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Department:Chemistry
Stage:Third**

Lectures in Coordination Chemistry

By

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Syllabus for Coordination chemistry of third stage

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Textbooks and references books

1. *Inorganic Chemistry, 5th Edition; Gary. L. Miessler and Donald . A. Tarr (2014).*
2. *Inorganic Chemistry” by Catherine. E. Housecroft and Alan G. Sharpe, Prentice Hall (4th Edition (2012).*
3. *Basic Inorganic Chemistry, 3rd ed., by F. A. Cotton et al., Wiley (2007).*
4. *Inorganic Chemistry principles of structure and reactivity 4th ed, by James E. Huhhey et al, Harper Collins college Puplishers (1993)*
5. *Shriver & Atkins'Inorganic Chemistry,by Atkins, Overton, Rourke, Weller, Armstrong, 5th Edition. Oxford (2010).*
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Introduction about transition element

What is a Transition Element?

Strictly a transition element is one whose element or at least one common oxidation state has an incomplete d-subshell (IUPAC).

IUPAC (International Union of Pure and Applied Chemistry)

The term '**transition**' arises from the elements' supposed *transitional* positions between the metallic elements of groups 1 and 2 and the predominantly non-metallic elements of groups 13 to 18. Typically, the transition elements are transition metals in view of their typical metallic properties.

Most of the elements exhibit a typical silvery metallic appearance, but gold and copper are unique in their reddish coloration and mercury is the only metal which is liquid at ambient temperatures. Compounds of the transition elements account for the majority of coloured inorganic materials, and many pigments are relatively simple derivatives of these elements; however, not all transition-element compounds are coloured. The transition elements comprise groups 3 to 12 and are found in the central region of the standard periodic table.

1A 1	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 H 1s ¹																	2 He 1s ²
2 Li 2s ¹	3 Be 2s ²											5 B 2s ² 2p ¹	6 C 2s ² 2p ²	7 N 2s ² 2p ³	8 O 2s ² 2p ⁴	9 F 2s ² 2p ⁵	10 Ne 2s ² 2p ⁶
3 Na 3s ¹	11 Mg 3s ²	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8 9 10			1B 11	2B 12	13 Al 3s ² 3p ¹	14 Si 3s ² 3p ²	15 P 3s ² 3p ³	16 S 3s ² 3p ⁴	17 Cl 3s ² 3p ⁵	18 Ar 3s ² 3p ⁶
4 K 4s ¹	19 Ca 4s ²	21 Sc 4s ² 3d ¹	22 Ti 4s ² 3d ²	23 V 4s ² 3d ³	24 Cr 4s ¹ 3d ⁵	25 Mn 4s ² 3d ⁵	26 Fe 4s ² 3d ⁶	27 Co 4s ² 3d ⁷	28 Ni 4s ² 3d ⁸	29 Cu 4s ¹ 3d ¹⁰	30 Zn 3d ¹⁰ 4s ²	31 Ga 4s ² 4p ¹	32 Ge 4s ² 4p ²	33 As 4s ² 4p ³	34 Se 4s ² 4p ⁴	35 Br 4s ² 4p ⁵	36 Kr 4s ² 4p ⁶
5 Rb 5s ¹	37 Sr 5s ²	39 Y 5s ² 4d ¹	40 Zr 5s ² 4d ²	41 Nb 5s ¹ 4d ⁴	42 Mo 5s ¹ 4d ⁵	43 Tc 5s ² 4d ⁵	44 Ru 5s ¹ 4d ⁷	45 Rh 5s ¹ 4d ⁸	46 Pd 4d ¹⁰	47 Ag 5s ¹ 4d ¹⁰	48 Cd 5s ² 4d ¹⁰	49 In 5s ² 5p ¹	50 Sn 5s ² 5p ²	51 Sb 5s ² 5p ³	52 Te 5s ² 5p ⁴	53 I 5s ² 5p ⁵	54 Xe 5s ² 5p ⁶
6 Cs 6s ¹	55 Ba 6s ²	71 Lu 6s ² 5d ¹ 4f ¹⁴	72 Hf 6s ² 5d ²	73 Ta 6s ² 5d ³	74 W 6s ² 5d ⁴	75 Re 6s ² 5d ⁵	76 Os 6s ² 5d ⁶	77 Ir 6s ² 5d ⁷	78 Pt 6s ¹ 5d ⁹	79 Au 6s ¹ 5d ¹⁰	80 Hg 6s ² 5d ¹⁰	81 Tl 6s ² 6p ¹	82 Pb 6s ² 6p ²	83 Bi 6s ² 6p ³	84 Po 6s ² 6p ⁴	85 At 6s ² 6p ⁵	86 Rn 6s ² 6p ⁶
7 Fr 7s ¹	87 Ra 7s ²	103 Lr 7s ² 5f ¹⁴ 6d ¹	104 Rf 7s ² 6d ²	105 Db 7s ² 6d ³	106 Sg 7s ² 6d ⁴	107 Bh 7s ² 6d ⁵	108 Hs 7s ² 6d ⁶	109 Mt 7s ² 6d ⁷	110 Ds 7s ² 6d ⁸	111 Rg 7s ² 6d ⁹	112 Cn 7s ² 6d ¹⁰	113 Nh 7s ² 7p ¹	114 Fl 7s ² 7p ²	115 Mc 7s ² 7p ³	116 Lv 7s ² 7p ⁴	(117) Ts 7s ² 7p ⁵	118 Og 7s ² 7p ⁶

57 La 6s ² 5d ¹	58 Ce 6s ² 4f ¹ 5d ¹	59 Pr 6s ² 4f ³	60 Nd 6s ² 4f ⁴	61 Pm 6s ² 4f ⁵	62 Sm 6s ² 4f ⁶	63 Eu 6s ² 4f ⁷	64 Gd 6s ² 4f ⁷ 5d ¹	65 Tb 6s ² 4f ⁹	66 Dy 6s ² 4f ¹⁰	67 Ho 6s ² 4f ¹¹	68 Er 6s ² 4f ¹²	69 Tm 6s ² 4f ¹³	70 Yb 6s ² 4f ¹⁴
89 Ac 7s ² 6d ¹	90 Th 7s ² 6d ²	91 Pa 7s ² 5f ² 6d ¹	92 U 7s ² 5f ³ 6d ¹	93 Np 7s ² 5f ⁴ 6d ¹	94 Pu 7s ² 5f ⁶	95 Am 7s ² 5f ⁷	96 Cm 7s ² 5f ⁷ 6d ¹	97 Bk 7s ² 5f ⁹	98 Cf 7s ² 5f ¹⁰	99 Es 7s ² 5f ¹¹	100 Fm 7s ² 5f ¹²	101 Md 7s ² 5f ¹³	102 No 7s ² 5f ¹⁴

The transition elements contain of four transition series which are all metals and are characterized by electrons being assigned to d orbitals. Stated differently, the d -transition elements contain electrons in both the ns and $(n - 1)d$ orbitals, but not in the np orbitals. The first transition series, Sc through Zn, has electrons in the $4s$ and $3d$ orbitals, but not in the $4p$ orbitals. They are referred to as

First transition series: $_{21}\text{Sc}$ through $_{30}\text{Zn}$ contain $3d^{1-10}, 4s^{1-2}$

Second transition series: $_{39}\text{Y}$ through $_{48}\text{Cd}$ contain $4d^{1-10}, 5s^{1-2}$

Third transition series: $_{71}\text{Lu}$ and $_{72}\text{Hf}$ through $_{80}\text{Hg}$ contain $5d^{1-10}, 6s^{1-2}$

Fourth transition series: $_{103}\text{Lr}$ and $_{104}\text{Rf}$ through $_{112}\text{Cn}$ contain $6d^{1-10}, 7s^{1-2}$

The electron configurations of the transition elements are presented in Table 1-1.

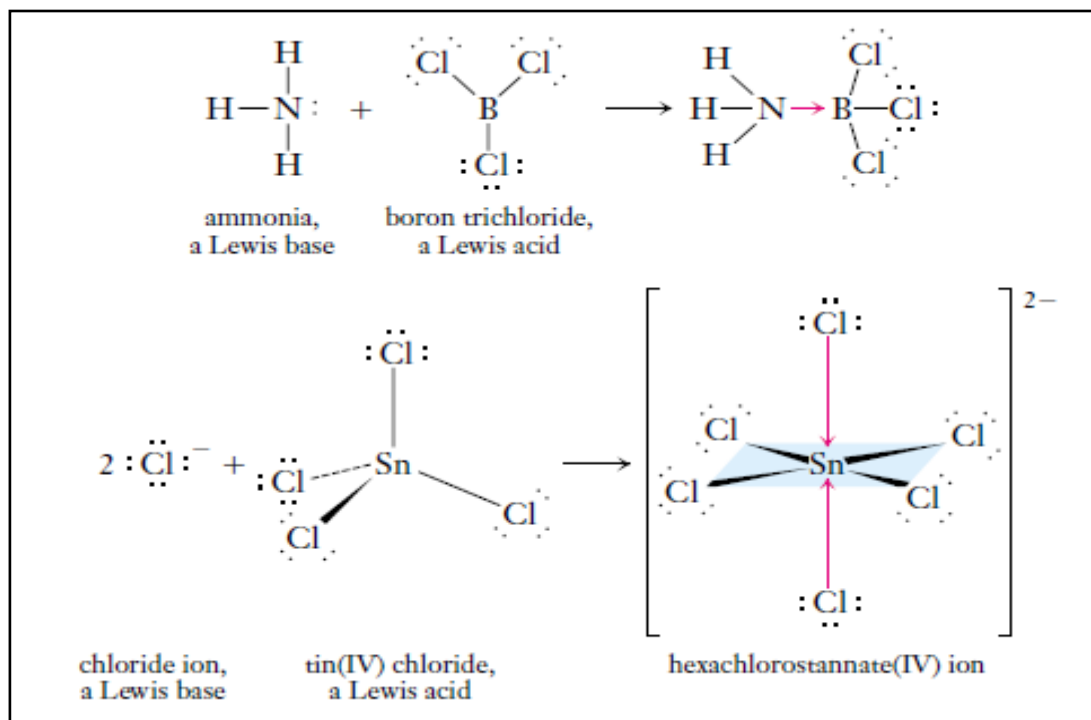
Table 1-1. The electronic configurations of the transition elements.

Scandium	$[\text{Ar}]3d^1 4s^2$	Yttrium	$[\text{Kr}]4d^1 5s^2$	Lanthanum	$[\text{Xe}]5d^1 6s^2$
Titanium	$[\text{Ar}]3d^2 4s^2$	Zirconium	$[\text{Kr}]4d^2 5s^2$	Hafnium	$[\text{Xe}]4f^{14} 5d^2 6s^2$
Vanadium	$[\text{Ar}]3d^3 4s^2$	Niobium	$[\text{Kr}]4d^4 5s^1$	Tantalum	$[\text{Xe}]4f^{14} 5d^3 6s^2$
Chromium	$[\text{Ar}]3d^5 4s^1$	Molybdenum	$[\text{Kr}]4d^5 5s^1$	Tungsten	$[\text{Xe}]4f^{14} 5d^4 6s^2$
Manganese	$[\text{Ar}]3d^5 4s^2$	Technetium	$[\text{Kr}]4d^5 5s^2$	Rhenium	$[\text{Xe}]4f^{14} 5d^5 6s^2$
Iron	$[\text{Ar}]3d^6 4s^2$	Ruthenium	$[\text{Kr}]4d^7 5s^1$	Osmium	$[\text{Xe}]4f^{14} 5d^6 6s^2$
Cobalt	$[\text{Ar}]3d^7 4s^2$	Rhodium	$[\text{Kr}]4d^8 5s^1$	Iridium	$[\text{Xe}]4f^{14} 5d^7 6s^2$
Nickel	$[\text{Ar}]3d^8 4s^2$	Palladium	$[\text{Kr}]4d^{10} 5s^0$	Platinum	$[\text{Xe}]4f^{14} 5d^9 6s^1$
Copper	$[\text{Ar}]3d^{10} 4s^1$	Silver	$[\text{Kr}]4d^{10} 5s^1$	Gold	$[\text{Xe}]4f^{14} 5d^{10} 6s^1$
Zinc	$[\text{Ar}]3d^{10} 4s^2$	Cadmium	$[\text{Kr}]4d^{10} 5s^2$	Mercury	$[\text{Xe}]4f^{14} 5d^{10} 6s^2$

Coordination chemistry

Coordination compounds, as the term is usually used in inorganic chemistry, include compounds composed of a metal atom or ion and one or more **ligands** (atoms, ions, or molecules) that formally donate electrons to the metal. This definition includes compounds with metal-carbon bonds, called **organometallic compounds**.

The name coordination compound comes from the coordinate covalent bond, Such bonds are often represented by arrows that point from the electron pair donor (Lewis base) to the acceptor (Lewis acid).



Most *d*-transition metal ions have vacant *d* orbitals that can accept shares in electron pairs. Many act as Lewis acids by forming coordinate covalent bonds in **coordination compounds (coordination complexes, or complex ions)**. Complexes of transition metal ions or molecules include **cationic complexes** (e.g., $[\text{Cr}(\text{OH}_2)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ag}(\text{NH}_3)_2]^+$), **anionic complexes** (e.g., $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{MnCl}_5]^{3-}$), and **neutral complexes** (e.g., $[\text{Fe}(\text{CO})_5]$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$). Complexes may contain all of the same type of ligand, in which case they are termed **homoleptic** such as $[\text{Co}(\text{NH}_3)_6]^{3+}$, or they may contain a variety of ligand types, whereby they are described as **heteroleptic** such as $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

History of bonding in TM complexes

Problem occurs because in a compound with formula $\text{CoCl}_3 \cdot 6\text{NH}_3$ and looking at advances in organic bonding theory only three other atoms should be attached to

Co - compare to 'normal' salts such as FeCl_3

Co was expected to have a 'valence' of three

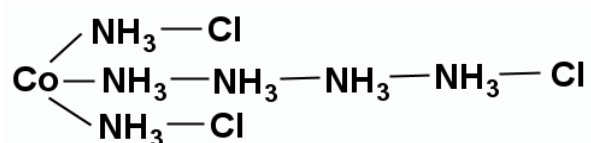
If the chlorides are assigned this role then what happens to six NH_3 ?

From observation of the following reactions

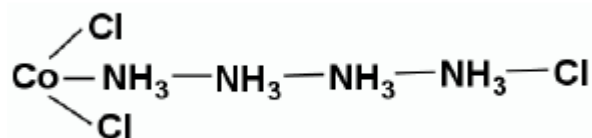
Colour	Formula			Product	Electrolyte
Yellow	$\text{CoCl}_3 \cdot 6\text{NH}_3$	+ excess Ag^+	—	3 AgCl	3 : 1
Purple	$\text{CoCl}_3 \cdot 5\text{NH}_3$	+ excess Ag^+	—	2 AgCl	2 : 1
Green	$\text{CoCl}_3 \cdot 4\text{NH}_3$	+ excess Ag^+	—	AgCl	1 : 1

Chain Theory

One theory, proposed first by C. W. Blomstrand (1826-1894) and developed further by S. M. Jorgensen (~1837-1914), was that the nitrogens could form chains much like those of carbon (and thus could have a valence of 5) and that chloride ions attached directly to cobalt were bonded more strongly than those bonded to nitrogen. e.g. $\text{CoCl}_3 \cdot 6\text{NH}_3$ with three available chlorides



e.g. $\text{CoCl}_3 \cdot 4\text{NH}_3$



Werner's coordination theory

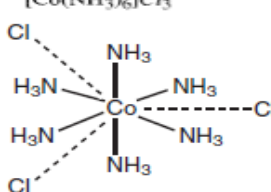
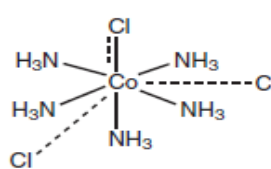
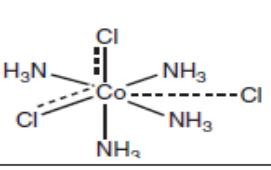
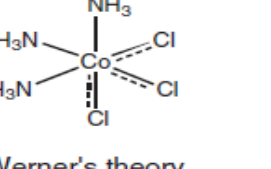
Alfred werner (1866-1919) suggested all six ammonias coordinate to Co in octahedral fashion and allowed for 'looser' bonding of some chlorides .

$\text{CoCl}_3 \cdot 6\text{NH}_3$ actually $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ actually $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$

Werner defined valency for the metal

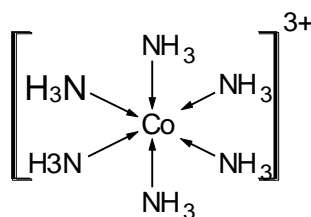
- Primary valency - Satisfied by negative ions (Cl) - we call this oxidation state
- Secondary valency - Satisfied by negative ions or neutral molecules (or some combination) - we call this coordination number.

The series of compounds in Table (below) illustrates how both the chain theory and Werner's coordination theory predict the number of ions to be formed by a series of cobalt complexes. Blomstrand's theory allowed dissociation of chlorides attached to ammonia but not of chlorides attached directly to cobalt. Werner's theory also included two kinds of chlorides. The number of chlorides attached to the cobalt (and therefore unavailable as ions) plus the number of ammonia molecules totaled six. The other chlorides were considered less firmly bound and could therefore form ions in solution.

Werner Formula (Modern Form)	of Ions Predicted	Blomstrand Chain Formula	of Ions Predicted
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ 	4	$\text{Co} \begin{array}{l} \text{NH}_3-\text{Cl} \\ \text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \text{NH}_3-\text{Cl} \end{array}$	4
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 	3	$\text{Co} \begin{array}{l} \text{NH}_3-\text{Cl} \\ \text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \text{Cl} \end{array}$	3
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ 	2	$\text{Co} \begin{array}{l} \text{Cl} \\ \text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \text{Cl} \end{array}$	2
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ 	0	$\text{Co} \begin{array}{l} \text{Cl} \\ \text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \text{Cl} \end{array}$	2
Werner's theory (non-electrolyte)			

Sidgwick's electronic concept of coordination bond

In 1916 Lewis introduced a concept of two-electron bond between two atoms in a molecule. According to this concept a covalent bond between two atoms of a molecule is formed by the sharing of an electron pair. Sidgwick (1927) extended this Lewis concept of covalent bond and introduced a new concept of coordinate bond which is also sometimes called polar or dative bond. According to this Sidgwick concept the ligand donates the electron pair to the central metal atom ion and thus forms a coordinate bond, $M \leftarrow L$, which indicates that the ligand, L (donor) has donated an electron pair to the metal ion, M (acceptor). This concept is based on the fact that all the ligands contain at least one lone pair of electrons. Thus on the basis of Sidgwick's concept, the structure of the complex ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, can be shown as given below:



Coordination bond formed is not very different from a covalent bond. The only difference lies in the mode of its formation.

Limitation of Sidgwick's concept of coordination bond

The donation of one electron pair by each of the ligands to the central metal ion to form, $M \leftarrow L$ coordinate bond in complexes accumulates negative charge on the central metal ion which is most unlikely. For example in $[\text{Co}(\text{NH}_3)_6]^{3+}$, six NH_3 molecules donate half share of 12 electrons (six negative charge) to Co^{3+} ion and thus $3+$ charge on cobalt atom is reduced to -3 . Such an accumulation of negative charge on the central metal atom is unlikely. **Pauling** suggested that the accumulation of

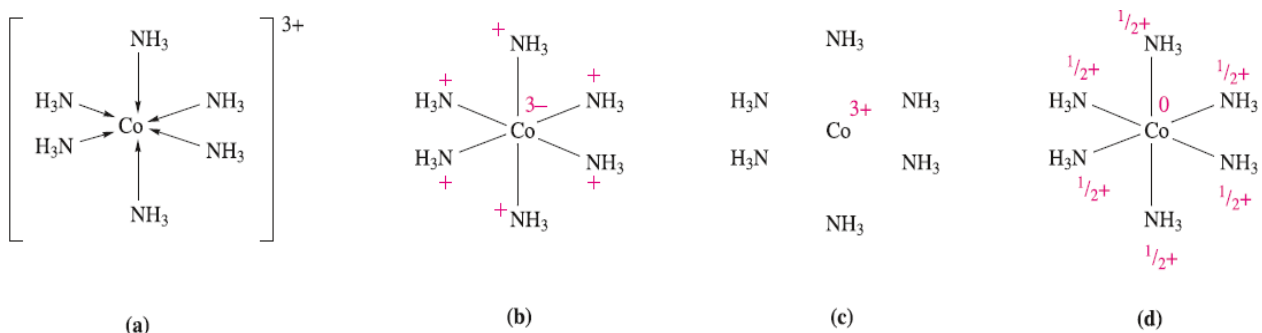
undue negative charge on the central metal ion can be prevented, if it is assumed that the metal-ligand bond has some ionic character (Electroneutrality principle)

Electroneutrality principle

Pauling's electroneutrality principle is an approximate method of estimating the charge distribution in molecules and complex ions. It states that the distribution of charge in a molecule or ion is such that the charge on any single atom is within the range +1 to -1 (ideally close to zero).

Consider the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$. Figure below (a) gives a representation of the complex which indicates that the coordinate bonds are formed by lone pair donation from the ligands to the Co(III) centre. It implies transfer of charge from ligand to metal, and (Fig. b) shows the resulting charge distribution. This is clearly unrealistic, since the cobalt(III) centre becomes more negatively charged than would be favourable given its electropositive nature. At the other extreme, we could consider the bonding in terms of a wholly ionic model (Fig. c): the 3+ charge remains localized on the cobalt ion and the six NH_3 ligands remain neutral. However, this model is also flawed. Experimental evidence shows that the $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion remains as an entity in aqueous solution, and the electrostatic interactions implied by the ionic model are unlikely to be strong enough to allow this to happen. Thus, neither of the extreme bonding models is appropriate.

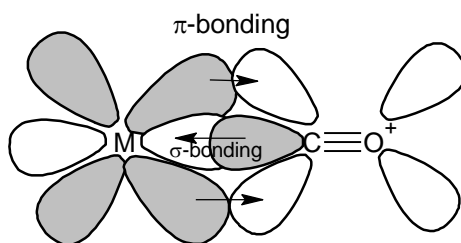
If we now apply the electroneutrality principle to $[\text{Co}(\text{NH}_3)_6]^{3+}$, then, ideally, the net charge on the metal centre should be zero. That is, the Co^{3+} ion may accept a total of *only three electrons* from the six ligands, thus giving the charge distribution shown in (Fig. d). The electroneutrality principle results in a bonding description for the $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion which is 50% ionic (or 50% covalent).



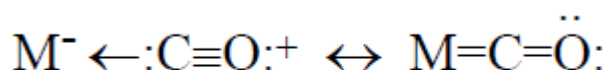
The complex cation $[\text{Co}(\text{NH}_3)_6]^{3+}$: (a) a conventional diagram showing the donation of lone pairs of electrons from ligands to metal ion; (b) the charge distribution that results from a 100% covalent model of the bonding; (c) the charge distribution that results from a 100% ionic model of the bonding; and (d) the approximate charge distribution that results from applying the electroneutrality principle.

A second way to remove electron density from a metal center is called **back-bonding**. If a metal atom has electron density in its *d*-orbitals, the electron density may be transferred to a ligand through the latter's π orbitals, e.g. CO. The central metal ion also form a π -bond with the ligand(**M** \rightarrow **L**) such as $\text{M} \rightarrow \text{CO}$.

π **bonding** is also called π **back-bonding**, with electrons from *d* orbitals of the metal donated back to the ligands(transfer of negative charge away from the metal ion).



This feeding of electron density into π^* orbitals on the ligand affects bond lengths in the complex. The M-C bond will shorten, while the C-O bond will lengthen. This can be easily seen using VB resonance structures:



Effective atomic number(EAN) rule or 18-electron rule.

On the basis of his concept of coordination bond, Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through $L \rightarrow M$ bonding, the total number of electrons on the central metal ion, including those gained from ligands in the bonding, is called the effective atomic number (EAN) of the central metal ion and in many cases this total number of electrons (*i.e.*, EAN) surrounding the coordinate metal ion is equal to the atomic number of the inert gas which follows the central metal atom in the periodic table. This is called ***Effective Atomic Number(EAN)Rule***. When the EAN is 36(Kr), 54(Xe) or 86(Rn), the rule is said to be followed.

To calculate EAN of the central metal atom in complexes

EAN of the central metal atom/ion in a given complex ion is given by:

$$\text{EAN} = (Z - x) + n \times y$$

Z=atomic number of the central metal atom, x= oxidation state of the central metal ion, n=number of ligands and y= number of electrons donated by one ligand.

Examples on EAN rule:

$$\text{Co}^{3+} = 24e$$

$$6\text{NH}_3 = 12e$$

$$\text{EAN} = 36e$$

Or $\text{EAN} = (27 - 3) + 6 \times 2 = 36e$

i.e., This metal ion obeys EAN rule



$$\text{Ag}^{1+} = 46e$$

$$2\text{NH}_3 = 4e$$

$$\text{EAN}=50e$$

This metal ion does not obey EAN rule

$$\text{Or } \text{EAN}=(47-1)+2\times 2=50e$$

$$3- \text{Ni}(\text{CO})_4 \quad \text{EAN}=(28-0)+4\times 2=36e \quad \text{This metal ion obey EAN rule}$$

$$4- [\text{ClMn}(\text{CO})_5] \quad \text{EAN}=(25-1)+5\times 2(\text{CO})+1\times 2(\text{Cl})=36e \quad \text{This metal ion obey EAN rule or}$$

$$\text{Mn}^{1+}=24e$$

$$5\text{CO}=10e$$

$$\text{Cl}=2e$$

$$\text{Total}=36e$$

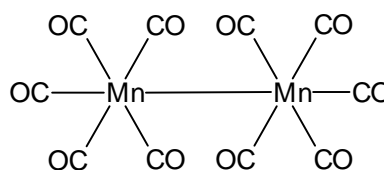
$$5- [\text{Mn}_2(\text{CO})_{10}]$$

$$\text{Mn}=25e$$

$$5\text{CO}=10e$$

$$\text{Mn-Mn}=1e$$

$$\text{EAN}=36e$$



$$6- \text{Co}_2(\text{CO})_8$$

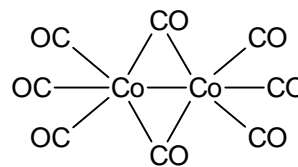
$$\text{Co}=27e$$

$$3\text{CO}=6e(\text{terminal})$$

$$2\mu_2\text{-CO}=2e(\text{bridging})$$

$$\text{Co-Co}=1e$$

$$\text{Total}=36e \quad \text{obey of EAN rule}$$



Oxidation State

Oxidation state is a frequently used concept which apportions charges and electrons within complex molecules and ions. The oxidation state of a metal is defined as the formal charge which would be placed upon that metal in a purely ionic description. For example, the metals in the gas phase ions Mn^{3+} and Cu^+ are assigned oxidation states of 3+ and 1+ respectively. These are usually denoted by placing the formal oxidation state in Roman numerals in parentheses after the element name; the ions Mn^{3+} and Cu^+ are examples of manganese(III) and copper(I).

It is usually easy to define the oxidation state for *simple* compounds of the transition metals. In the case of neutral compounds, we assign charges as if the compound were ionic. Thus, MnCl_2 is regarded as $(\text{Mn}^{2+}, 2\text{Cl}^-)$ and is correctly described as manganese (II) chloride. Similarly, WO_3 as $(\text{W}^{6+}, 3\text{O}_2^-)$ is tungsten(VI) oxide. Since ligands which bear no formal charges in an ionic formulation may be ignored, $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ is a chromium(III) compound, and $\text{Ni}(\text{OH})_2$ and NiBr_2 , are nickel(II) compounds.

Problems with the assignment of oxidation state can arise with even apparently simple compounds. Consider, for example, Fe_3O_4 . If the compound were ionic, we would have four O^{2-} ions. In order for the entire compound to be neutral, the three iron atoms must possess an overall charge of +8. The ensuing assignment of an oxidation state of +8/3 to each iron is not particularly meaningful. A compound of this type is best regarded as a mixed oxidation state oxide, $(\text{FeO} + \text{Fe}_2\text{O}_3)$ or $\text{Fe}(\text{II})\text{Fe}_2(\text{III})\text{O}_4$, in which there are both iron(II) and iron(III) centres.

Cations and anions are treated in an exactly similar manner, remembering to take the overall charge of the species into account. If only neutral ligands are present, the oxidation state of the metal ion is equal to the overall charge on the ion. Thus, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ are iron(III) and nickel(II) complexes respectively. If charged ligands are present, formal charges are assigned on the basis of an ionic description. Thus, the ion $[\text{Ni}(\text{CN})_4]^{2-}$ is treated as containing a cationic nickel centre

and four anionic cyanides. Since the four cyanides give a total charge of -4, the nickel must be assigned a charge of +2 in order for the ion to possess an overall charge of -2, and it is therefore a nickel(II) complex. Similarly, $[\text{MnO}_4]^-$ is treated as $(\text{Mn}^{7+}, 4\text{O}_2^-)$ and is a manganese(VII) compound.

It is quite possible for a metal centre to possess a zero or negative oxidation state. Thus, the species $[\text{Cr}(\text{CO})_6]$ and $[\text{Fe}(\text{CO})_4]^{2-}$ are chromium(0) and iron(-2) complexes.

Oxidation states of first row transition-metals

Available oxidation states											
Sc				0			3				
Ti				0	1	2	3	4			
V				0	1	2	3	4	5		
Cr			−1	0	1	2	3	4	5	6	
Mn	−3	−2	−1	0	1	2	3	4	5	6	7
Fe			−1	0	1	2	3	4	5	6	
Co				0	1	2	3	4	5		
Ni				0	1	2	3	4			
Cu				0	1	2	3				
Zn				0		2					

Common oxidation states are shaded. Note the pattern in maximum oxidation states. NB - in the 2nd and 3rd row, Ru and Os can attain the +VIII state as MO_4 .

Other method

Table 1-5. The oxidation states of first row transition-metals.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0 and lower			√	√	√	√	√	√	√	
+1			√	√	√	√	√	√	√	
+2		√	√	√	√	√	√	√	√	√
+3	√	√	√	√	√	√	√	√	√	
+4		√	√	√	√	√	√	√		
+5			√	√	√		√			
+6				√	√	√				
+7					√					

√ Known
√√ Commonest oxidation states

Type of ligands

1- **Monodentate** (one-toothed) - bind by donating one lone pair. The majority of ligands are either neutral or anionic. Those which coordinate to a metal ion through a single atom are described as **monodentate or unidentate**. Examples of such ligands : water (H_2O), ammonia (NH_3) and chloride (Cl^-). A more extensive listing of common ligands is found in Table 3.

2- Polydentate (many-toothed) - bond through more than one donor atom

Ligands which interact with a metal ion through two or more donor atoms are of particular importance in coordination chemistry. a **didentate (or bidentate)** ligand interacts with metals through two donor atoms, a **tridentate (or terdentate)** through three, and so on.

If two or more of the donor atoms are interacting with the same metal centre, the ligands are described as **chelating** and the complexes as **chelates**. It is generally found that there is an extra stability associated with complexes which contain chelating ligands - the so-called **chelate effect**.

In Table 4 there are list some common polydentate ligands together with the abbreviations by which they are commonly known. Once again, note that both neutral and anionic ligands are found, and that the range of donor atoms is great. A new feature of these polydentate ligands is that they may contain mixtures of different donor atoms within the same ligand. Note also that a range of **cyclic ligands** is known, each of which provides a central cavity for a metal ion. The study of such **macrocyclic or encapsulating ligands** is of considerable current interest.

Table (3)Some typical monodentate ligands and representative complexes that they form

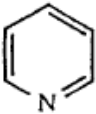
Monodentate ligands	Donor atom	Example
O^{2-}	O	$[MnO_4]^-$
Halides, F^- , Cl^- , Br^- , I^-	F, Cl, Br, I	$[NiCl_4]^{2-}$, $[CrF_6]^{3-}$
H^-	H	$[ReH_9]^{2-}$
NCS^-	N or S	$[Cr(NH_3)_5(NCS)]^{2+}$ $[Cr(NH_3)_5(NCS)]^{2+}$
NO_2^-	N or O	$[Co(NH_3)_5(NO_2)]^{2+}$ $[Co(NH_3)_5(ONO)]^{2+}$
RS^-	S	$[Fe(SPh)_4]^-$
CN^-	C	$[Fe(CN)_6]^{3-}$
HO^-	O	$[Zn(OH)_4]^{2-}$
H_2O	O	$[Mn(H_2O)_6]^{2+}$
NH_3	N	$[Co(NH_3)_6]^{3+}$
phosphines, PR_3	P	$[Pt(PMe_3)_4]$
 pyridine, py	N	$[Ni(py)_6]^{2+}$
CO	C	$[Mn(CO)_5]^-$
RCN	N	$[Ru(NH_3)_5(NCMe)]^{2+}$
$(CH_3)_2S$	S	$[Pt\{(CH_3)_2S\}_2Cl_2]$

Table (4)Some typical polydentate ligands and their complexes .

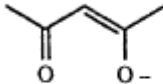
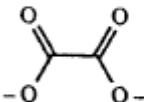
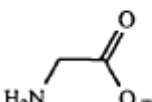
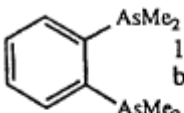
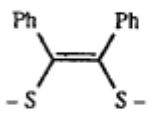
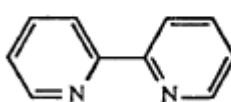
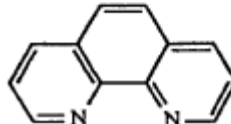
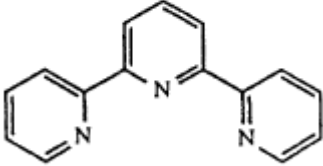
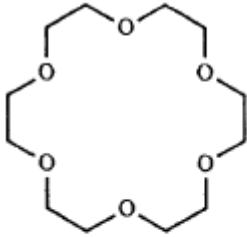
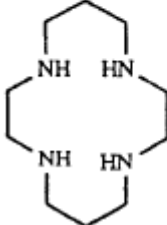
Polydentate ligands	Donor atoms	Example
<i>Didentate</i>		
 acetylacetonate, pentane-2,4-dionate, acac	O,O'	[Cr(acac) ₃]
 oxalato, ox	O,O'	[Fe(ox) ₃] ³⁻
 glycinato, gly	N,O	[Cu(gly) ₂]
H ₂ NCH ₂ CH ₂ NH ₂ 1,2-diaminoethane, ethylenediamine, en.	N,N'	[Co(en) ₃] ³⁺
Ph ₂ PCH ₂ CH ₂ PPh ₂ bis(diphenylphosphino)-ethane, dppe	P,P'	[Fe(dppe) ₂ (CO)]
 1,2-bis(dimethylarsino)- benzene, diars	As,As'	[CrCl ₄ (diars)] ⁻
 -S- -S-	S,S'	[Re(S ₂ C ₂ Ph ₂) ₃]
 2,2'-bipyridine, 2,2'-dipyridyl, bipy, bpy	N,N'	[Mn(bpy) ₃] ²⁺
 1,10-phenanthroline, phen	N,N'	[Ru(phen) ₃] ²⁺

Table (4) continued

Polydentate ligands	Donor atoms	Example
<i>Tridentate</i>		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ Diethylenetriamine, 1,4,7-triazaheptane, bis(2-aminoethyl)amine, dien.	N,N',N''	$[\text{Co}(\text{dien})_2]^{3+}$
 2,2':6,2''-terpyridine, terpyridyl, tpy, terpy	N,N',N''	$[\text{Cr}(\text{tpy})_2]^{3+}$
<i>Macrocyclic</i>		
 18-crown-6	O ₆	$[\text{K}(\text{18-crown-6})]^+$
 1,4,8,11-tetrazacyclo- tetradecane, cyclam	N,N',N'',N'''	$[\text{Ni}(\text{cyclam})]^{2+}$

Nomenclature

Organic (and some inorganic) ligands are frequently named with older trivial names rather than with IUPAC (International Union of Pure and Applied Chemistry) names. The IUPAC names are more correct, but trivial names and abbreviations are still commonly used. Tables 5, 6, and 7 list some of the common ligands.

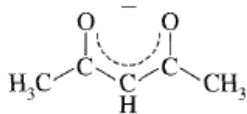
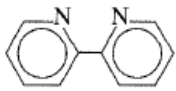
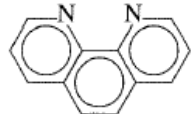
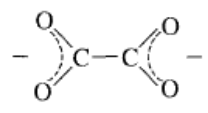
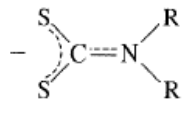
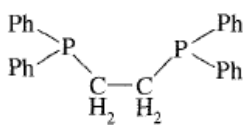
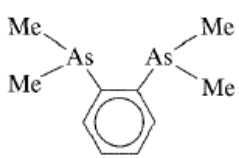
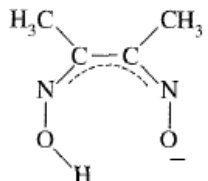
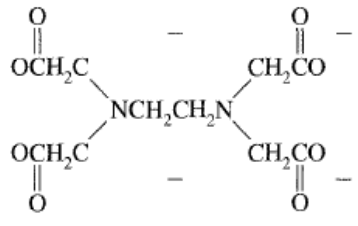
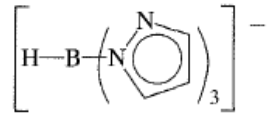
Table (5) common monodentate ligands

<i>Common Name</i>	<i>IUPAC Name</i>	<i>Formula</i>
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
azido	azido	N_3^-
cyano	cyano	CN^-
thiocyano	thiocyanato-S (S-bonded)	SCN^-
isothiocyano	thiocyanato-N (N-bonded)	NCS^-
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito-N (N-bonded)	NO_2^-
nitrito	nitrito-O (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine	py
ammine	ammine	NH_3
methylamine	methylamine	$MeNH_2$
amido	amido	NH_2^-

Table (6) common chelating ligands

<i>Chelating Points</i>	<i>Common Name</i>	<i>IUPAC Name</i>	<i>Abbreviation</i>	<i>Formula</i>
monodentate	ammine, methylamine	ammine, methylamine		NH_3, CH_3NH_2
bidentate	ethylenediamine	1,2-ethanediamine	en	$NH_2CH_2CH_2NH_2$
tridentate	diethylenetriamine	2,2'-diaminodiethylamine or 1,4,7-triazaheptane	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
tetradentate	triethylenetetraamine	1,4,7,10-tetraazadecane	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	β, β', β'' -triaminotriethylamine	β, β', β'' -tris(2-aminoethyl)amine	tren	$ \begin{array}{c} NH_2CH_2CH_2NCH_2CH_2NH_2 \\ \\ CH_2CH_2NH_2 \end{array} $
pentadentate	tetraethylenepentamine	1,4,7,10,13-pentaaazatridecane		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyl (dinitrilo) tetraacetate	EDTA	$ \begin{array}{c} ^-OOCCH_2CH_2 \quad \quad \quad CH_2CH_2OO^- \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ \quad \quad \quad NCH_2CH_2N \\ \diagup \quad \quad \quad \diagdown \\ ^-OOCCH_2CH_2 \quad \quad \quad CH_2CH_2OO^- \end{array} $

Table (7) common multidentate ligands (chelating) ligands

Common Name	IUPAC Name	Abbreviation	Formula and Structure
acetylacetonato	2,4-pentanediono	acac	$\text{CH}_3\text{COCHCOCH}_3^-$ 
2,2'-bipyridine	2,2'-bipyridyl	bipy	$\text{C}_{10}\text{H}_8\text{N}_2$ 
1,10-phenanthroline phenanthroline	1,10-diaminophenanthrene	phen, o-phen	$\text{C}_{12}\text{H}_8\text{N}_2$ 
oxalato	oxalato	ox	$\text{C}_2\text{O}_4^{2-}$ 
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	S_2CNR_2^- 
1,2-bis (diphenylphosphino)ethane	1,2-ethanediylbis (diphenylphosphane)	dppe	$\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ 
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsane)	diars	$\text{C}_6\text{H}_4(\text{As}(\text{CH}_3)_2)_2$ 
dimethylglyoximato	butanediene dioxime	DMG	$\text{HONCC}(\text{CH}_3)\text{C}(\text{CH}_3)\text{NO}^-$ 
ethylenediaminetetraacetato	1,2-ethanediyl (dinitrilo)tetraacetato	EDTA	$(^-\text{OOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$ 
pyrazolylborato	hydrotris-(pyrazo-1-yl)borato		 

Nomenclature rules

1. The positive ion (cation) comes first, followed by the negative ion (anion). This is also the common order for simple salts.

Examples: diamminesilver(I) chloride, $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
potassium hexacyanoferrate(III), $\text{K}_3[\text{Fe}(\text{CN})_6]$

2. The inner coordination sphere is enclosed in square brackets in the formula. Within the coordination sphere, the ligands are named before the metal, but in formulas the metal ion is written first.

Examples: tetraamminecopper(II) sulfate, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
hexaamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

3. The number of ligands of one kind is given by the following prefixes. If the ligand name includes these prefixes or is complicated, it is set off in parentheses and the second set of prefixes is used.

di	bis
tri	tris
tetra	tetrakis
penta	pentakis
hexa	hexakis
hepta	heptakis
octa	octakis
nona	nonakis
deca	decakis

Examples: dichlorobis(ethylenediamine)cobalt(III), $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$
tris(bipyridine)iron(II), $[\text{Fe}(\text{C}_5\text{H}_4\text{N}-\text{C}_5\text{H}_4\text{N})_3]^{+2}$

4- Ligands are named in alphabetical order (according to the name of the ligand, not

the prefix), although exceptions to this rule are common. An earlier rule gave anionic ligands first, then neutral ligands, each listed alphabetically.

Examples: tetraamminedichlorocobalt(III), $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 (tetraammine is alphabetized by *a* and dichloro by *c*, not by the prefixes)
 amminebromochloromethylamineplatinum(II), $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{CH}_3\text{NH}_2)]$

5. Anionic ligands are given an *o* suffix. Neutral ligands retain their usual name. Coordinated water is called *aqua* and coordinated ammonia is called *ammine*.

Examples: chloro, Cl^- methylamine, CH_3NH_2
 bromo, Br^- ammine, NH_3 (the double m distinguishes NH_3
 sulfato, $\text{SO}_4^{=}$ from alkyl amines)
 aqua, H_2O

6. Two systems exist for designating charge or oxidation number:

a. The Stock system puts the calculated oxidation number of the metal ion as a Roman numeral in parentheses after the name of the metal. This is the more common convention, although there are cases in which it is difficult to assign oxidation numbers.

b. The Ewing-Bassett system puts the charge on the coordination sphere in parentheses after the name of the metal.

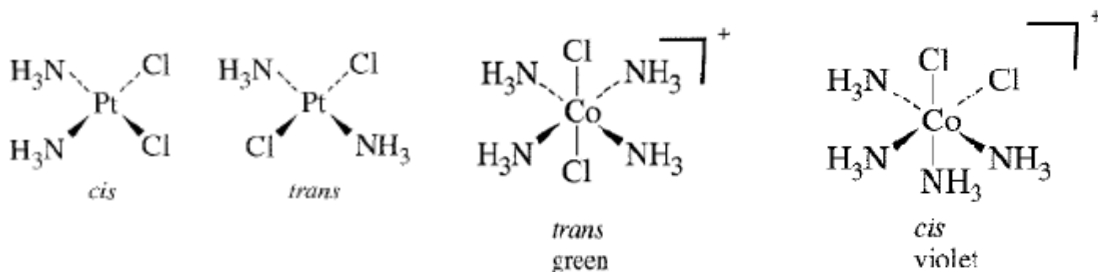
In either case, if the charge is negative, the suffix *-ate* is added to the name of the coordination sphere.

Examples: tetraammineplatinum(II) or tetraammineplatinum(2+), $[\text{Pt}(\text{NH}_3)_4]^{+2}$
 tetrachloroplatinate(II) or tetrachloroplatinate(2-), $[\text{PtCl}_4]^{2-}$
 hexachloroplatinate(IV) or hexachloroplatinate(2-), $[\text{PtCl}_6]^{2-}$

7. The prefixes *cis*- and *trans*- designate adjacent and opposite geometric locations.

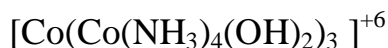
Examples: *cis*- and *trans*-diamminedichloroplatinum(II), $[\text{PtCl}_2(\text{NH}_3)_2]$

cis- and *trans*-tetraamminedichlorocobalt(III), $[\text{CoCl}_2(\text{NH}_3)_4]^+$

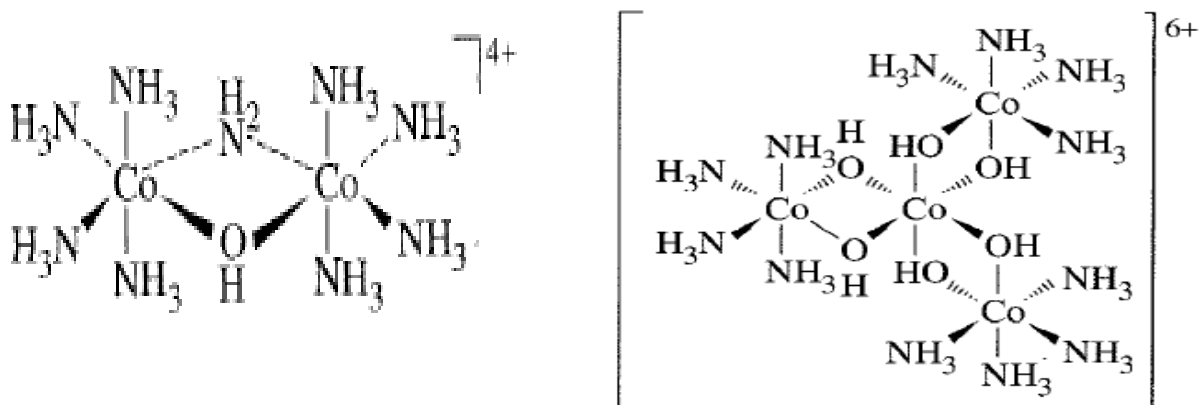


8. Bridging ligands between two metal ions have the prefix μ -

Examples: tris(tetraammine- μ -dihydroxocobalt)cobalt(6+),



μ -amido- μ -hydroxobis(tetramminecobalt)(4+),



9. When the complex is negatively charged, the names for the following metals are derived from the sources of their symbols, rather than from their English names:

iron (Fe) ferrate

lead (Pb) plumbate

silver (Ag) argentate

tin(Sn) stannate

gold(Au) aurate

Examples: tetrachloroferrate(III) or tetrachloroferrate(1-), $[\text{FeCl}_4]^-$

dicyanoaurate(I) or dicyanoaurate(1-), $[\text{Au}(\text{CN})_2]^-$

Isomerism In Coordination Compounds

Isomers are different compounds that have the same molecular formula; they have the same number and kinds of atoms arranged differently. The term *isomers* comes from the Greek word meaning “equal weights.” *Because their structures are different, isomers have different physical and chemical properties.*

There are two major classes of isomers: **structural (constitutional) isomers** and **stereoisomers**. For coordination compounds, each can be further subdivided as follows.

Structural Isomers

1. ionization isomers
2. hydrate isomers
3. coordination isomers
4. linkage isomers

Stereoisomers

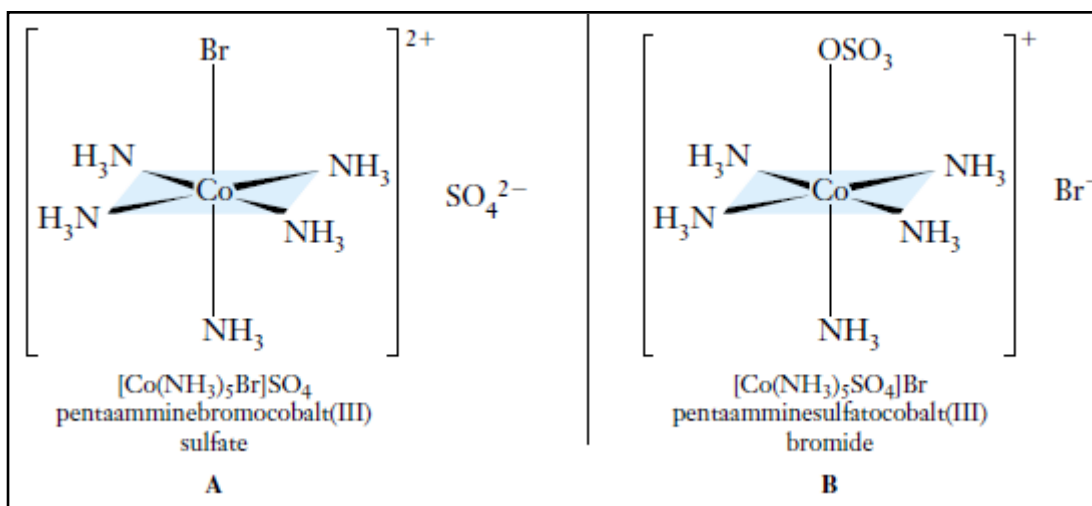
1. geometric (positional) isomers
2. optical isomers

Differences between **structural isomers** involve either more than one coordination sphere or different donor atoms on the same ligand. They contain *different atom-to-atom bonding sequences*. Simple stereoisomers of coordination compounds involve only one coordination sphere and the same ligands and donor atoms. Before considering stereoisomers, we will describe the four types of structural isomers.

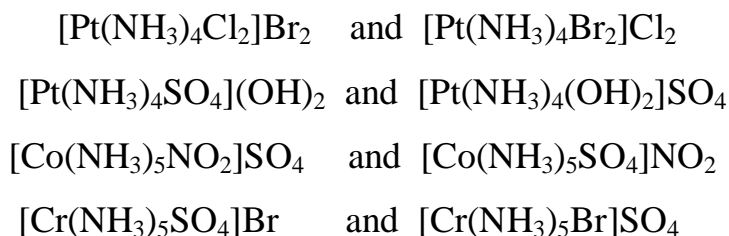
Structural (Constitutional) Isomers

1- Ionization (Ion–Ion Exchange) Isomers

Non-coordinated and coordinated ionic ligands are exchanged. For example, red-violet $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and red $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are ionization isomers.



In structure A the SO_4^{2-} ion is free and is not bound to the cobalt(III) ion. A solution of A reacts readily with a solution of barium, BaCl_2 , to precipitate BaSO_4 , but does not react readily with AgNO_3 . In structure B the SO_4^{2-} ion is bound to the cobalt(III) ion and so it does not react with BaCl_2 in aqueous solution. The Br^- ion is free, however, and a solution of B reacts with AgNO_3 to precipitate AgBr . *Equimolar* solutions of A and B also have different electrical conductivities. The sulfate solution, A, conducts electric current better because its ions have 2+ and 2- charges rather than 1+ and 1-. Other examples of this type of isomerism include:



2- Hydrate Isomers

In some crystalline complexes, water can be *inside* and *outside* the coordination sphere. The standard example is $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$, which can have three distinctly different crystalline compounds, now known as $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (blue-green), and $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green). A fourth isomer, $[\text{CrCl}_3(\text{H}_2\text{O})_3]$ (yellow-green) also occurs at high concentrations of HCl . The three cationic isomers can be separated by cation ion exchange from

commercial $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, in which the major component is $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ in the *trans* configuration.

3- Coordination isomerism

Examples of a complete series of coordination isomers require at least two metal ions and sometimes more. The total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. This is best described by example.

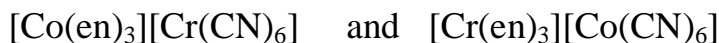
For the empirical formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, there are three possibilities:



$[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$ (This compound apparently has not been reported, but the individual ions are known.)

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ (Magnus' green salt, the first platinum ammine, was discovered in 1828.)

Other examples are possible with different metal ions and with different oxidation states:



4- Linkage (ambidentate) isomerism

Some ligands can bond to the metal through different atoms. The most common early examples were thiocyanate, SCN^- , and nitrite, NO_2^- . Class (a) metal ions (hard acids) tend to bond to the nitrogen of thiocyanate and class (b) metal ions (soft acids) bond through the sulfur, but the differences are small and the solvent used influences the bonding.

Compounds of rhodium and iridium with the general formula $[\text{M}(\text{PPh}_3)_2(\text{CO})(\text{NCS})_2]$ form M - S bonds in solvents of large dielectric constant and M-N bonds in solvents of low dielectric constant, as shown in Figure (1)(a). There are also compounds with both M-SCN (thiocyanato) and M-NCS (isothiocyanato)

[isothiocyanatothiocyanato(1-**diphenylphosphino-3-dimethylaminopropane**) palladium(II); Figure (1)(b)].

M-NCS combinations are linear and M-SCN combinations are bent at the S atom in all thiocyanate complexes. This bend means that the MSCN isomer has a larger steric effect, particularly if it can rotate about the M-S bond.

The nitrite isomers of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{+2}$ was studied by Jorgensen and Werner, who observed that there were two compounds of the same chemical formula but of different colors. A red form of low stability converted readily to a yellow form. The red form was thought to be the M-ONO nitrito isomer and the yellow form the M-NO₂ nitro isomer, based on comparison with compounds of similar color. In a more recent example, the stable O-N-Ru form of $[\text{Ru}(\text{NO})_5(\text{OH})]^{-2}$ is in equilibrium with the metastable N-O -Ru form .

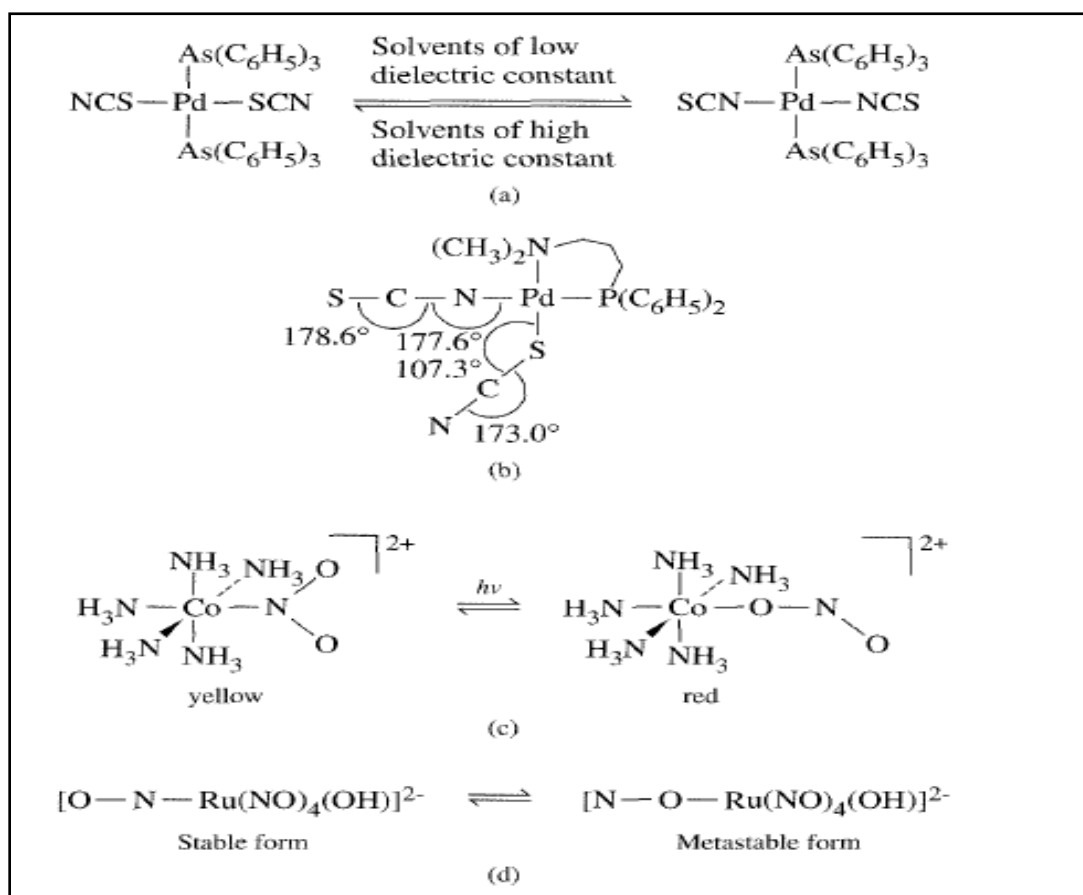


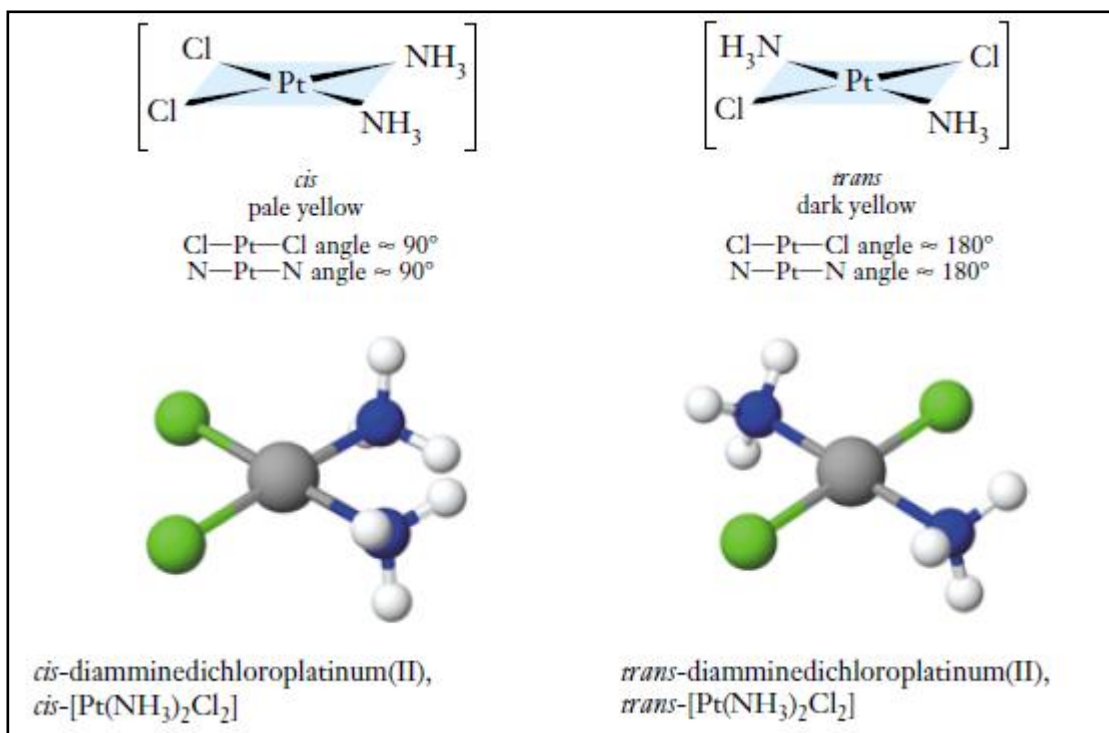
Figure shows Linkage (Ambidentate) isomers

STEREISOMERS

Compounds that contain the same atoms and the same atom-to-atom bonding sequences, but that differ only in the spatial arrangements of the atoms relative to the central atom, are **stereoisomers**. Complexes with only *simple* ligands can exist as stereoisomers *only if* they have coordination number 4 or greater. The most common coordination numbers among coordination complexes are 4 and 6, and so they will be used to illustrate stereoisomerism.

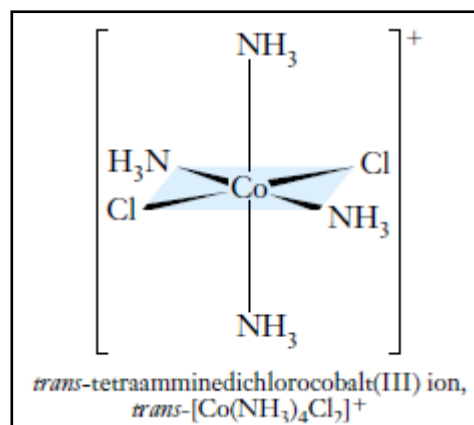
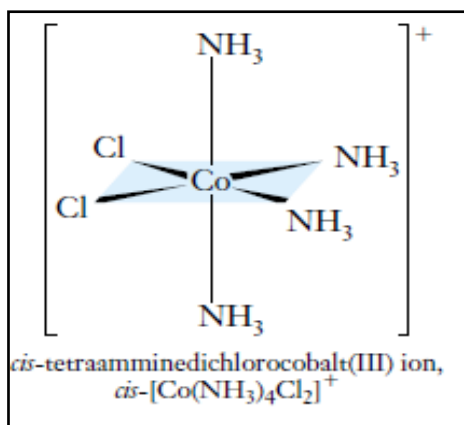
1- Geometric (*cis-trans*) Isomers

In **geometric isomers**, or ***cis-trans* isomers**, of *coordination compounds*, the same ligands are arranged in different orders within the coordination sphere. Geometric isomerism occurs when atoms or groups of atoms can be arranged on two sides of a rigid structure. *Cis* means “adjacent to” and *trans* means “on the opposite side of.” *Cis*- and *trans*-diamminedichloroplatinum(II) are shown below.

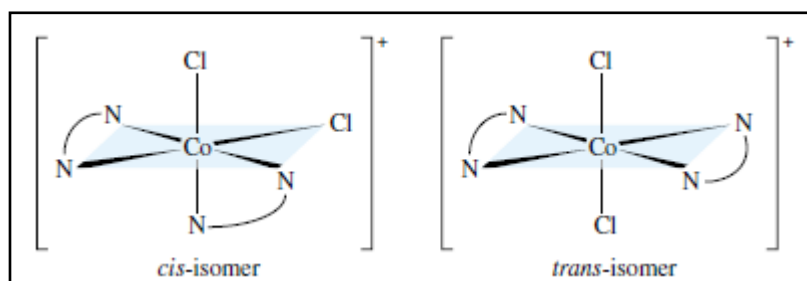


In the *cis* isomer, the chloro groups are closer to each other (on the same side of the square) than they are in the *trans* isomer. The ammine groups are also closer together in the *cis* complex.

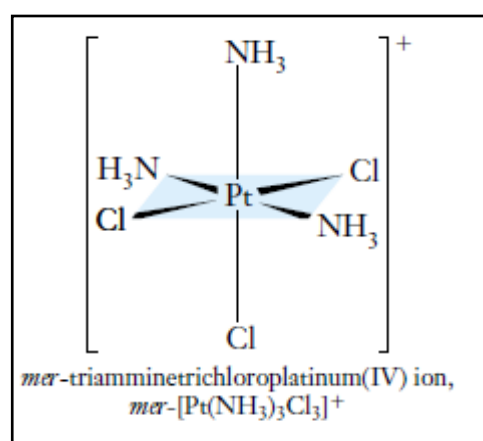
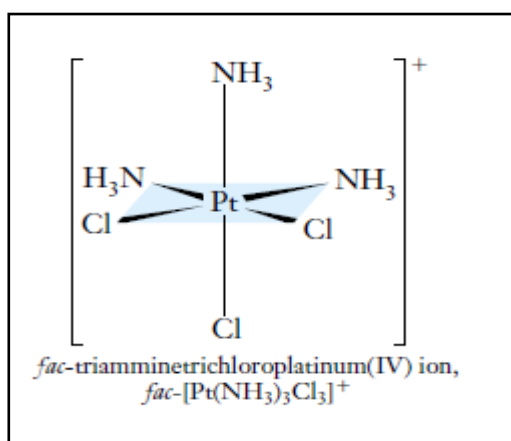
Geometric isomerism is possible for octahedral complexes. For example, complexes of the type MA_4B_2 can exist in two isomeric forms. Consider as an example the complex ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The two like ligands (Cl^-) can be either *cis* or *trans* to each other. These two complexes are different colors: solutions and salts of the *cis* isomer are violet and those of the *trans* isomer are green.



Complexes type $[\text{M}(\text{A}\cap\text{A})_2\text{B}_2]$ involving bidentate ligands $\text{A}\cap\text{A}$, such as ethylenediamine, can also exhibit this kind of isomerism, as shown below.



Octahedral complexes with the general formula MA_3B_3 can exhibit another type of geometric isomerism, called ***mer-fac isomerism***. This can be illustrated with the complex ion $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$. In one isomer the three similar ligands (e.g., the Cl^- ligands) are mutually cis to each other; this is called the ***fac isomer*** (for *facial*). In the other isomer, two of the same ligands (e.g., the Cl^- ligands) are mutually trans to each other; this is called the ***mer isomer***.



Complexes of the type $[\text{MA}_2\text{B}_2\text{C}_2]$ can exist in several isomeric forms. Consider as an example $[\text{Cr}(\text{OH}_2)_2(\text{NH}_3)_2\text{Br}_2]^+$. First, the members of all three pairs of like ligands may be either *trans* to each other (A) or *cis* to each other (B).

