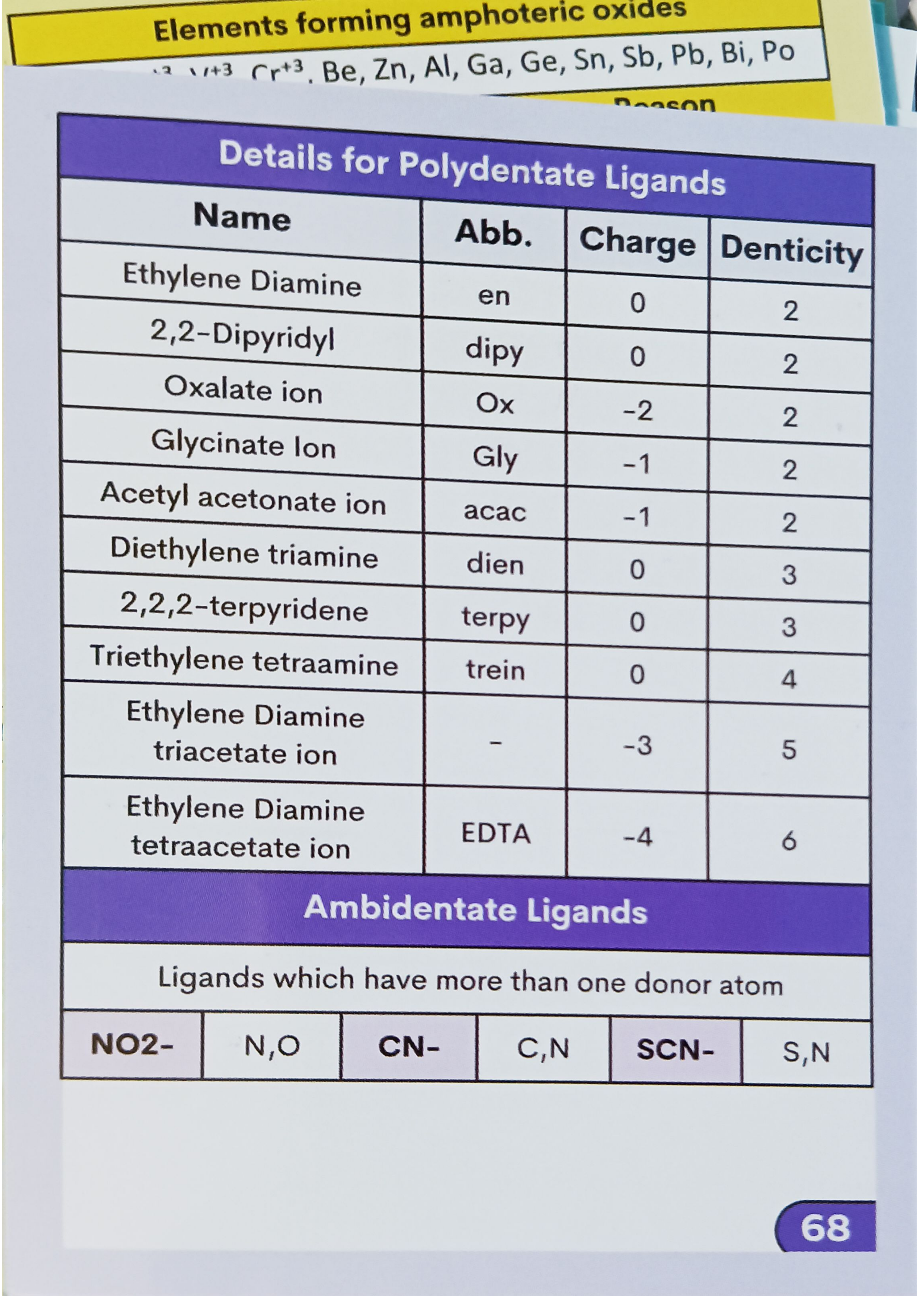
COORDINATION COMPOUNDS

Addition Compounds

- Compounds formed by joining together stiochiometric amounts of two or more stable compounds
- e.g. $KCl. MgCl_2.6H_2O$ (Carnalite).
  $K_2SO_4.Al_2(SO_4)_3.24\ H_2O$ (Potash Alum)

Double Salt	Complex Compound
Exist only in solid state (Dissociates in Aqueous)	Exist in both solid and aqueous state
Two Salts are equimolar	Two Salts may/may not be equimolar
Ionic compounds with no coordinate bond	Complex always contains coordinate bond
Metal shows normal valency	Metal satisfies both primary and secondary valency
Properties same as constituent compounds	Properties are different then constituent compounds
Lose identity in solution	Do not lose their identity
Potash alum	**$K_4[Fe(CN)_6]$**



Elements forming amphoteric oxides

Cr^{+3}, Be, Zn, Al, Ga, Ge, Sn, Sb, Pb, Bi, Po

Details for Polydentate Ligands

Name	Abb.	Charge	Denticity
Ethylene Diamine	en	0	2
2,2-Dipyridyl	dipy	0	2
Oxalate ion	Ox	-2	2
Glycinate Ion	Gly	-1	2
Acetyl acetonate ion	acac	-1	2
Diethylene triamine	dien	0	3
2,2,2-terpyridene	terpy	0	3
Triethylene tetraamine	trein	0	4
Ethylene Diamine triacetate ion	-	-3	5
Ethylene Diamine tetraacetate ion	EDTA	-4	6

Ambidentate Ligands

Ligands which have more than one donor atom

NO2-	N,O	**CN-**	C,N	**SCN-**	S,N

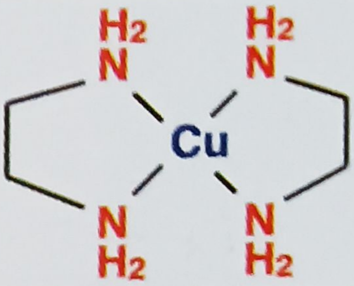
Werner's Theory

1° Valency	2° Valency
• Non Directional • Ionisable in nature • Corresponds to charge on metal	• Directional • Doesn't ionise • Corresponds to coordination No.

In $[Co(NH_3)_6]Cl_3$, 1° val. = 3 ; 2° val. = 6

Salt	Complex	ppt.	(+ : -)	Cond.
$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	3	4(3:1)	Highest
$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	2	3(2:1)	high
$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	1	2(1:1)	low
$CoCl.3NH_3$	$[Co(NH_3)_3Cl_3]$	0	Neutral	lowest

Chelation



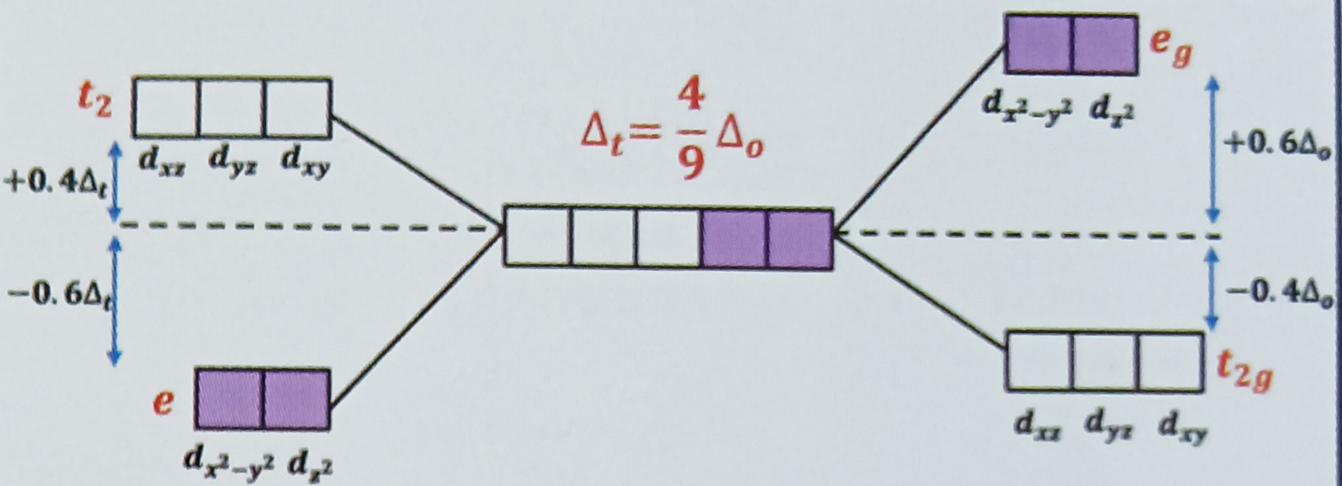
$[Cu(en)_2]^{2+}$

Forming two 5-membered rings

- Poly-dentate ligands using it's two or more donor sites to form a closed ring structure is called chelation.
- Chelating ligands form more stable complexes
- Entropy increases due to chelation
- 5 > 6 ring size stability (using saturated ligands)
- 6 > 5 ring size stability (using unsaturated ligan

VALENCE BOND THEORY

Molecule	Hyb/ Geometry	unp. e-	Dia/ Para, Mag. Moment
$[V(H_2O)_6]^{+3}$	d^2sp^3/ octa	2	Para,2.82BM
$[Cr(CN)_6]^{-3}$	d^2sp^3/ octa	3	Para,3.87BM
$[Cr(CO)_6]$	d^2sp^3/ octa	0	Dia, 0
$[Cr(CN)_6]^{-4}$	d^2sp^3/ octa	2	Para, 2.82
$[Mn(CN)_6]^{-4}$	d^2sp^3/ octa	1	Para,1.732
$[Mn(H_2O)_6]^{+2}$	sp^3d^2/octa	5	Para,5.92
$[Mn(CN)_6]^{-3}$	d^2sp^3/ octa	2	Para, 2.82
$[Fe(H_2O)_6]^{+2}$	sp^3d^2/octa	4	Para,4.89
$[Fe(CN)_6]^{4-}$	d^2sp^3/ octa	0	Dia, 0
$[Fe(H_2O)_6]^{+3}$	sp^3d^2/octa	5	Para,5.92
$[Fe(CN)_6]^{-3}$	d^2sp^3/ octa	1	Dia, 1.732
$[Co(H_2O)_6]^{+2}$	sp^3d^2/octa	3	Para,3.87
$[CoCl_4]^{-2}$	sp^3,tetra	3	Para,3.87
$[Ni(CO)_4]$	sp^3,tetra	0	Dia,0
$[NiCl_4]^{-2}$	sp^3,tetra	2	Para,2.82
$[Ni(CN)_4]^{-2}$	dsp^2,SP	0	Dia,0
$[Cu(NH3)_4]^{+2}$	dsp^2,SP	1	Para,1.7



CRYSTAL FIELD SPLITTING ENERGY

$\Delta_o > P$ = Low spin complex (Strong field Ligand)
$\Delta_o < P$ = High spin complex (Weak field Ligand)

If Δ = Splitting energy P = Pairing Energy

- **For Octahedral complexes**
CFSE = $[-0.4x + 0.6y]\Delta_o$
  - x = no. of e^- in t_2g
  - y = no. of e^- in eg
	- **For tetrahedral complexes**
	CFSE = $[-0.6x + 0.4y]\Delta_t$
	  - **x = no. of e^- in t_2**
	  - **y = no. of e^- in e**

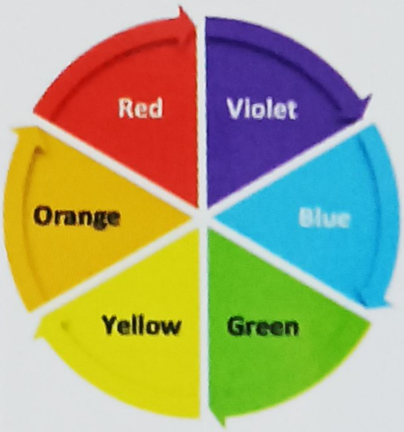
Electrochemical Series : $I^- < Br^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < EDTA^{4-} < NH_3 <$ en $< NO_2^- < CN^- < CO$

Splitting (Δ) $\propto$ Oxidation number of metal $\propto$ Field strength of ligands $\propto$ Size (3d < 4d < 5d)

1. For 3d series, +2 oxidation state, NO_2^-, CN^- and CO acts as strong field ligands (CN=6)
2. For 4d and 5d series, all ligands are strong field.
3. For CN = 4 with +3 ox. no, all ligands are strong field
4. For Co^{+3} ,O-donors behave as strong field ligan

Colour Complementary Theory ($E=hc/\lambda$)

Strong Field Ligand		Weak Field ligand	
Absorption	**Emission**	**Absorption**	**Emission**
E = high	E = low	E = Low	E = High
λ = low	λ = high	λ = high	λ = low



Intensity of colour is inversly proportional to ligand field strength

For λ absorption,

$[Ni(NO_2)_6]^{4-} < Ni(NH_3)_6]^{2+} < Ni(H_2O)_6]^{2+}$

For E Absorption,

$[Ni(NO_2)_6]^{4-} > Ni(NH_3)_6]^{2+} > Ni(H_2O)_6]^{2+}$

Remember : 1kJ = 83.7cm^{-1}

Metal Carbonyl - Synergic bonding

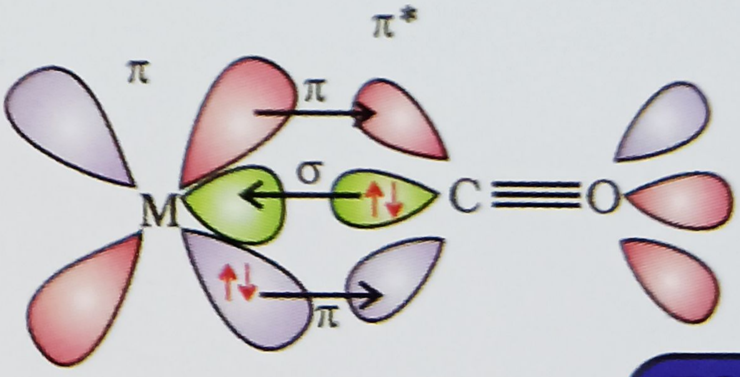
- M–C bond posses both σ & Π Character.
- σ bond → Lone pair donated from CO to vacant orbital of metal
- Π bond → e- from filled metal d orbital to anti-bonding Π^* of CO.

Frequency of bond

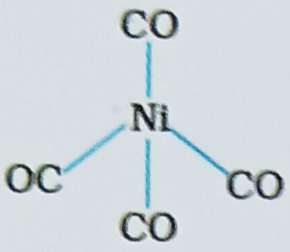
$\propto$ Bond strength

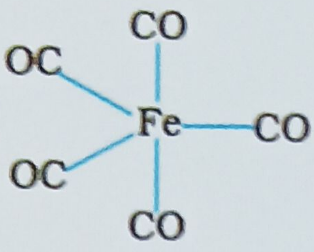
$\propto$ bond order

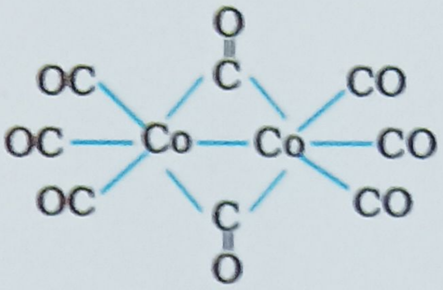
$\propto$ 1/bond length

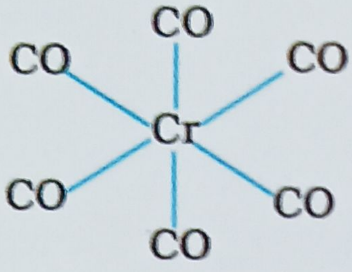


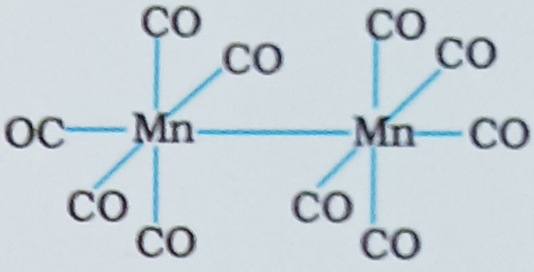
Important metal carbonyls


$Ni(CO)_4$
Tetrahedral


$Fe(CO)_5$
Trigonal bipyramidal


$[Co_2(CO)_8]$


$Cr(CO)_6$ Octahedral


$[Mn_2(CO)_{10}]$

Effective Atomic number (EAN Rule)

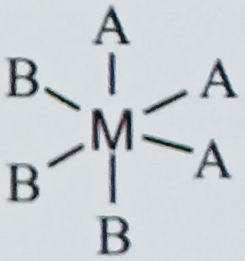
EAN (Should match inert gas) = Atomic number of Central metal – Oxidation state + 2 (coordination number).

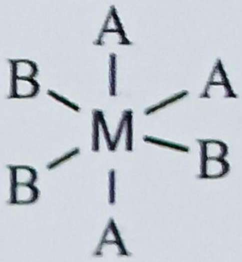
$K_4[Fe(CN)_6]$, EAN = 26-2+12 = 36 (Stable complex)

Geometrical and Optical Isomers

Cis isomers	**Trans Isomers**
Similar Ligands at 90°	Similar Ligands at 180°
Facial	**Meridional**
Three similar ligands at 90°	Two ligands at 90°, One at 180°

Facial





Meridional

Structural Isomers

Type	Examples	
Ionisation	$[Co(NH_3)_5Cl]SO_4$	$[Co(NH_3)_5\ SO_4]Cl$
Hydrate	$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2.H_2O$
Linkage	$[Co(NH_3)_5NO_2]^{2+}$	$[Co(NH_3)_5ONO]^{2+}$
Coordination	$[Co(NH_3)_6][Cr(CN)_6]$	$[Cr(NH_3)_6]\ [Co(CN)_6]$

Number of GI and EP

(GI /TI= Geometrical/Total Isomers, EP = Enantiomeric Pairs)

Type	GI	EP	TI	Examples
MA_4B_2	2	0	2	$[Cr(NH_3)_4Cl_2]^+$
MA_4BC	2	0	2	$[Pt(NH_3)_4BrCl]$
MA_3B_3	2	0	2	$[RhCl_3(py)_3]$
MABCDEF	15	15	30	$[Pt(NH_3)Cl(Br)(I)(NO_2)(Py)]$
$M(AA)_3$	0	1	2	$[Co(en)_3]^{3+}$
$M(AB)_3$	2	2	4	$[Cr(gly)_3]$
$M(AA)_2a_2$	5	3	8	$[Co(en)_2Cl_2]+$
$M(AA)_2ab$	6	5	11	$[Co(en)_2(NH_3)(Cl)]^{+2}$
MA_2B_2	2	0	2	$[Pt(NH_3)_2Cl_2]$
MA_2BC	2	0	2	$[Pt(py)_2(NH_3)Cl]+$
MABCD	3	0	3	$[Pt(NH_3)(py)(Cl)(Br)]$