COORDINATION COMPOUNDS

DEFINITIONS OF SOME IMPORTANT TERMS PERTAINING TO COORDINATION COMPOUNDS

✤ CENTRAL METAL ATOM / ION

The central ion serves as a receptor (Lewis's acid) and is required to accept electron pairs donated by the donor atom of the ligand, necessitating the presence of vacant orbitals. This clarifies why transition metals with available d-orbitals readily create coordination compounds.

For instance, in the complexes $[Ni (NH_3)_6]^{2+}$ and $[Fe (CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} serve as the central metal ions, respectively.

LIGANDS

Entities that are directly connected to the central metal atom/ion in a complex ion are referred to as ligands. These ligands are bound to the central metal atom/ion through a coordinate or dative bond, and free ligands typically possess at least one lone pair.

Therefore, the ligands function as Lewis bases, while the central metal ions/atoms act as Lewis's acids. Ligands can be classified into different types based on the number of donor atoms they contain:

(i) Mono / Unidentate Ligands

They have one donor atom, i.e., they can donate only one electron pair to the central metal atom /ion eg., F⁻, Cl⁻, Br⁻, H₂O, NH₃, CN⁻, NO₂⁻, OH⁻, CO etc.

(ii) Bidentate Ligands

Ligands which have two donor atoms and have the ability to link with the central metal atom /ion at two positions are called bidentate ligands e.g.



(iii) Tridentate Ligands

Ligands having three donor atoms are called tridentate ligands.

Examples are:



(iv) Tetradentate Ligands

These ligands possess four donor atoms.

Examples are:



(v) Pentadentate Ligands

They have five donor atoms.

For example, ethylenediamine triacetate ion.



(vi) Hexadentate Ligands

They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



(vii) Ambidentate ligands:

Certain ligands possess multiple donor atoms, yet when they form complexes, only one donor atom becomes attached to the metal/ion. These ligands are referred to as ambidentate ligands.

Examples of such ligands include:



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- (viii) Ligands with more than two donor atoms are termed polydentate or multidentate ligands. Multidentate ligands, known as chelating ligands, give rise to the creation of a stable cyclic ring, which leads to the formation of complexes referred to as chelates. Typically, chelating ligands are organic compounds.
- (ix) Chelate ligand:

A chelate ligand is a di- or polydentate ligand that employs two or more donor atoms to bind to a single metal ion, creating a ring structure. The resulting complex is termed a chelate complex, and the process of forming such chelates is known as chelation. The number of these ligating groups on the ligand is referred to as its denticity. Chelate rings may consist of various numbers of atoms, with the most common ones containing five or six atoms, including the metal ion. Smaller rings exhibit smaller angles and distances, leading to strain, while larger rings often lead to crowding both within the ring and between adjacent ligands. Some ligands have the ability to form multiple rings; for example, ethylene diamine tetraacetate (EDTA) can form five rings by utilizing its four carboxylate groups and two amine nitrogen's, as depicted in the structures.



The chelate complexes exhibit higher stability when compared to complexes containing unidentate ligands with similar characteristics. This enhanced stability of chelate complexes, in contrast to regular complexes, is referred to as the chelate effect.

For example,

$$Ni^{2+}(aq) + 6 NH_{3}(aq) \rightleftharpoons [Ni(NH_{3})_{6}]^{2+}(aq) K_{formation} = 10^{8}$$

 $Ni^{2+}(aq) + 3 NH_{2}CH_{2}CH_{2}NH_{2}(aq) \rightleftharpoons [Ni(en)_{3}]^{2+}(aq)K_{formation} = 10^{18}$

The five and six membered rings are more stable.

Denticity and Chelation: Common Monodentate Ligands

Common Name	IUPAC Name	Formula
methyl isocyanide	methylisocyanide	CH ₃ NC
triphenyl phosphine	triphenyl phosphine	PPh ₃
	/triphenyl phosphene	
pyridine	pyridine	C5H5N(PY)
ammonia	ammine	NH ₃
methyl amine	methylamine	MeNH ₂
water	aqua or aquo	H ₂ O
carbonyl	carbonyl	СО
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO
Fluoro	Fluoro or fluorido*	F ⁻
Chloro	chloro or chlorido*	Cl ⁻
bromo	bromo or bromido*	Br ⁻
iodo	iodo or iodido*	Ι-
cyano	cyanido or cyanido-C*	Cn ⁻
	(C-bonded)	
Isocyano	isocyanido or cyanido-N*	NC ⁻
	(N-bonded)	
thio cyano	thiocyanato-S(S-bonded)	SCN ⁻
isothiocyano	thiocyanato-N(N-bonded)	NCS ⁻
cyanate (cyanate)	cyanato-0 (0-bonded)	OCN ⁻
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO-
hydroxo	hydroxo or hydroxide*	OH-
nitro	nitrito–N (N–bonded)	NO ₂
nitrito	nitrito-0 (0-bonded)	ONO ⁻
nitrate	nitrato	NO ₃
amido	amido	NH ₂
imido	imido	NH ²⁻
nitride	nitrido	N ³⁻
azido	azido	NO ₃
hydride	hydrido	H-
oxide	oxido	02-
peroxide	peroxido	02-
superoxide	superoxido	0_2
acetate	acetato	CH ₃ COO ⁻

Chemistry

sulphate	sulphato	SO ₄ ²⁻	
thiosulphate	thiosulphato	$S_2 O_3^{2-}$	
sulphite	sulphito	SO ₃ ²⁻	
hydrogen sulphite	hydrogensulphito	HSO ₃	
sulphide	sulphido or thio	S ²⁻	
hydrogen sulphide	hydrogensulphido or	HS ⁻	
	mercapto		
thionitrito	thionitrito	(NOS) ⁻	
nitrosylium	nitrosylium or nitrosonium	NO ⁺	
nitronium	nitronium	SNO ⁺ ₂	
*The 2004 IUPAC draft recommends that anionic ligands will end with-ido.			

Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbre- viation	Formula
bidentate	propane diamine	1,2-propane- diamine	pn	NH2-CH-CH2-NH2 I CH3
Tri- dentate	Diethylene- triamine	[N-(2- aminoethyl)-1 2-ethane-diamine or diethylene- triamine	dien	NH2CH2CH2NHCH2 CH2NH2
Tetra- dentate	Triethylene- tetramine	[N, N'-bis-(2- aminoethyl)-1, 2-ethane-diamine or triethylene- tetraamine	trien	NH2CH2CH2NHCH2 CH2NHCH2CH2NH2
	Triamino- triethylamine	-tris(2-aminoe- thyl) amine.	tren	NH2CH2CH2NCH2CH2 NH2 CH2CH2NH2
Penta- dentate	tetraethyl- lenepen- taamine	1,4,7,10 pentaaza- tridecane or tetraethyl- lenepentaamine		NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ CH ₂ NHCH ₂ 2CH ₂ NH ₂
Hexa- dentate	Ethy- lenediamine- tetraacetate	1,2–ethanediol (dinitrilo) tetraacetate or ethylenediamine- tetraacetate	EDTA	-00CH2C CH2COO- \ / NCH2CH2N / \ -00CH2C CH2COO-

Common Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbrevi	Formula	Structure
Name		auon		
Acetylace- tonato	2,4- pentanediono or acetylaceto- nato	acac	CH ₃ COCHCOCH ₃	
2,2'- bipyridine	2,2'-bipyridyl	bipy	C ₁₀ H ₈ N ₂	$\langle \bigcirc \\ \rangle \\ \langle \bigcirc \rangle \\ \rangle \\ $
1,10- phenanthroli ne/ phenanthroli ne	1,10- diaminophena nthrene	phen, o- phen	C12H8N2	
oxalato	Oxalato	OX	C2 <i>0</i> ₄ ²⁻	
dialkyldithioc arbamato	dialkylcarbam odithioato	dtc	S2CNR ₂	S
1,2- bis(diphenyl phophine)eth ane	1,2- ethanediylbis (dipheylphos phene)	dppe	Ph2PC2H4PPh2	Ph Ph Ph Ph Ph Ph Ph Ph Ph
o- phenylenebis (dimethylarsi ne)	1,2- phenylenebis (dimethyl- larsene)	Diars	C ₆ H ₄ (AS(CH ₃) ₂) ₂	Me As Mc
dimethylglyo ximato	butanedienedi oxime or dimethylgly- oximato	DMG	HONC(CH ₃)C(CH 3)NO-	

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ethylenediam	1,2-ethanediyl	EDTA	(-00CCH2)2	= 0
inetetraaceta	(dinitrilo)tetr		NCH ₂	тоён₂с сн₂ёот
to	aacetato		CH ₂ N(CH ₂ COO-) ₂	NC-,CH,N
	or			_očH³čcH⁵ď
	ethylenediami			0 0
	netetraacetato			
Pyrazoly-	hydrotris-			$\Gamma = (N, N, T)^{-1}$
lborato	(pyrazo-1-yl)			H-B-NO
	borato			

(x) Flex dentate Ligand:

It's important to understand that not all of the donor atoms within polydentate ligands need to establish coordinate bonds with the central metal atom or ion. In other words, when a polydentate ligand exhibits varying denticity in different coordination compounds, it is termed a flex dentate ligand. It's worth noting that within a specific complex, the denticity of a given ligand remains fixed and cannot change.

For instance, EDTA has the capability to function as a hexa-, penta-, or tetra-dentate ligand.

EDTA usually acts as hexadentate ligand but in [Cr (III)(OH)(EDTA)]^{2–} and [Co (III)Br (EDTA)]^{2–} as pentadentate and in [Pd (II)H₂(EDTA)]⁰ as a tetradentate ligand.

Sulphate ion, SO_4^{2-} can also be mono or bi dentate ligand.

For example;



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Effective atomic number -EAN (Sidgwick Theory and EAN Rule):

The total number of electrons on the central metal atom/ion after receiving electron pairs from donor atoms of ligands through coordinate bonds is referred to as the Electron-Acceptance Number (E.A.N.) of the central metal atom/ion.

$$E.A.N = Z - O.S. + 2 \times C.N.$$

Sidgwick further proposed that the metal ion will continue to accept electron pairs until the combined total of electrons within the metal ion and those donated by ligands matches the electron count of the nearest noble gas. This collective count of electrons is referred to as the Effective Atomic Number (EAN) of the metal/ion.

This will become clear by taking the example of hexamine cobalt (III) ion $[Co(NH_3)_6]^{3+}$

Atomic number of cobalt = 27

In the present complex, cobalt is present in the oxidation state of +3.

:. E.A.N. of $Co^{3+} = Z - O.S. + 2 \times C.N.$ = 27 - 3 + 2 × 6 = 36

In the given example, as the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be considered stable. Although the EAN rule, which asserts that complexes are stable when their EAN matches the atomic number of the next noble gas, applies to many metal carbonyl complexes, there are several instances where the EAN rule is not followed.