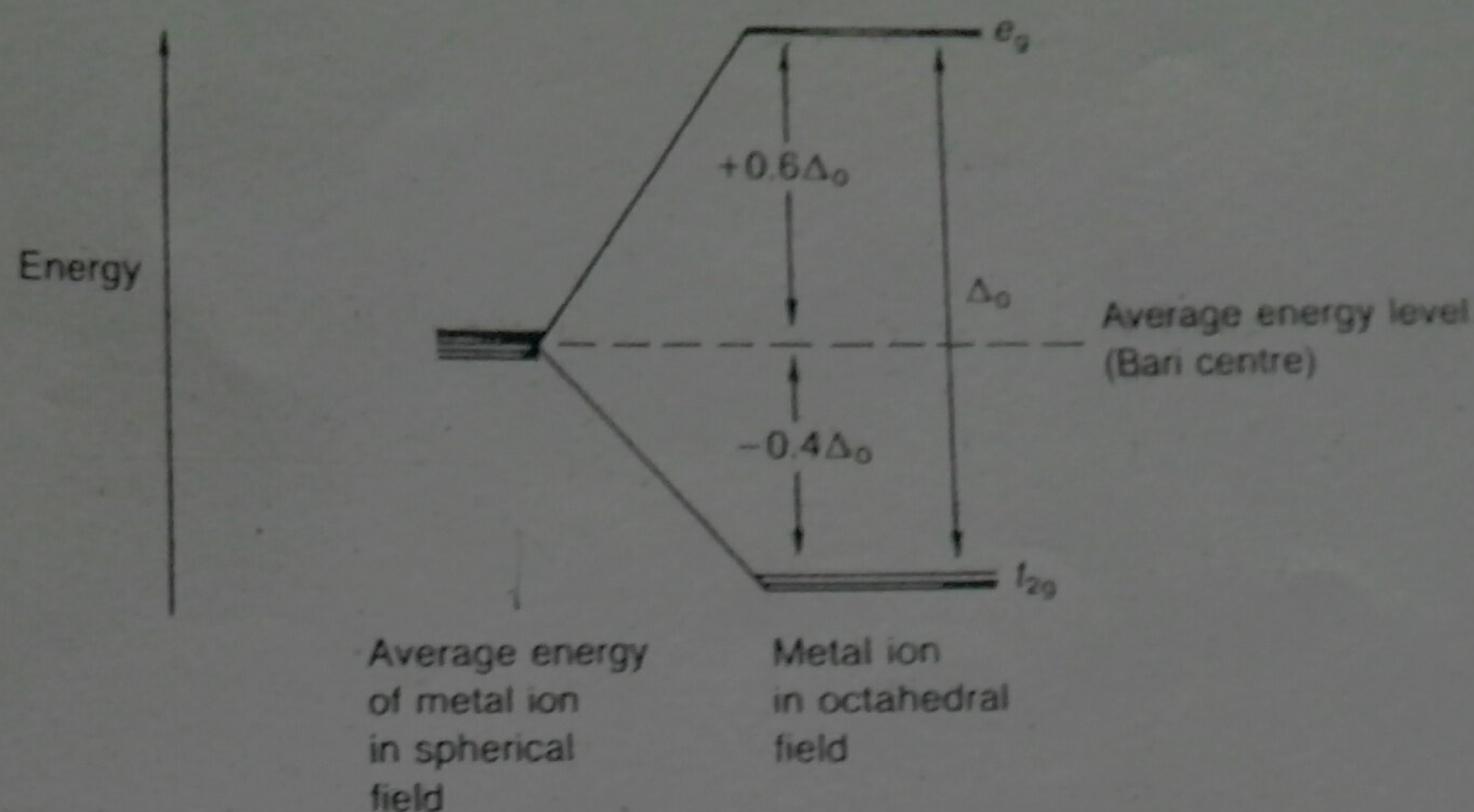


Figure 7.9 Diagram of the energy levels of d orbitals in an octahedral field.

the e_g orbitals are $+0.6\Delta_o$ above the average level, and the t_{2g} orbitals are $-0.4\Delta_o$ below the average (Figure 7.9).

The size of the energy gap Δ_o between the t_{2g} and e_g levels can be measured easily by recording the UV-visible spectrum of the complex. Consider a complex like $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. The Ti^{3+} ion has one d electron. In the complex this will occupy the orbital with the lowest energy, that is one of the t_{2g} orbitals (Figure 7.10a). The complex absorbs light of the correct wavelength (energy) to promote the electron from the t_{2g} level to the e_g level (Figure 7.10b).

The electronic spectrum for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is given in Figure 7.11. The steep part of the curve from 27000 to 30000 cm^{-1} (in the UV region) is due to charge transfer. The $d-d$ transition is the single broad peak with a maximum at 20300 cm^{-1} . Since $1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$, the value of Δ_o

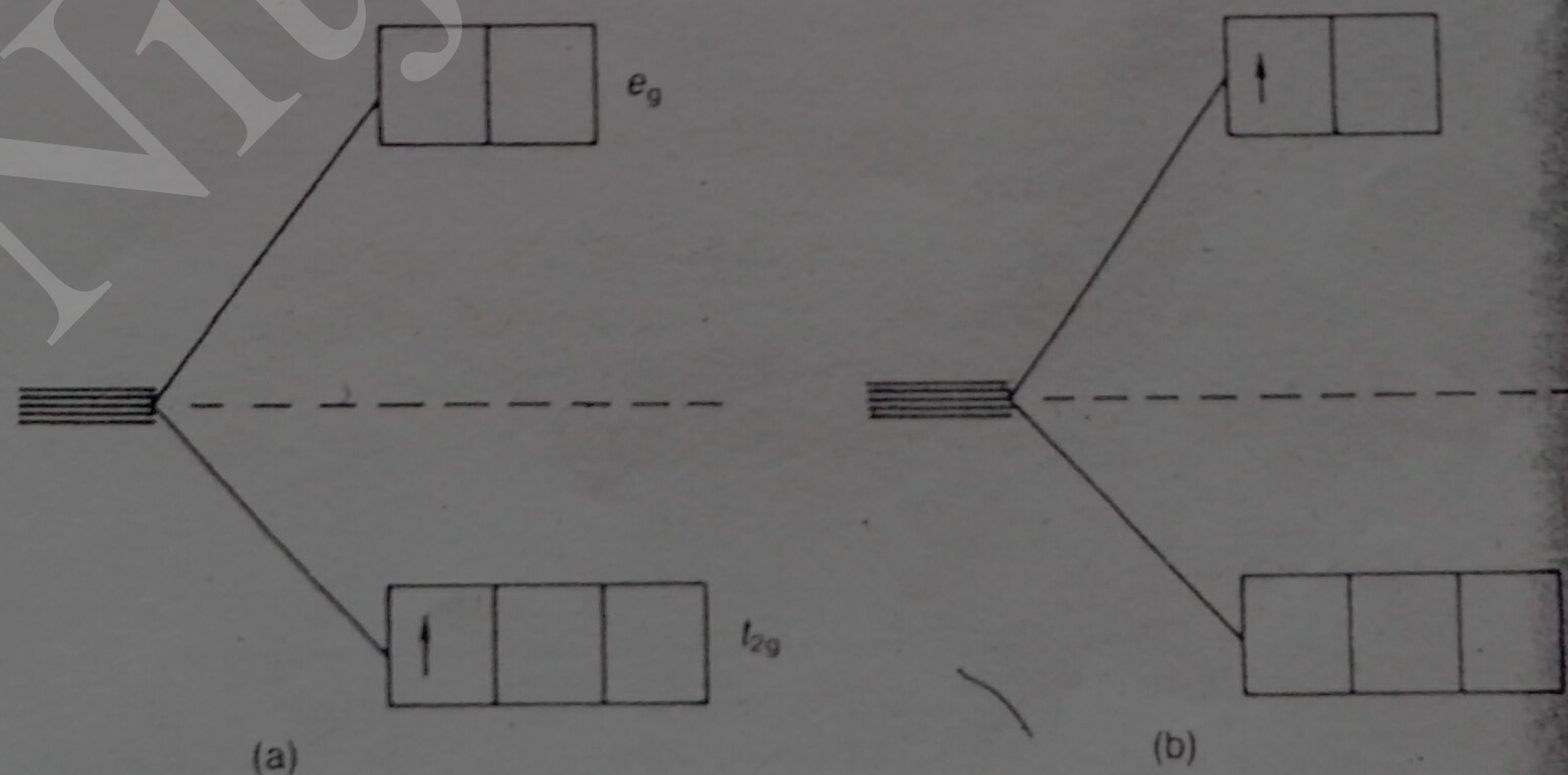
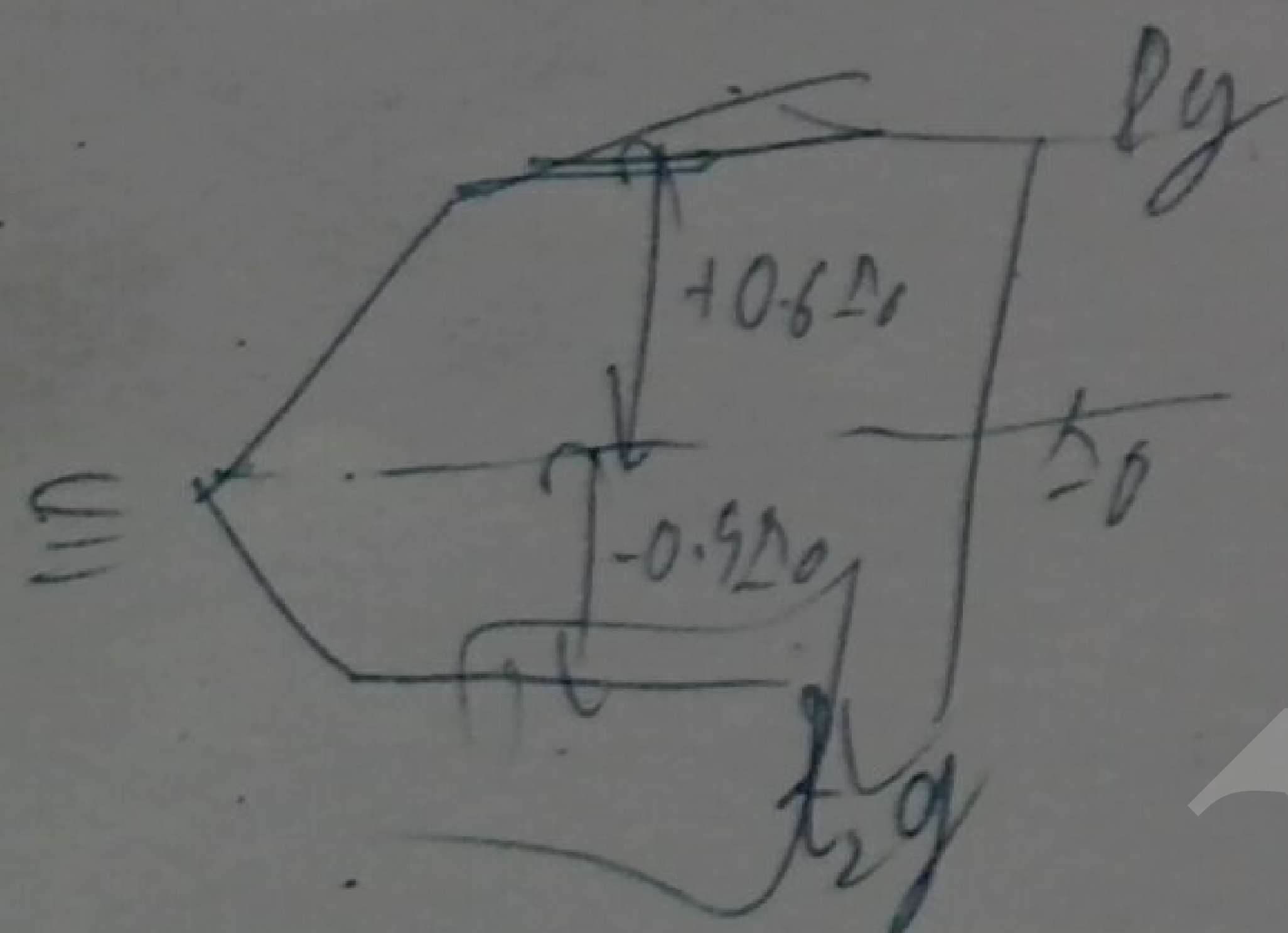


Figure 7.10 d^1 configuration: (a) ground state, (b) excited state.

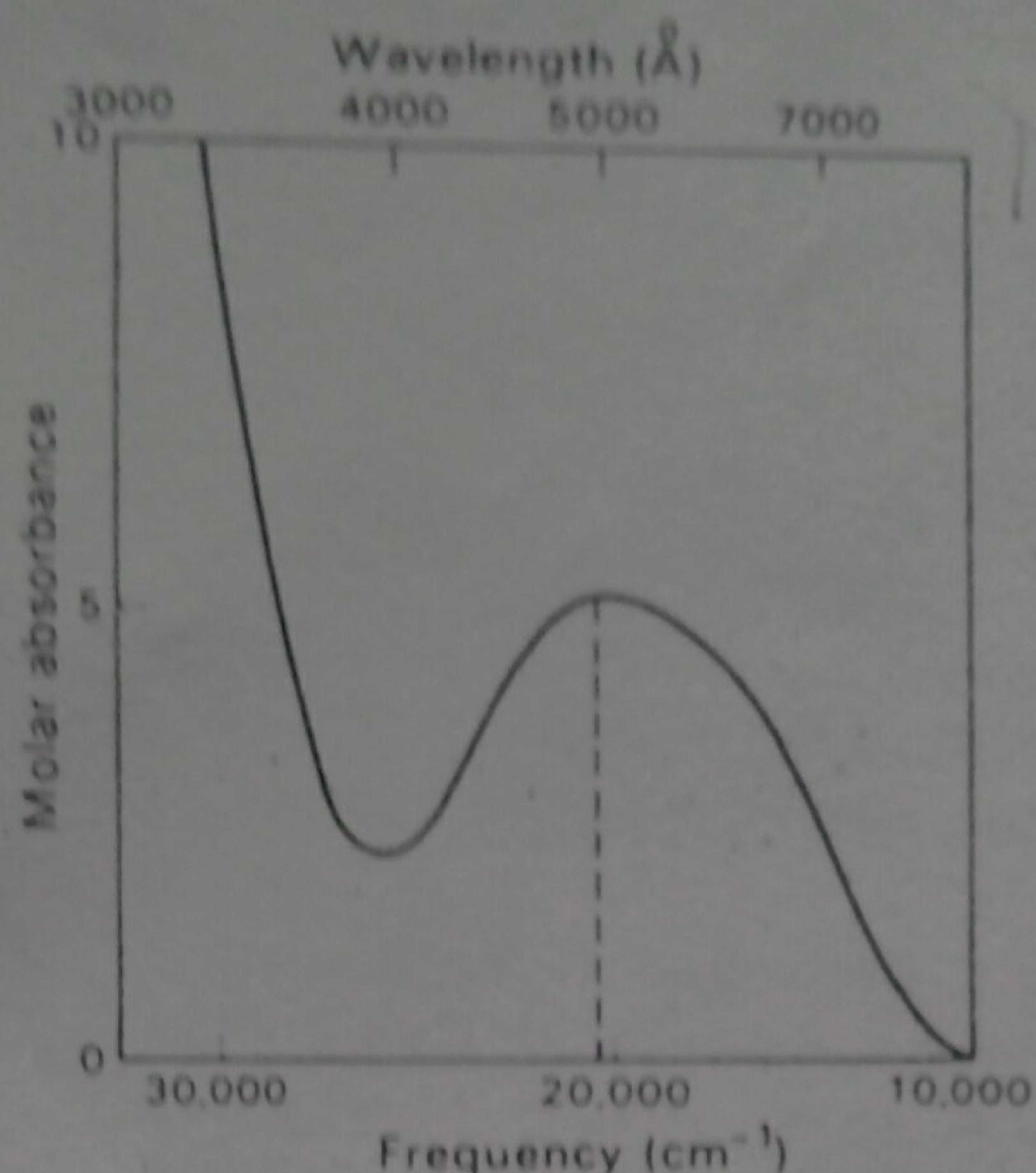


Figure 7.11 Ultraviolet and visible absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

for $[\text{Ti}(\text{H}_2\text{O})]^{3+}$ is $20\,300/83.7 = 243 \text{ kJ mol}^{-1}$. This is much the same as the energy of many normal single bonds (see Appendix F).

The above method is the most convenient way of measuring Δ_0 values. However, Δ_0 values can also be obtained from values of observed lattice energies and those calculated using the Born-Landé equation (see Chapter 3).

Solutions containing the hydrated Ti^{3+} ion are reddish violet coloured. This is because yellow and green light are absorbed to excite the electron. Thus the transmitted light is the complementary colour red-violet (Table 7.7).

Because of the crystal field splitting of d orbitals, the single d electron in $[\text{Ti}(\text{H}_2\text{O})]^{3+}$ occupies an energy level $2/5\Delta_0$ below the average energy of the d orbitals. As a result the complex is more stable. The crystal field stabilization energy (CFSE) is in this case $2/5 \times 243 = 97 \text{ kJ mol}^{-1}$.

Table 7.7 Colours absorbed and colours observed

Colour absorbed	Colour observed	Wavenumber observed (cm^{-1})
yellow-green	red-violet	24 000–26 000
yellow	indigo	23 000–24 000
orange	blue	21 000–23 000
red	blue-green	20 000–21 000
purple	green	18 000–20 000
red-violet	yellow-green	17 300–18 000
indigo	yellow	16 400–17 300
blue	orange	15 300–16 400
blue-green	red	12 800–15 300

Table 7.8 Crystal field splittings by various ligands

Complex	Absorption peak	
	(cm^{-1})	(kJ mol^{-1})
$[\text{Cr}^{\text{III}}\text{Cl}_6]^{3-}$	13 640	163
$[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$	17 830	213
$[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}$	21 680	259
$[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$	26 280	314

The magnitude of Δ_o depends on three factors:

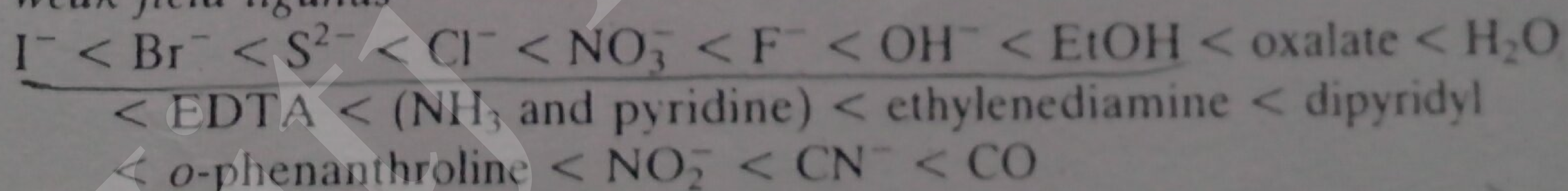
1. The nature of the ligands.
2. The charge on the metal ion.
3. Whether the metal is in the first, second or third row of transition elements.

Examination of the spectra of a series of complexes of the same metal with different ligands shows that the position of the absorption band (and hence the value of Δ_o) varies depending on the ligands which are attached (Table 7.8).

Ligands which cause only a small degree of crystal field splitting are termed weak field ligands. Ligands which cause a large splitting are called strong field ligands. Most Δ values are in the range 7000 cm^{-1} to 30000 cm^{-1} . The common ligands can be arranged in ascending order of crystal field splitting Δ . The order remains practically constant for different metals, and this series is called the spectrochemical series (see Further Reading Tsuchida, 1938; Jørgensen, 1962).

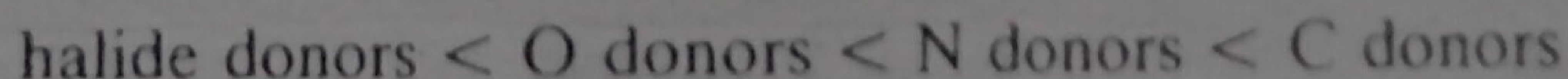
Spectrochemical series

weak field ligands



strong field ligands

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effects of σ and π bonding. The halides are in the order expected from electrostatic effects. In other cases we must consider covalent bonding to explain the order. A pattern of increasing σ donation is followed:



The crystal field splitting produced by the strong field CN^- ligand is about double that for weak field ligands like the halide ions. This is attributed to π bonding in which the metal donates electrons from a filled t_{2g} orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π acceptors.

The magnitude of Δ_o increases as the charge on the metal ion increases.

Table 7.9 Crystal field splittings for hexa-aqua complexes of M^{2+} and M^{3+}

Oxidation state		Ti	V	Cr	Mn	Fe	Co	Ni	Cu
(+II)	Electronic configuration	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
	Δ_o in cm^{-1}	-	12 600	13 900	7 800	10 400	9 300	8 500	12 600
	Δ_o in kJ mol^{-1}	-	151	(166)	93	124	111	102	(151)
(+III)	Electronic configuration	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
	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	-	-

Values for d^4 and d^9 are approximate because of tetragonal distortion.

Table 7.10 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	489

For first row transition metal ions, the values of Δ_o for M^{3+} complexes are roughly 50% larger than the values for M^{2+} complexes (Table 7.9).

The value of Δ_o also increases by about 30% between adjacent members down a group of transition elements (Table 7.10). The crystal field stabilization energy in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, which has a d^1 configuration, has previously been shown to be $-0.4\Delta_o$. In a similar way, complexes containing a metal ion with a d^2 configuration will have a CFSE of $2 \times -0.4\Delta_o = -0.8\Delta_o$, by singly filling two of the t_{2g} orbitals. (This is in agreement with Hund's rule that the arrangement with the maximum number of unpaired electrons is the most stable.) Complexes of d^3 metal ions have a CFSE of $3 \times -0.4\Delta_o = -1.2\Delta_o$.

Complexes with a metal ion with a d^4 configuration would be expected to have an electronic arrangement in accordance with Hund's rule (Figure 7.12a) with four unpaired electrons, and the CFSE will be $(3 \times -0.4\Delta_o) + (0.6\Delta_o) = -0.6\Delta_o$. An alternative arrangement of electrons which does not comply with Hund's rule is shown in Figure 7.12b. This arrangement has two unpaired electrons, and the CFSE is $(4 \times -0.4\Delta_o) = -1.6\Delta_o$. The CFSE is larger than in the previous case. However, the energy P used to pair the electrons must be allowed for, so the total stabilization energy is $-1.6\Delta_o + P$. These two arrangements differ in the number of unpaired electrons. The one with the most unpaired electrons is called 'high-spin' or 'spin-free', and the other one the 'low-spin' or 'spin-paired' arrangement. Both arrangements have been found to exist. Which arrangement occurs for any particular complex depends on whether the energy to promote an

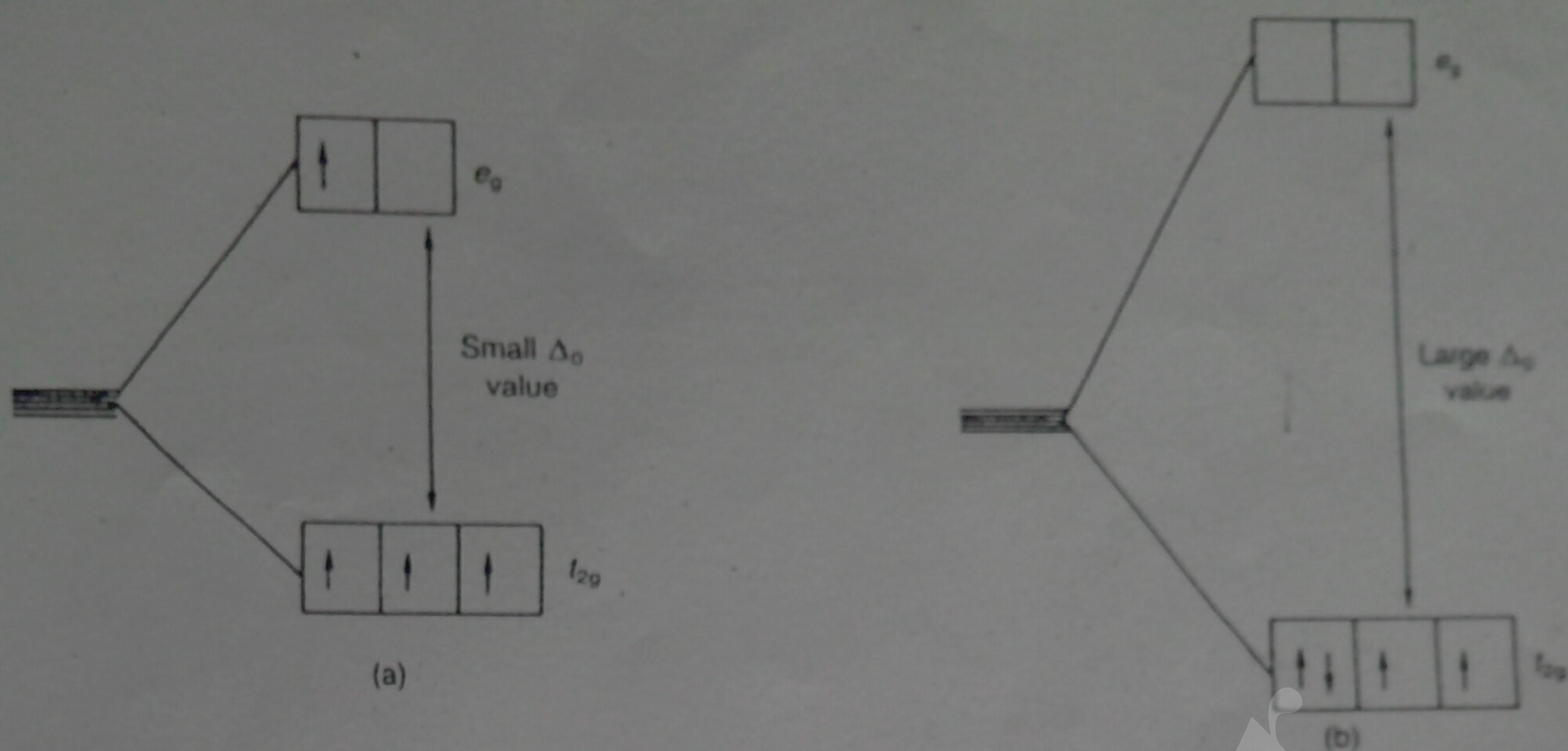


Figure 7.12 High- and low-spin complexes: (a) d^4 high-spin arrangement (weak ligand field); (b) d^4 low-spin arrangement (strong ligand field).

Table 7.11 CFSE and pairing energy for some complexes

Complex	Configuration	Δ_o (cm^{-1})	P (cm^{-1})	Predicted	Found
$[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$	d^6	10 400	17 600	high spin	high spin
$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$	d^6	32 850	17 600	low spin	low spin
$[\text{Co}^{\text{III}}\text{F}_6]^{3-}$	d^7	13 000	21 000	high spin	high spin
$[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$	d^7	23 000	21 000	low spin	low spin

electron to the upper e_g level (that is the crystal field splitting Δ_o) is greater than the energy to pair electrons (that is P) in the lower t_{2g} level. For a given metal ion P is constant. Thus the amount of crystal field splitting is determined by the strength of the ligand field. A weak field ligand such as Cl^- will only cause a small splitting of energy levels Δ_o . Thus it will be more favourable energetically for electrons to occupy the upper e_g level and have a high-spin complex, rather than to pair electrons. In a similar way, strong field ligands such as CN^- cause a large splitting Δ_o . In this case it requires less energy to pair the electrons and form a low-spin complex.

Similar arguments apply to high- and low-spin complexes of metal ions with d^5 , d^6 and d^7 configurations. These are summarized in Table 7.12.

EFFECTS OF CRYSTAL FIELD SPLITTING

In octahedral complexes, the filling of t_{2g} orbitals decreases the energy of a complex, that is makes it more stable by $-0.4\Delta_o$ per electron. Filling e_g

Table 7.12 CFSE and electronic arrangements in octahedral complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$
d^1	\uparrow \square \square	\square \square	-0.4	1.73	\uparrow \square \square	\square \square	-0.4	1.73
d^2	\uparrow \uparrow \square	\square \square	-0.8	2.83	\uparrow \uparrow \square	\square \square	-0.8	2.83
d^3	\uparrow \uparrow \uparrow	\square \square	-1.2	3.87	\uparrow \uparrow \uparrow	\square \square	-1.2	3.87
d^4	\uparrow \uparrow \uparrow	\uparrow \square	-1.2 +0.6 = -0.6	4.90	$\uparrow\downarrow$ \uparrow \uparrow	\square \square	-1.6	2.83
d^5	\uparrow \uparrow \uparrow	\uparrow \uparrow	-1.2 +1.2 = -0.0	5.92	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	\square \square	-2.0	1.73
d^6	$\uparrow\downarrow$ \uparrow \uparrow	\uparrow \uparrow	-1.6 +1.2 = -0.4	4.90	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\square \square	-2.4	0.00
d^7	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	\uparrow \uparrow	-2.0 +1.2 = -0.8	3.87	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow \square	-2.4 +0.6 = -1.8	1.73
d^8	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow \uparrow	-2.4 +1.2 = -1.2	2.83	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow \uparrow	-2.4 +1.2 = -1.2	2.83
d^9	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow	-2.4 +1.8 = -0.6	1.73	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow	-2.4 +1.8 = -0.6	1.73
d^{10}	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	-2.4 +2.4 = 0.0	0.00	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	-2.4 +2.4 = 0.0	0.00

orbitals increases the energy by $+0.6\Delta_o$ per electron. The total crystal field stabilization energy is given by

$$\text{CFSE}_{(\text{octahedral})} = -0.4n_{(t_{2g})} + 0.6n_{(e_g)}$$

where $n_{(t_{2g})}$ and $n_{(e_g)}$ are the number of electrons occupying the t_{2g} and e_g orbitals respectively. The CFSE is zero for ions with d^0 and d^{10} configurations in both strong and weak ligand fields. The CFSE is also zero for d^5 configurations in a weak field. All the other arrangements have some

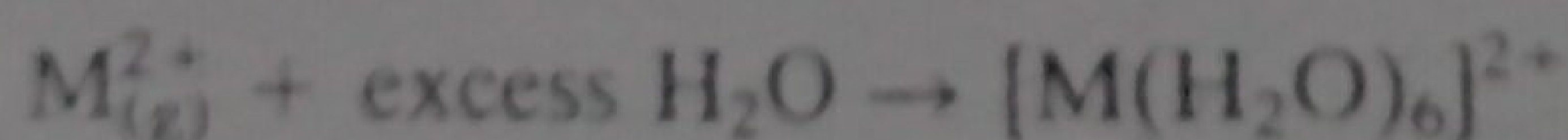
Table 7.13 Measured and calculated lattice energies

Compound	Structure	Measured lattice energy (kJ mol ⁻¹)	Calculated lattice energy (kJ mol ⁻¹)	Difference (measured - calculated) (kJ mol ⁻¹)
NaCl	Sodium chloride	-764	-764	0
AgCl	Sodium chloride	-916	-784	-132
AgBr	Sodium chloride	-908	-759	-149
MgF ₂	Rutile	-2908	-2915	+7
MnF ₂	Rutile	-2770	-2746	-24
FeF ₂	Rutile	-2912	-2752	-160
NiF ₂	Rutile	-3046	-2917	-129
CuF ₂	Rutile	-3042	-2885	-157

CFSE, which increases the thermodynamic stability of the complexes. Thus many transition metal compounds have a higher measured lattice energy (obtained by calculations using the terms in the Born-Haber cycle) than is calculated using the Born-Landé, Born-Meyer or Kapustinskii equations. In contrast, the measured (Born-Haber) and calculated values for compounds of the main groups (which have no CFSE) are in close agreement (Table 7.13). There is also close agreement in MnF₂ which has a d^5 configuration and a weak field ligand; hence there is no CFSE.

A plot of the lattice energies of the halides of the first row transition elements in the divalent state is given in Figure 7.13. In the solid, the coordination number of these metals is 6, and so the structures are analogous to octahedral complexes. The graphs for each halide show a minimum at Mn²⁺, which has a d^5 configuration. In a weak field this has a high-spin arrangement with zero CFSE. The configurations d^0 and d^{10} also have zero CFSE. The broken line through Ca²⁺, Mn²⁺ and Zn²⁺ represents zero stabilization. The heights of other points above this line are the crystal field stabilization energies.

The hydration energies of the M²⁺ ions of the first row transition elements are plotted in Figure 7.14a.



The ions Ca²⁺, Mn²⁺ and Zn²⁺ have d^0 , d^5 and d^{10} configurations, and have zero CFSE. An almost straight line can be drawn through these points. The distance of the other points above this line corresponds to the CFSE. Values obtained in this way agree with those obtained spectroscopically. A similar graph of the M³⁺ ions is shown in Figure 7.14b: here the d^0 , d^5 and d^{10} species are Sc³⁺, Fe³⁺ and Ga³⁺.

The ionic radii for M²⁺ ions might be expected to decrease smoothly from Ca²⁺ to Zn²⁺ because of the increasing nuclear charge, and the poor shielding by d electrons. A plot of these radii is given in Figure 7.15. The change in size is not regular.

A smooth (broken) line is drawn through Ca²⁺, Mn²⁺ and Zn²⁺. These

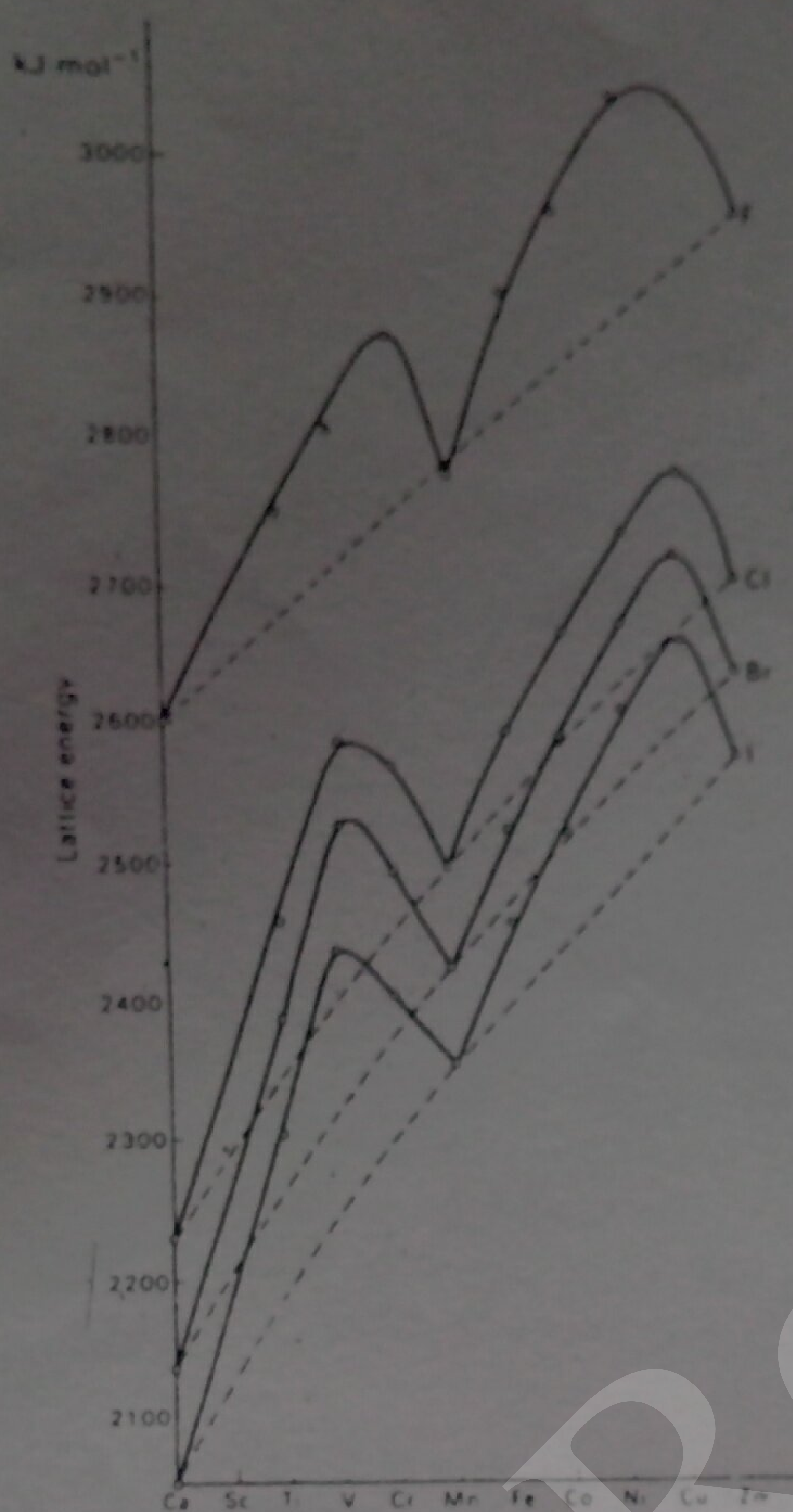


Figure 7.13 CFSE of dihalides of the first transition series. (After T. C. Waddington, Lattice energies and their significance in inorganic chemistry, *Advances in Inorganic Chemistry and Radiochemistry*, 1, Academic Press, New York, 1959.)

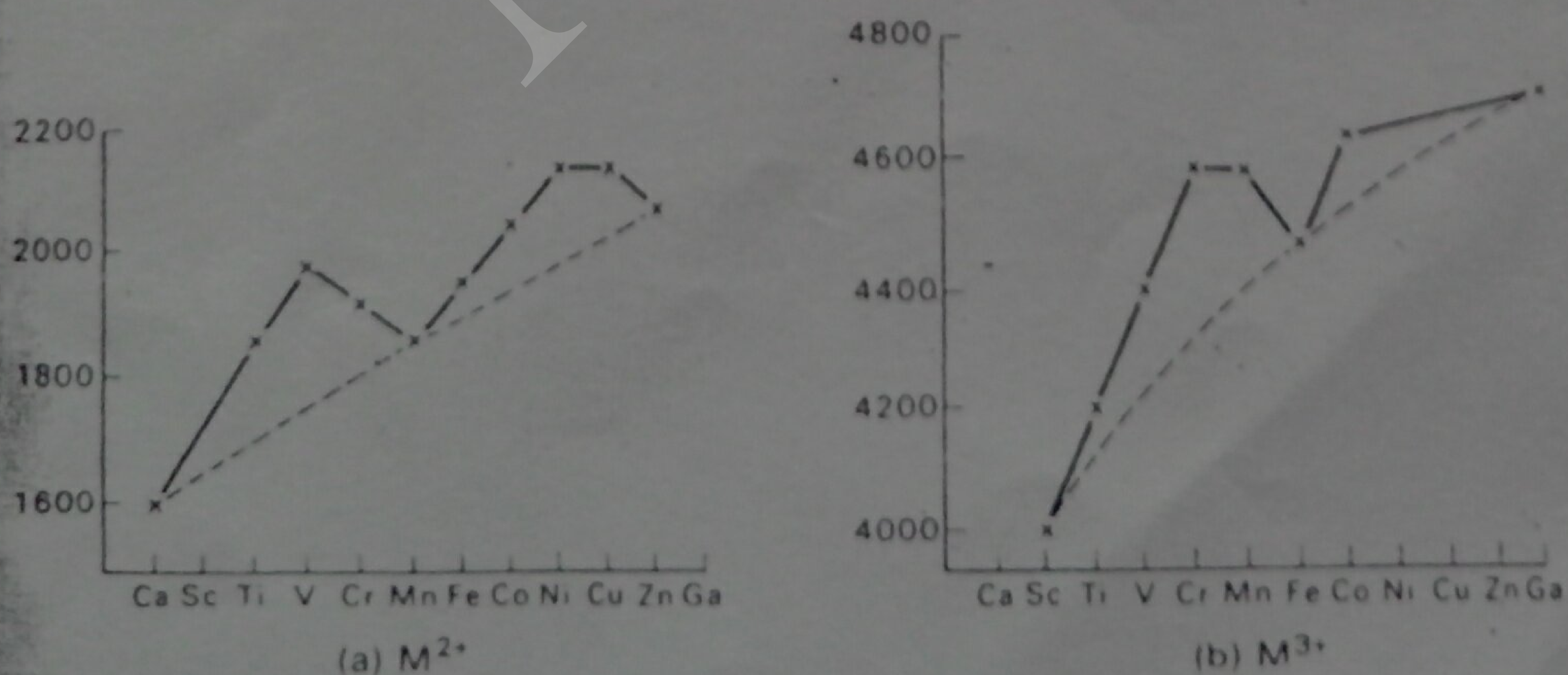


Figure 7.14 Enthalpies of hydration for M^{2+} and M^{3+} , in kJ mol^{-1}

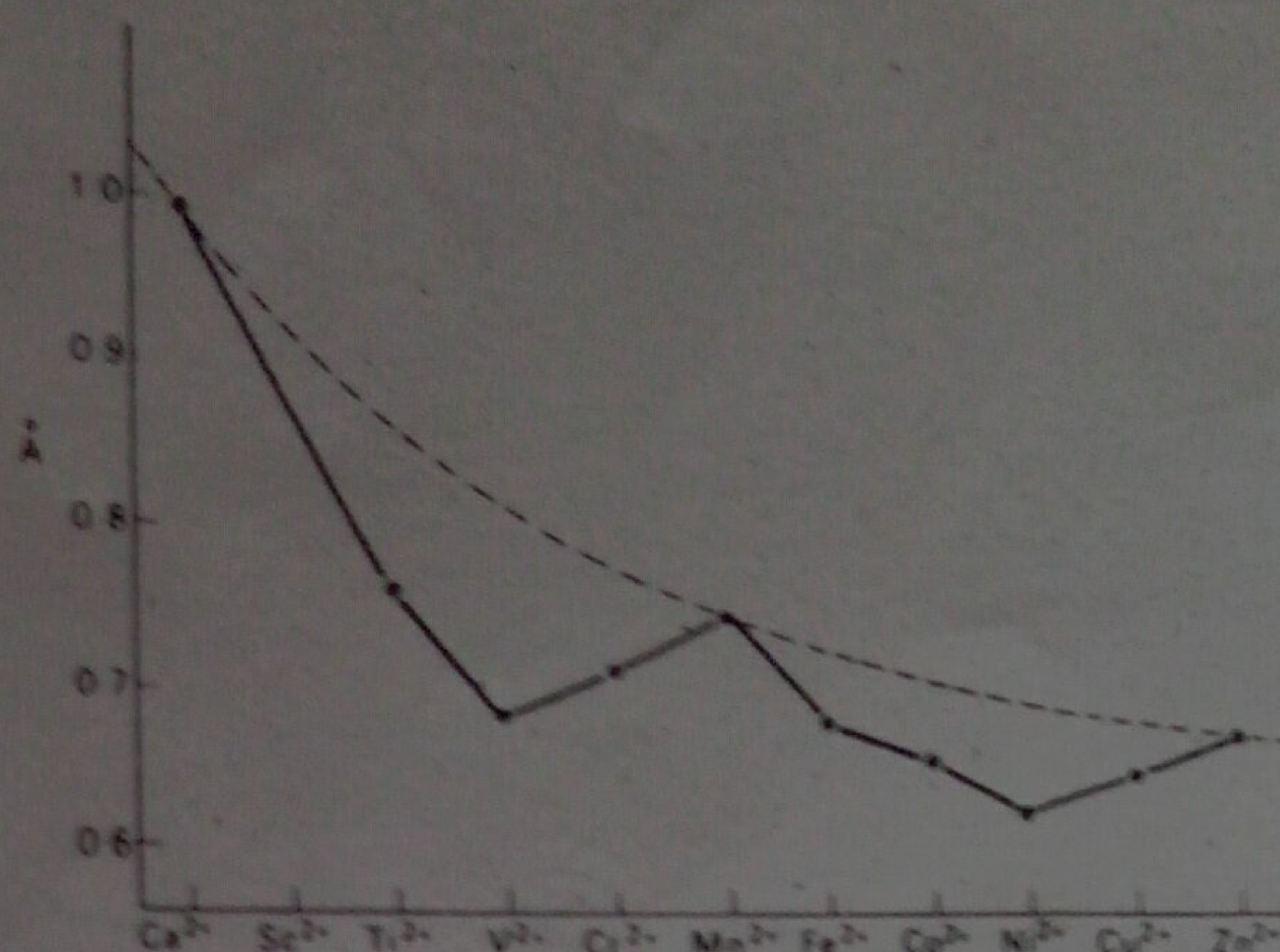


Figure 7.15 Octahedral ionic radii of M^{2+} for first row transition elements.

have d^0 , d^5 and d^{10} configurations as the d orbitals are empty, half full or full. These arrangements constitute an almost spherical field round the nucleus. In Ti^{2+} the d electrons occupy orbitals away from the ligands, providing little or no shielding of the nuclear charge. Thus the ligands are drawn closer to the nucleus. The increased nuclear charge has an even greater effect in the case of V^{2+} . At Cr^{2+} the e_g level contains one electron. This is concentrated in the direction of the ligands, thus providing very good shielding. Thus the ligands can no longer approach so closely and the ionic radius increases. This increase in size is continued with the filling of the second e_g orbital at Mn^{2+} . The screening by the e_g orbitals is so good that the radius of Mn^{2+} is slightly smaller than it would be if it were in a truly spherical field. The same sequence of size changes is repeated in the second half of the series.

TETRAGONAL DISTORTION OF OCTAHEDRAL COMPLEXES (JAHN-TELLER DISTORTION)

The shape of transition metal complexes is determined by the tendency of electron pairs to occupy positions as far away from each other as possible. This is the same as for the main group compounds and complexes. In addition, the shapes of transition metal complexes are affected by whether the d orbitals are symmetrically or asymmetrically filled.

(Repulsion by six ligands in an octahedral complex splits the d orbitals on the central metal into t_{2g} and e_g levels.) It follows that there is a corresponding repulsion between the d electrons and the ligands. If the d electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron. The symmetrical arrangements of d electrons are shown in Table 7.14.

All other arrangements have an asymmetrical arrangement of d electrons. If the d electrons are asymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted because some ligands are prevented from approaching the metal.

Table 7.14 Symmetrical electronic arrangements

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^0	$\square \square \square$	$\square \square$	Strong or weak	$\text{Ti}^{\text{IV}}\text{O}_2$, $[\text{Ti}^{\text{IV}}\text{F}_6]^{2-}$ $[\text{Ti}^{\text{IV}}\text{Cl}_6]^{2-}$
d^3	$\uparrow \uparrow \uparrow$	$\square \square$	Strong or weak	$[\text{Cr}^{\text{III}}(\text{oxalate})_3]^{3-}$ $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$
d^5	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$	Weak	$[\text{Mn}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Fe}^{\text{III}}\text{F}_6]^{3-}$
d^6	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\square \square$	Strong	$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$
d^8	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \uparrow$	Weak	$[\text{Ni}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$
d^{10}	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow$	Strong or weak	$[\text{Zn}^{\text{II}}(\text{NH}_3)_6]^{2+}$ $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$

as closely as others. The e_g orbitals point directly at the ligands. Thus asymmetric filling of the e_g orbitals results in some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the t_{2g} orbitals do not point directly at the ligands, but point in between the ligand directions. Thus asymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. Distortion caused by asymmetric filling of the t_{2g} orbitals is usually too small to measure. The electronic arrangements which will produce a large distortion are shown in Table 7.15.

The two e_g orbitals d_{z^2} and $d_{x^2-y^2}$ are normally degenerate. However, if they are asymmetrically filled then this degeneracy is destroyed, and the two orbitals are no longer equal in energy. If the d_{z^2} orbital contains one

Table 7.15 Asymmetrical electronic arrangements

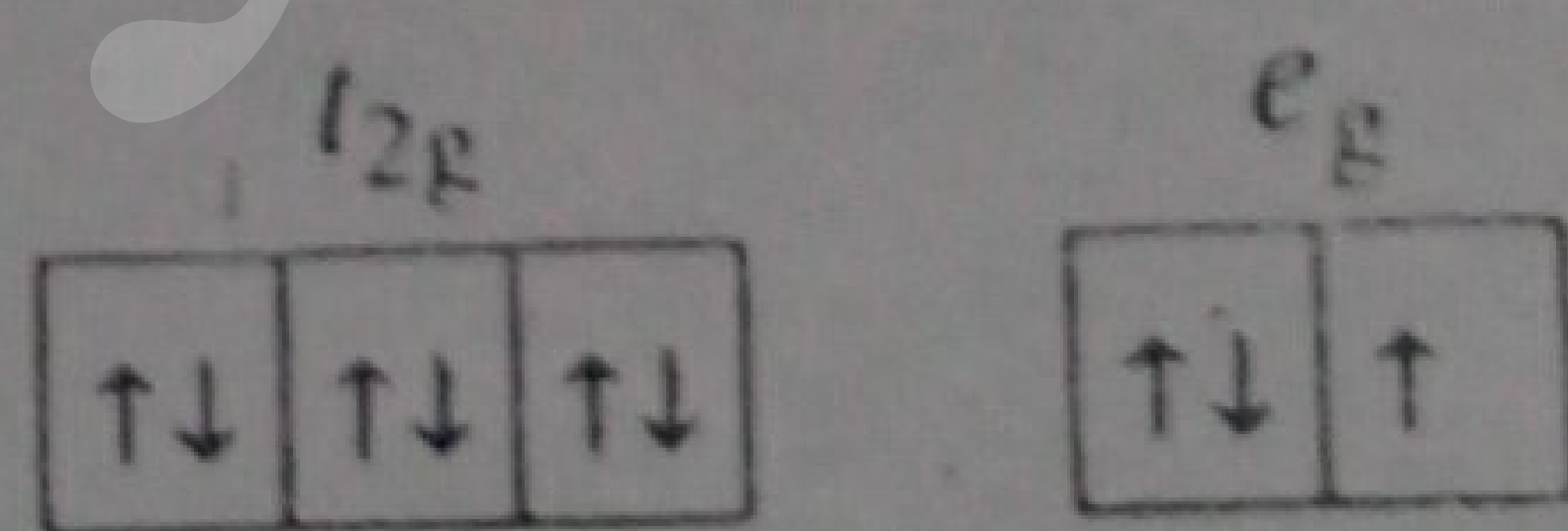
Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^4	$\uparrow \uparrow \uparrow$	$\uparrow \square$	Weak field (high-spin complex)	$\text{Cr}(+II)$, $\text{Mn}(+III)$
d^4	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow \square$	Strong field (low-spin complex)	$\text{Co}(+II)$, $\text{Ni}(+III)$
d^9	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow \uparrow$	Either strong or weak	$\text{Cu}(+II)$

more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along $+z$ and $-z$ will encounter greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the z axis. This is called tetragonal distortion. Strictly it should be called tetragonal elongation. This form of distortion is commonly observed.

If the $d_{x^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y axes. This means that the ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z axis, and is called tetragonal compression. Tetragonal elongation is much more common than tetragonal compression, and it is not possible to predict which will occur.

For example, the crystal structure of CrF_2 is a distorted rutile (TiO_2) structure. Cr^{2+} is octahedrally surrounded by six F^- , and there are four $\text{Cr}-\text{F}$ bonds of length 1.98–2.01 Å, and two longer bonds of length 2.43 Å. The octahedron is said to be tetragonally distorted. The electronic arrangement in Cr^{2+} is d^4 . F^- is a weak field ligand, and so the t_{2g} level contains three electrons and the e_g level contains one electron. The $d_{x^2-y^2}$ orbital has four lobes whilst the d_{z^2} orbital has only two lobes pointing at the ligands. To minimize repulsion with the ligands, the single e_g electron will occupy the d_{z^2} orbital. This is equivalent to splitting the degeneracy of the e_g level so that d_{z^2} is of lower energy, i.e. more stable, and $d_{x^2-y^2}$ is of higher energy, i.e. less stable. Thus the two ligands approaching along the $+z$ and $-z$ directions are subjected to greater repulsion than the four ligands along $+x$, $-x$, $+y$ and $-y$. This causes tetragonal distortion with four short bonds and two long bonds. In the same way MnF_3 contains Mn^{3+} with a d^4 configuration, and forms a tetragonally distorted octahedral structure.

Many $\text{Cu}(+II)$ salts and complexes also show tetragonally distorted octahedral structures. Cu^{2+} has a d^9 configuration:



To minimize repulsion with the ligands, two electrons occupy the d_{z^2} orbital and one electron occupies the $d_{x^2-y^2}$ orbital. Thus the two ligands along $+z$ and $-z$ are repelled more strongly than are the other four ligands (see Chapter 27, under +II state for copper).

The examples above show that whenever the d_{z^2} and $d_{x^2-y^2}$ orbitals are unequally occupied, distortion occurs. This is known as Jahn–Teller distortion. The Jahn–Teller theorem states that 'Any non-linear molecular system in a degenerate electronic state will be unstable, and will undergo some sort of distortion to lower its symmetry and remove the degeneracy.' More simply, molecules or complexes (of any shape except linear), which have an unequally filled set of orbitals (either t_{2g} or e_g), will be distorted. In octahedral complexes distortions from the t_{2g} level are too small to be

detected. However, distortions resulting from uneven filling of the e_g orbitals are very important.

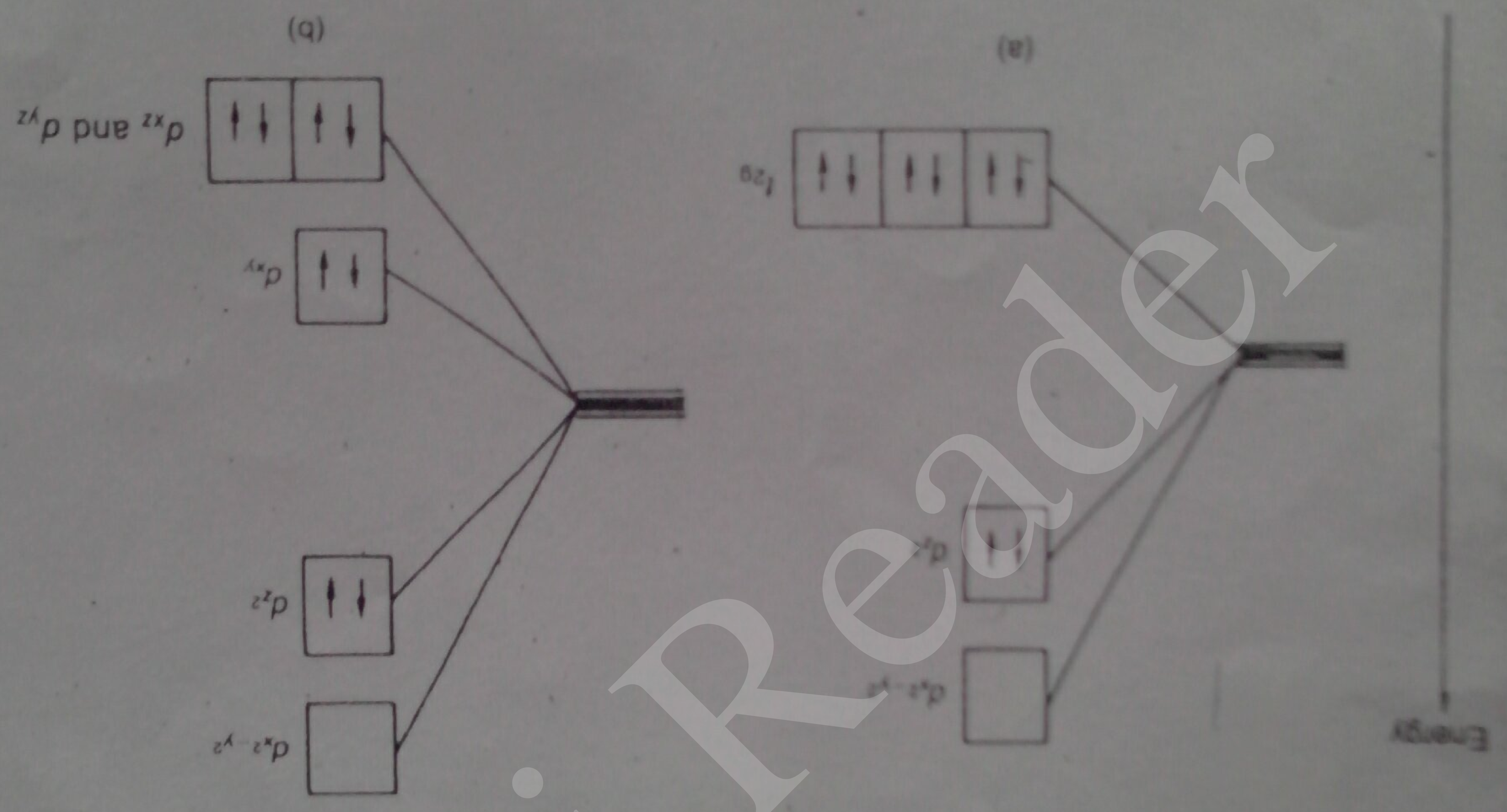


Figure 7.16 d^6 arrangement in weak octahedral field.

Figure 7.17 d^8 arrangement in very strong octahedral field. Tetragonal distortion splits (a) the e_g level; and (b) also splits the t_{2g} level. The d_{xy} orbital is higher in energy than the d_{xz} or d_{yz} . (For simplicity this is sometimes ignored.)

SQUARE PLANAR ARRANGEMENTS

If the central metal ion in a complex has a d^8 configuration, six electrons will occupy the t_{2g} orbitals and two electrons will occupy the e_g orbitals. The arrangement is the same in a complex with weak field ligands. The electrons are arranged as shown in Figure 7.16. The orbitals are symmetrically filled, and a regular octahedral complex is formed, for example by $[Ni^{II}(H_2O)_6]^{2+}$ and $[Ni^{II}(NH_3)_6]^{2+}$.

The single electron in the $d_{z^2-y^2}$ orbital is being repelled by four ligands, whilst the electron in the d_{z^2} orbital is only being repelled by two ligands. Thus the energy of the $d_{z^2-y^2}$ increases relative to that of d_{z^2} . If the ligand field is sufficiently strong, the difference in energy between these two orbitals becomes larger than the energy needed to pair the electrons. Under these conditions, a more stable arrangement arises when both the e_g electrons pair up and occupy the lower energy d_{z^2} orbital. This leaves the $d_{z^2-y^2}$ orbital empty (Figure 7.17). Thus four ligands can now approach along the $+x$, $-x$, $+y$ and $-y$ directions without any difficulty, as the $d_{z^2-y^2}$ orbital is empty. However, ligands approaching along the $+z$ and $-z$ directions meet very strong repulsive forces from the filled d_{z^2} orbital (Figure 7.18). Thus only four ligands succeed in bonding to the metal. A square planar complex is formed, the attempt to form an octahedral complex being unsuccessful.

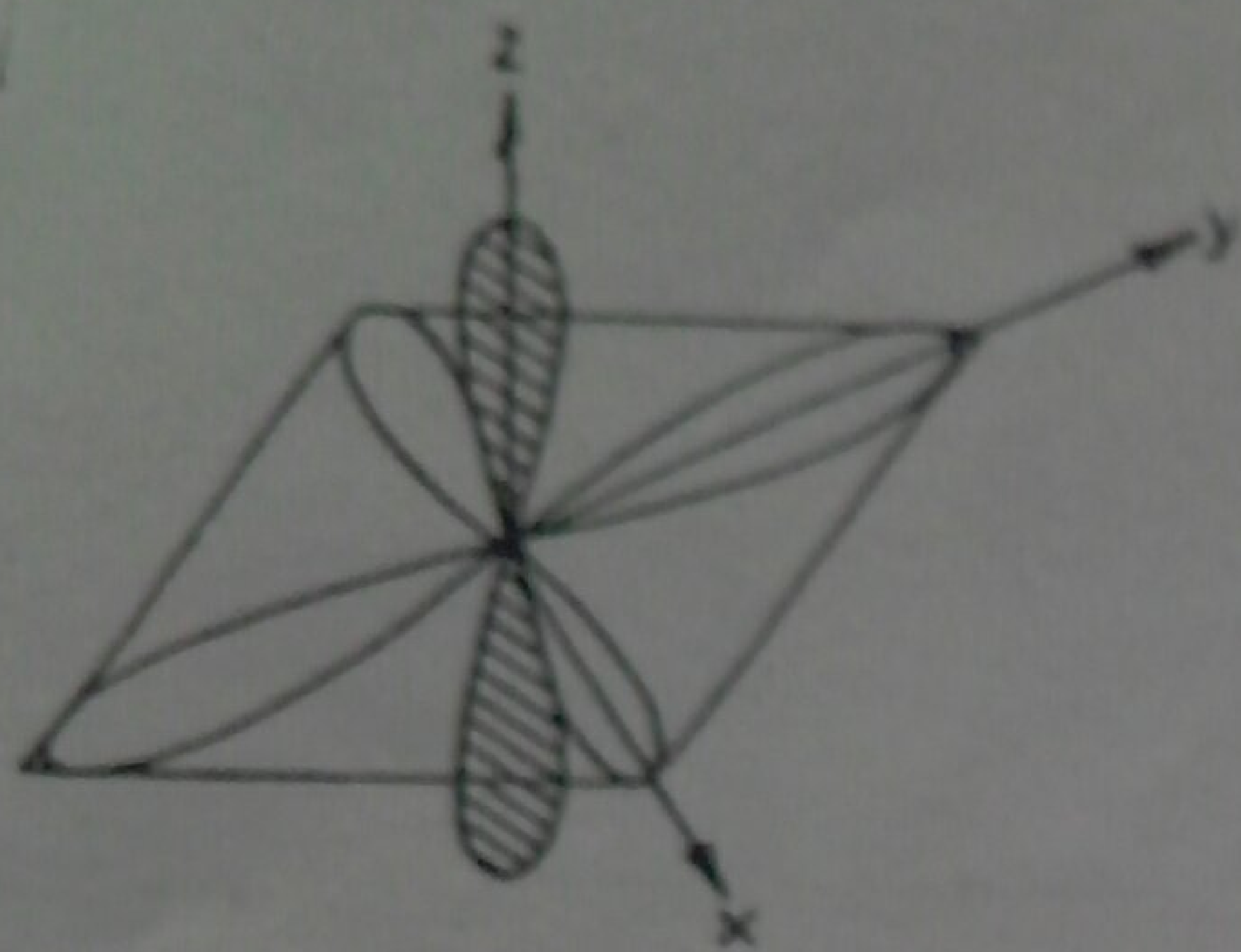


Figure 7.18 d^8 arrangement, strong field. (The d_{z^2} orbital is full, the $d_{z^2-y^2}$ empty.)

The amount of tetragonal distortion that occurs depends on the particular metal ion and ligands. Sometimes the tetragonal distortion may become so large that the d_{z^2} orbital is lower in energy than the d_{xy} orbital as shown in Figure 7.19. In square planar complexes of Co^{II} , Ni^{II} and Cu^{II} the d_{z^2} orbital has nearly the same energy as the d_{xy} and d_{xz} orbitals. In $[\text{PtCl}_4]^{2-}$ the d_{z^2} orbital is lower in energy than the d_{xz} and d_{yz} orbitals.

Square planar complexes are formed by d^8 ions with strong field ligands, for example $[\text{Ni}^{II}(\text{CN})_4]^{2-}$. The crystal field splitting Δ_o is larger for second and third row transition elements and for more highly charged species. All the complexes of $\text{Pt}(+II)$ and $\text{Au}(+III)$ are square planar - including those with weak field ligands such as halide ions.

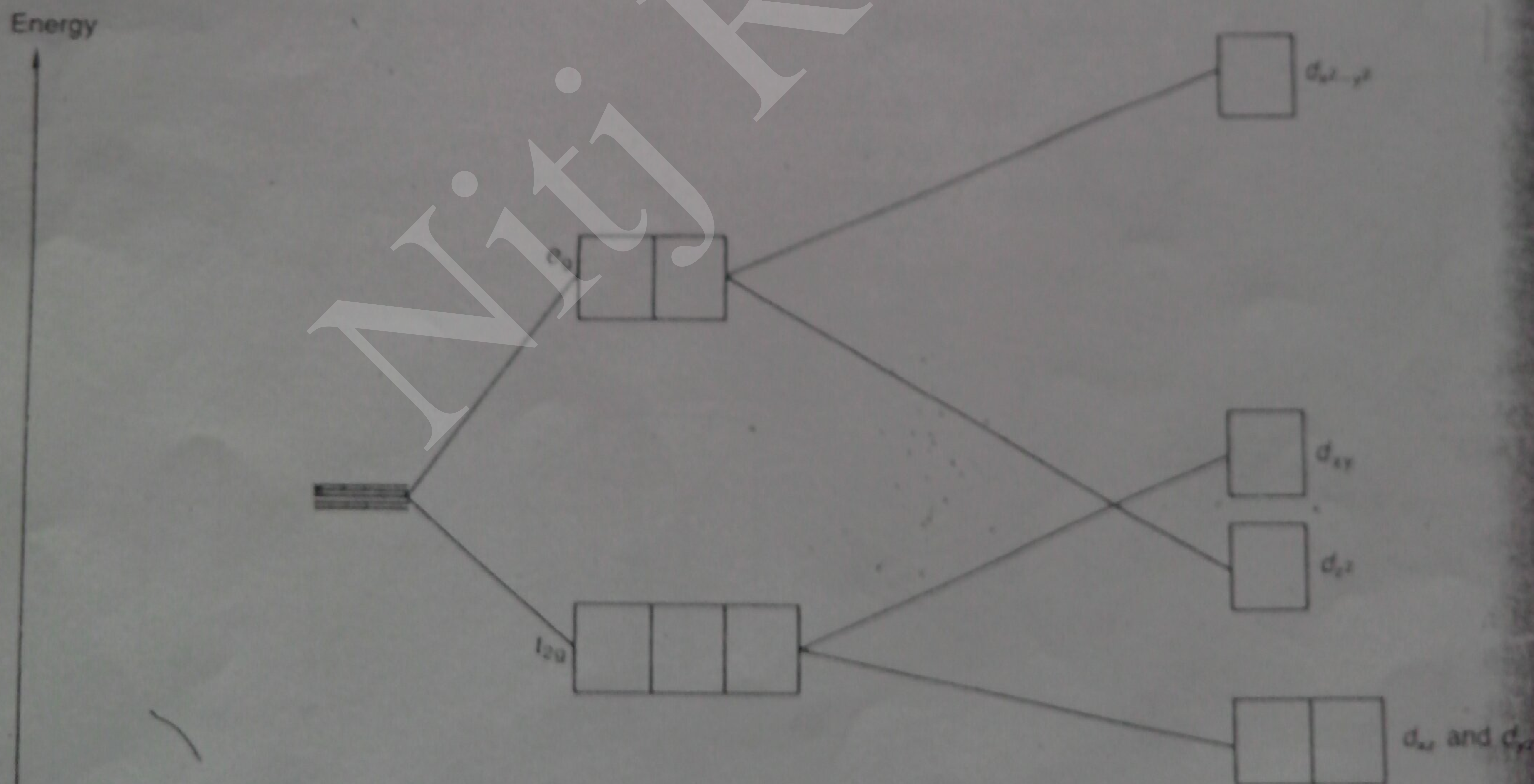


Figure 7.19 Tetragonal distortion.

Table 7.16 Ions that form square planar complexes

Electronic configuration	Ions	Type of field	Number of unpaired electrons
d^4	Cr(+II)	Weak	4
d^6	Fe(+II)	(Haem)	2
d^7	Co(+II)	Strong	1
d^8	Ni(+II), Rh(+I), Ir(+I)	Strong	0
d^9	Pd(+II), Pt(+II), Au(+III)	Strong and weak	0
	Cu(+II), Ag(+II)	Strong and weak	1

Square planar structures can also arise from d^4 ions in a weak ligand field. In this case the d_{z^2} orbital only contains one electron.

TETRAHEDRAL COMPLEXES

A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Figure 7.20.

The directions x , y and z point to the centres of the faces of the cube. The e_g orbitals point along x , y and z (that is to the centres of the faces). The t_{2g} orbitals point between x , y and z (that is towards the centres of the edges of the cube) (Figure 7.21).

The direction of approach of the ligands does not coincide exactly with

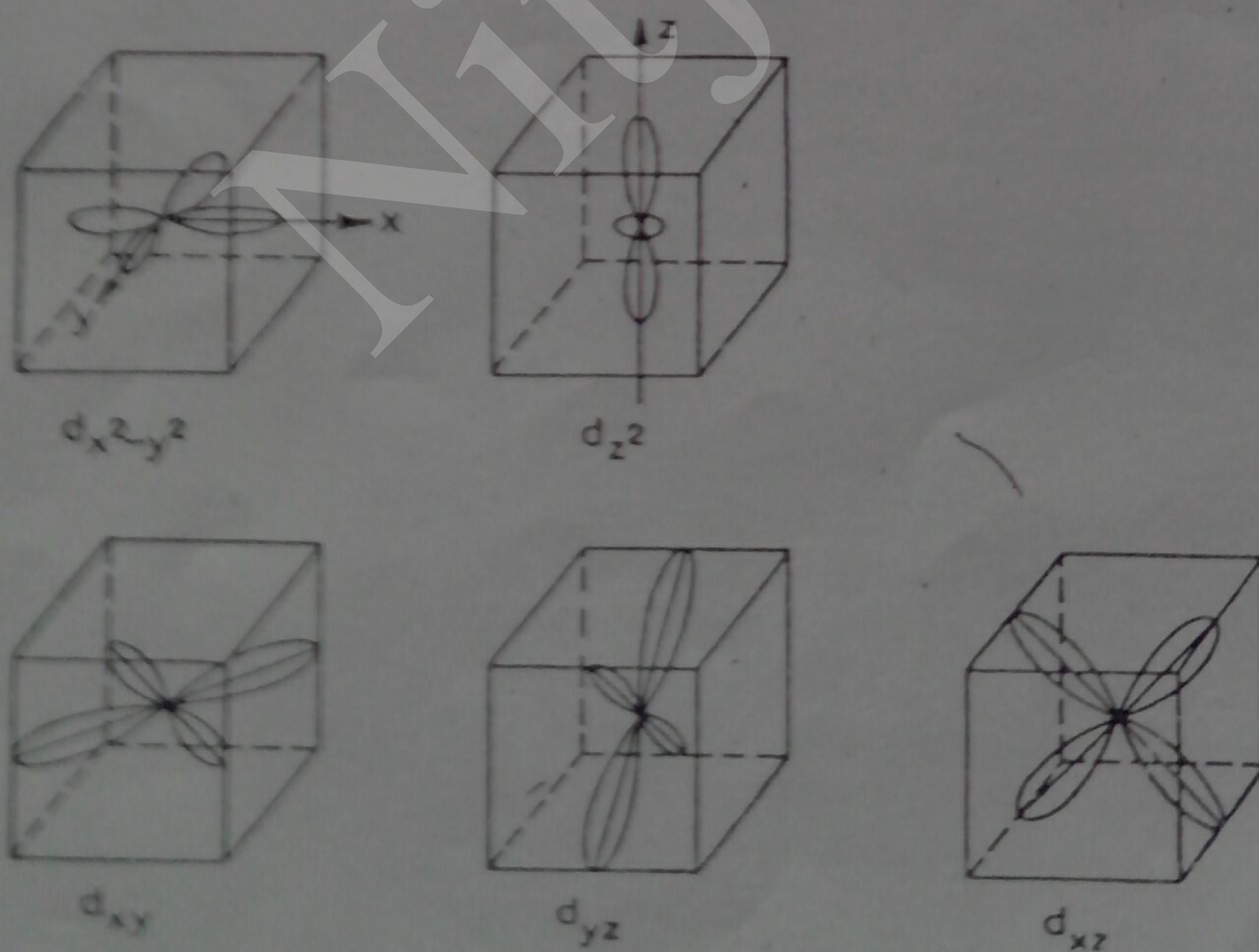
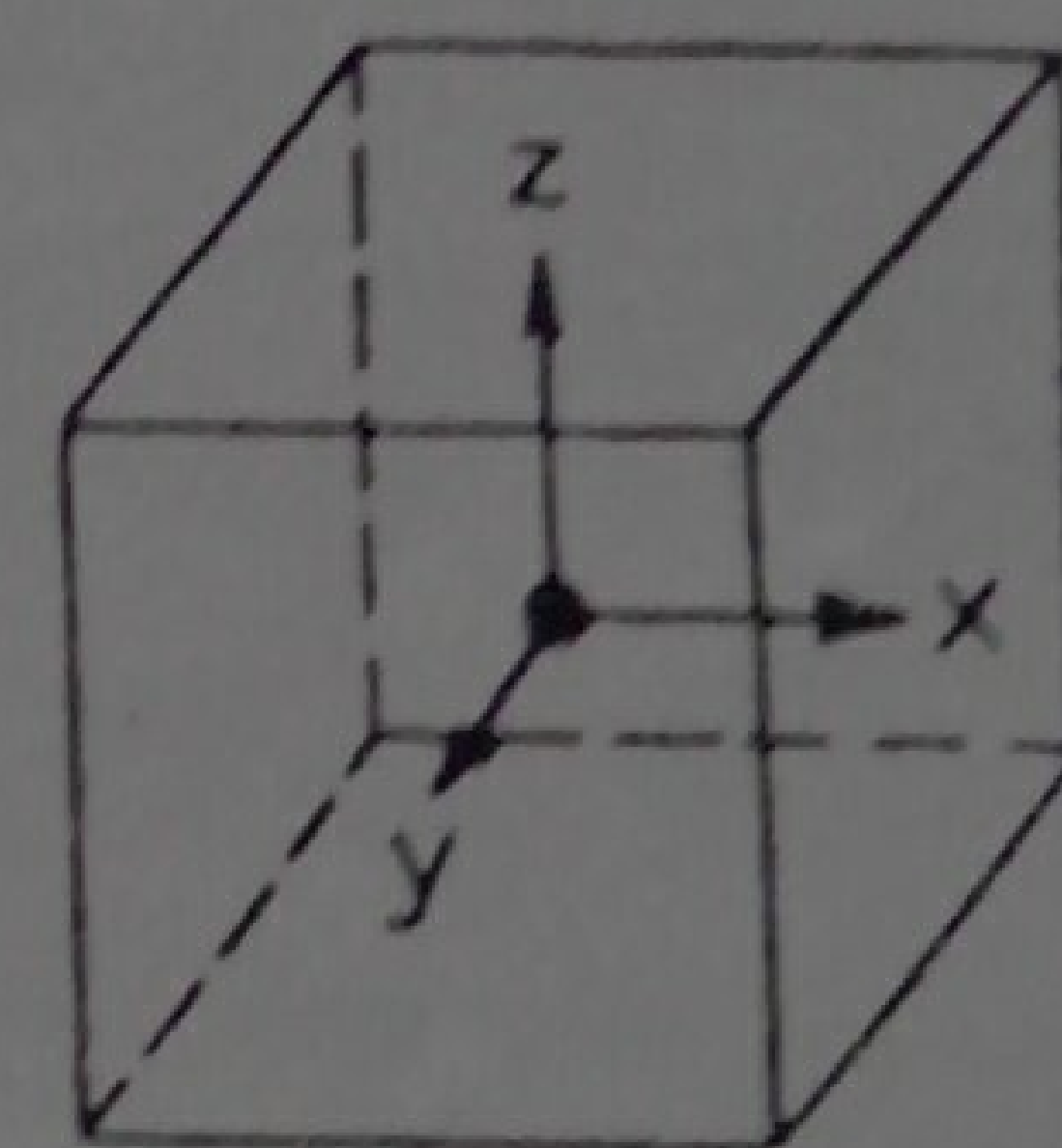
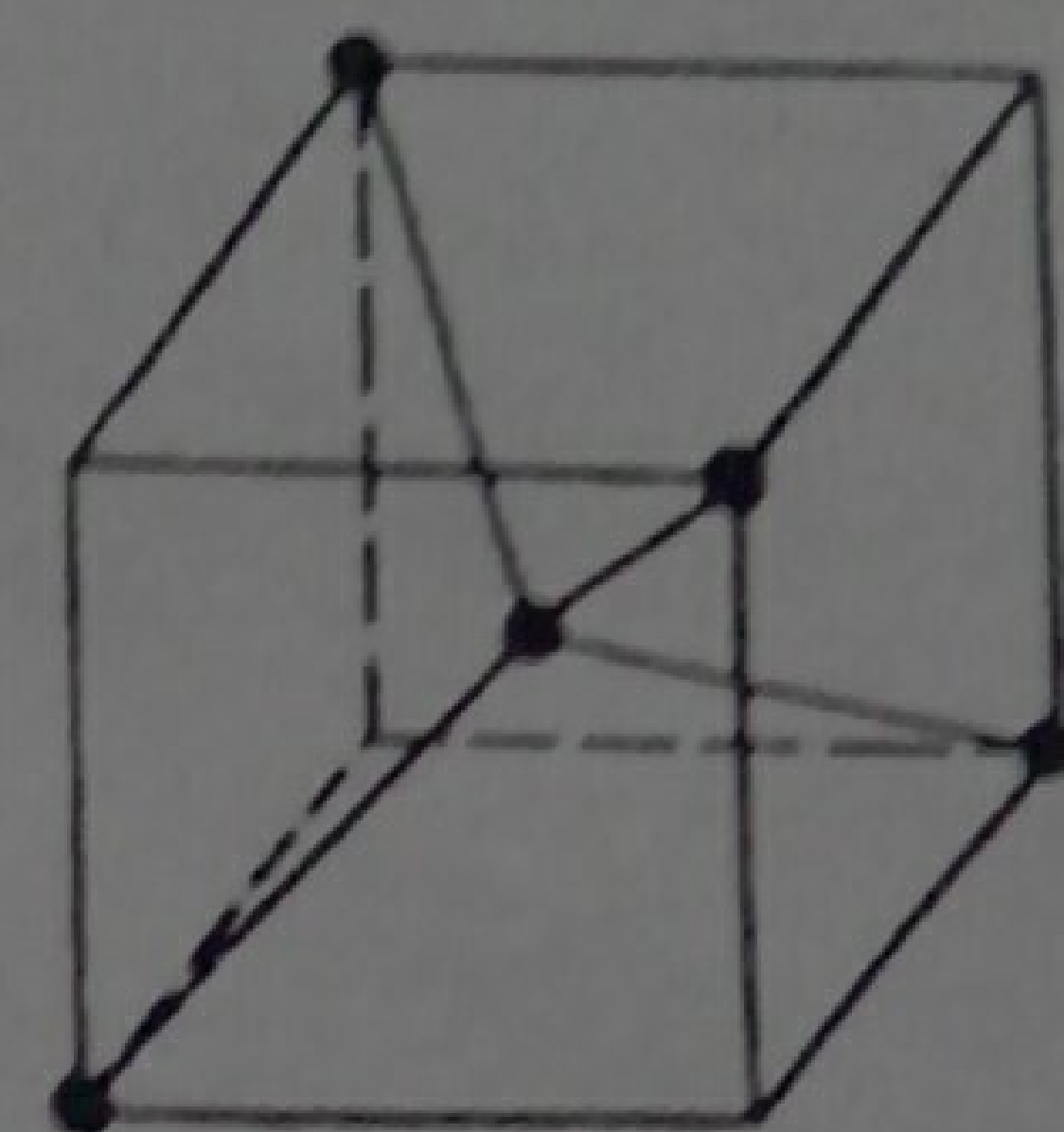
Figure 7.21 Orientation of d orbitals relative to a cube.

Figure 7.20 Relation of a tetrahedron to a cube.

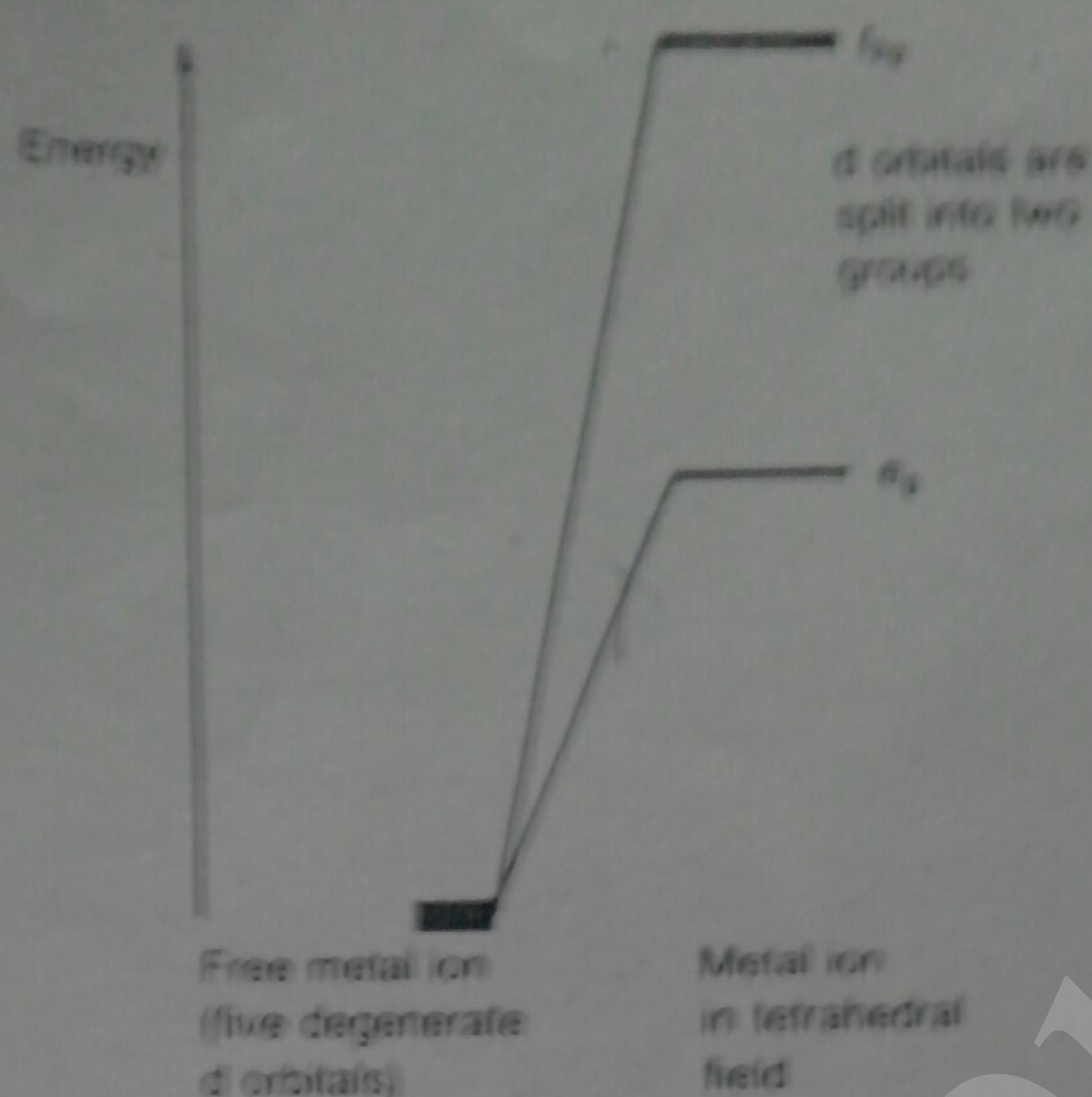


Figure 7.22 Crystal field splitting of energy levels in a tetrahedral field.

either the e_g or the t_{2g} orbitals. The angle between an e_g orbital, the central metal and the ligand is half the tetrahedral angle = $109^\circ 28' / 2 = 54^\circ 44'$. The angle between a t_{2g} orbital, the central metal and the ligand is $35^\circ 16'$. Thus the t_{2g} orbitals are nearer to the direction of the ligands than the e_g orbitals. (Alternatively the t_{2g} orbitals are half the side of the cube away from the approach of the ligands, whilst the e_g orbitals are half the diagonal of the cube away.) The approach of the ligands raises the energy of both sets of orbitals. The energy of the t_{2g} orbitals is raised most because they are closest to the ligands. This crystal field splitting is the opposite way round to that in octahedral complexes (Figure 7.22).

The t_{2g} orbitals are $0.4\Delta_t$ above the weighted average energy of the two groups (the Bary centre) and the e_g orbitals are $0.6\Delta_t$ below the average (Figure 7.23).

The magnitude of the crystal field splitting Δ_t in tetrahedral complexes is considerably less than in octahedral fields. There are two reasons for this:

1. There are only four ligands instead of six, so the ligand field is only two thirds the size: hence the ligand field splitting is also two thirds the size.
2. The direction of the orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting by roughly a further two thirds.

Thus the tetrahedral crystal field splitting Δ_t is roughly $2/3 \times 2/3 = 4/9$ of the octahedral crystal field splitting Δ_o . Strong field ligands cause a bigger energy difference between t_{2g} and e_g than weak field ligands. However, the tetrahedral splitting Δ_t is always much smaller than the octahedral splitting Δ_o . Thus it is never energetically favourable to pair electrons, and all tetrahedral complexes are high-spin.

34

JAHN TELLER THEOREM:-

The theorem states that any non-linear molecule (Octahedral, tetrahedral, square planar complex) with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes the degeneracy of orbitals, because the distortion lowers the overall energy of the complex.

This theorem explains why 6-coordinated complexes undergo distortion to assume distorted octahedral (ie Tetragonal) geometry.

Distorted octahedral complexes are those complexes in which all six distances between metal and ligand are not same.

The symmetrical t_{2g} orbitals are t_{2g0} , t_{2g3} , t_{2g6} .

The Un-symmetrical t_{2g} orbitals are t_{2g1} , t_{2g2} , t_{2g4} , t_{2g5} .

The symmetrical e_g orbitals are e_{g0} , e_{g4} .

The Un-symmetrical e_g orbitals are e_{g1} , e_{g3} .

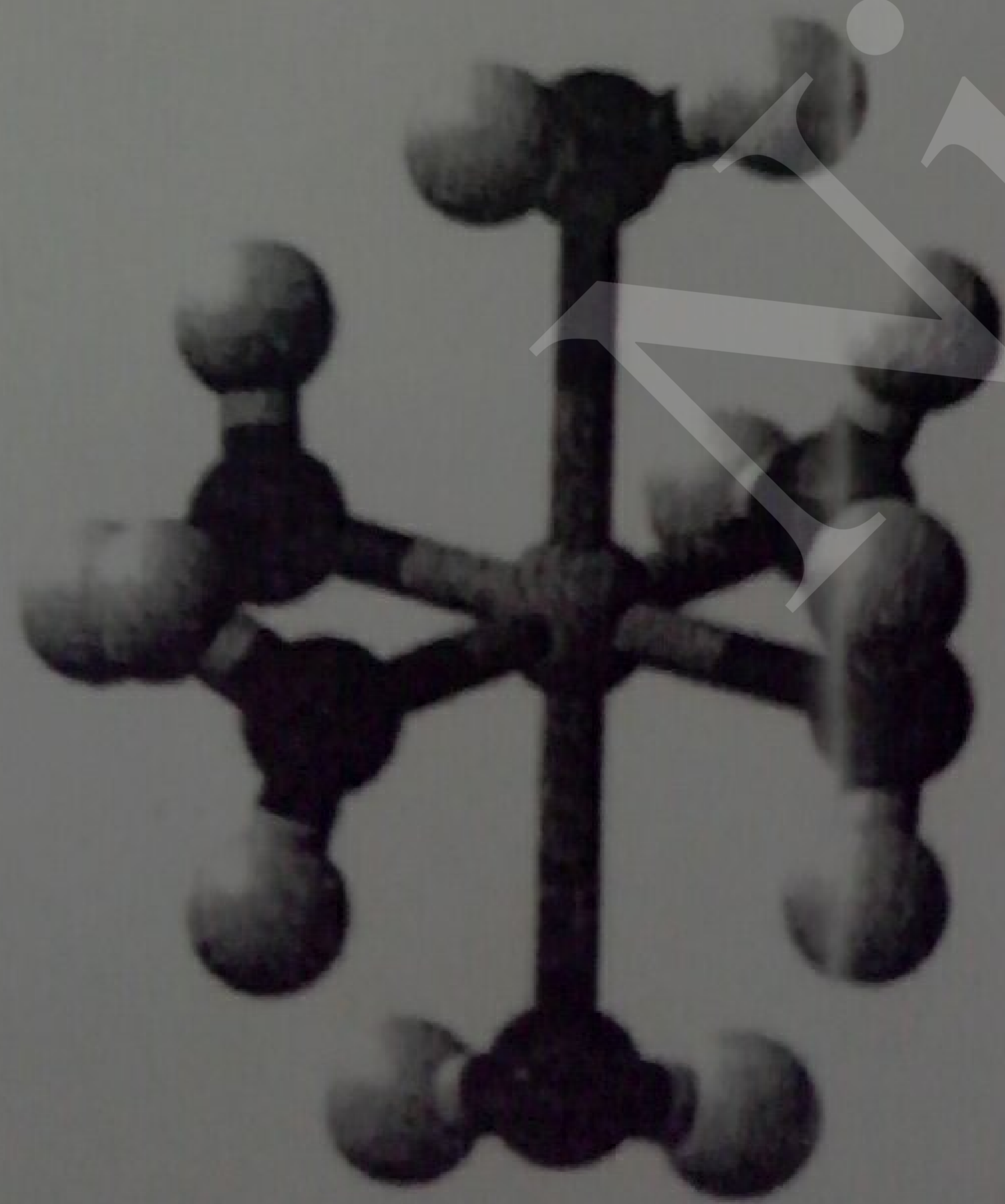
The e_{g2} is symmetrical is when configuration is $(dx^2-y^2)1$ and $dz^2 1$ and

is Un-symmetrical when configuration is $(dx^2-y^2)0$ and $dz^2 2$.

t_{2g} symmetrical + e_g symmetrical = No Distortion

t_{2g} Un-symmetrical = Slight Distortion

e_g Un-symmetrical = Large Distortion



The Jahn-Teller effect is most often encountered in octahedral complexes of the transition metals, and is very common in six-coordinate copper(II) complexes.

35

The d^3 electronic configuration of this ion gives three electrons in the two degenerate e_g orbitals, leading to a doubly degenerate electronic ground state.

Such complexes distort along one of the molecular fourfold axes (always labelled the z axis), which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy.

The distortion normally takes the form of elongating the bonds to the ligands lying along the z -axis, but occasionally as a shortening of these bonds may occur.

When such an elongation occurs, the effect is to lower the electrostatic repulsion between the electron-pair on the ligand and any electrons in orbitals with a z -component, thus lowering the energy of the complex.

In octahedral complexes, the Jahn-Teller effect is most pronounced when an odd number of electrons occupy the e_g orbitals; *i.e.*, in d^9 , low-spin d^7 or high-spin d^4 complexes, all of which have doubly degenerate ground states. This is because the e_g orbitals involved in the degeneracy point directly at the ligands, so distortion can result in a large energetic stabilisation.

Strictly speaking, the effect should also occur when there is a degeneracy due to the electrons in the t_{2g} orbitals (*i.e.* configurations such as d^1 or d^2 , both of which are triply degenerate). However, the effect is much less noticeable, because there is a much smaller lowering of repulsion on taking ligands further away from the t_{2g} orbitals, which don't point *directly* at the ligands involved. The same is true in tetrahedral complexes; distortion is less because there is less stabilisation to be gained because the ligands are not pointing directly at the orbitals.

Two examples are discussed. 36 student
discusses even one example, full credit
may be given.

Sangita Oberoi

Examples - Crystal structure of CrF_2 is distorted structure. In this case Cr^{2+} is octahedrally surrounded by six F^- ions, 4 ($\text{Cr}-\text{F}$) bonds are of length $1.98-2.01 \text{ \AA}$ whereas two bonds of length 2.43 \AA . So octahedron is said to be tetragonal distorted, its electronic arrangement is $\text{Cr}^{2+} (d^4)$. Here t_{2g} level contains 3 e^- & e_g contains one electron.

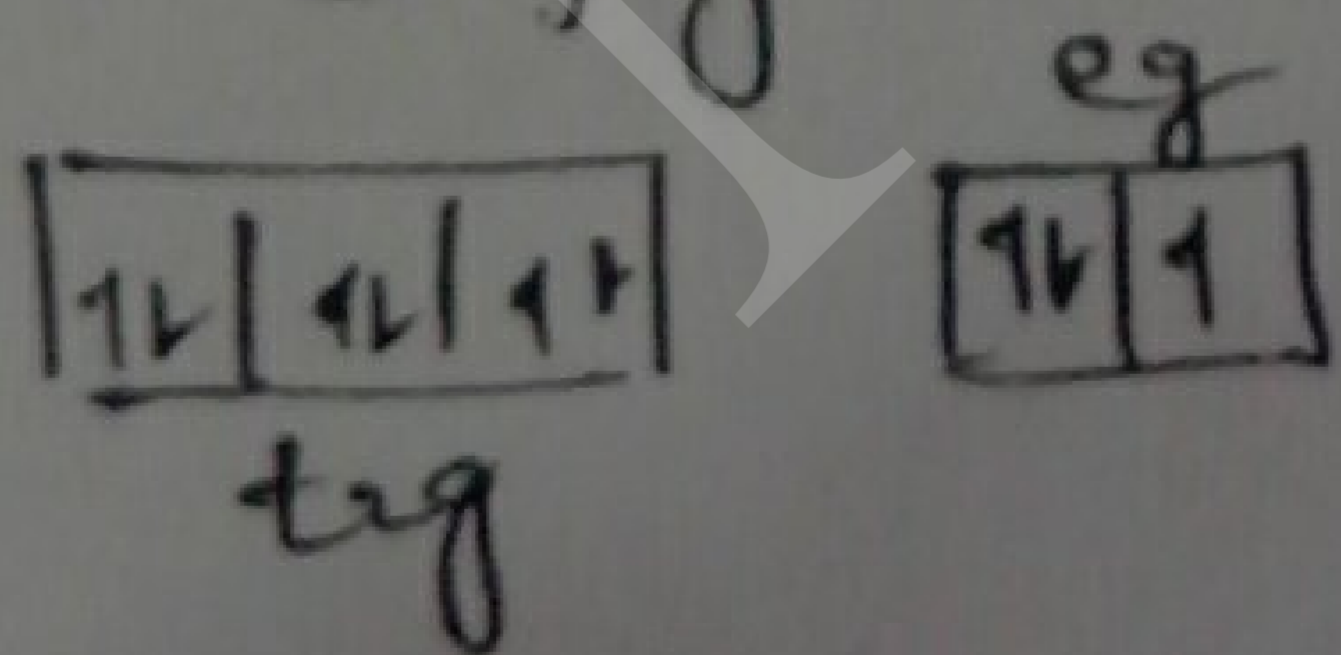
$d_{x^2-y^2}$ - 4 lobes \rightarrow pointing at the ligand

d_{z^2} - 2 lobes

To minimize repulsion with the ligand, e_g ^{single} e^- will occupy the d_{z^2} orbital, it splits the degeneracy of e_g level, so that d_{z^2} of low energy (more stable) whereas $d_{x^2-y^2}$ (higher energy i.e. less stable).

Two ligand approaches \uparrow towards z directions subjecting greater repulsion than the four ligands along (x, y, z) directions. it causes tetragonal distortion.

1) Cu(II) d^9 Configuration in this case 2 e^- occupy d_{z^2} orbital & 1 e^- occupy $d_{x^2-y^2}$ orbital



2 e^- 2 ligands along \rightarrow z & \uparrow z

are more strongly repelled than other four ligands.

So, above examples shows that whenever d_{z^2} & $d_{x^2-y^2}$ orbitals are unequally occupied, distortion occurs. This is called as Jahn-Teller distortion.

36