### CH 3101 - 2025

July 2025							
S	M	Т	WT		F	S	
		1	2	3	4	5	
6	7	8	9	10	11	12	
13	14	15	16	17	18	19	
20	21	22	23	24	25	26	
27	28	29	30	31			

	August 2025							
S	M	M T W T F				S		
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3		5	6	7		9		
10	11		13	14	X	16		
17			20	21		23		
24			27	28		30		
31								

	September 2025							
S	M	Т	W	T	F	S		
			3	4		6		
7						3		
14		10	17	18	1	20		
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20	29	30						

October 2025							
S	M	Т	W	Т	F	S	
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12			15	16		18	
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26		., 20		30			

	November 2025							
S	M	T	W	Т	F	S		
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16			19	20		22		
23	24	25	26	27	28	29		
<del>30</del>								

December 2025							
S	M	Т	W	Т	F	S	
	1	2	3	4	5	6	
7	8	9	10	11	12	13	
14	15	16	17	18	19	20	
21	22	23	24	25	26	27	
28	29	30	31				

### **Syllabus**

Nomenclature and isomerism: structures and isomers of coordination compounds

**CFSE** and Structural effects: Jahn-Teller Distortions,

Bonding in metal complexes: ML 4 and ML 6 MO types (sigma donor-pi donor, sigma donor, sigma donor-pi acceptor) Ligand Field Theory: Symmetry and Group Theoretical approach, spectrochemical series and its correlation to the MO diagram, metal carbonyl bonding, metal olefin bonding, MO diagram of Ferrocene, Metal-Metal Bond

Microstates, selection rule, Hunds rule, Orgel diagram, Tanabe-Sugano diagrams (1 L), Spin-states, Interpretation of Spectra d 1 -d 9 (Octahedral, Tetrahedral, high-spin, low spin, Charge-transfer Spectra,

Orbital and spin magnetic moments, spin only moments of d n ions and their correlation with effective magnetic moments, Curie law, paraferro, anti-ferro and ferri-magnetic systems, Oxidation States and Structural trends, Representative compounds, Lanthanides and Actinides

Reaction mechanism of complexes: Inorganic Reaction Mechanisms, Ligand Substitution Reaction, Kinetics, Stereochemical aspects of Octahedral, Square-Planar complexes, Trans effect, Isomerization reactions, Inner-sphere reaction, Outer-sphere reaction, Marcus Equation, Robin-Day Classification, Electrophilic Substitutions, Photochemical reactions, Photochemistry of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and related complexes.

### **Transition metals**

	1																	18
1	Ĥ	2											13	14	15	16	17	He
2	Li	Be											B	ů	Ň	°	, F	Ne
3	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	si Si	15 <b>P</b>	16 <b>S</b>	CI	Ar
4	K K	Ca	SC 21	Ti	V 23	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	sr Sr	39 <b>Y</b>	Žr	Nb	Mo	TC 43	ĸ Ru	Rh	Pd	Åg	<sup>48</sup> Cd	In	Sn Sn	Sb	Te	53	Xe
6	Cs S	Ba	*	Hf	Ta	W 74	Re	OS	ir	Pt	Au	₩g	TI	Pb	Bi	Po	At	Rn 86
7	Fr	** Ra	**	Rf	Db	Sg	Bh	HS	Mt	DS	Rg	Cn	Nh	FI	MC	LV	117 <b>T</b> S	Og Og
	Lantha	nides*	Ľa	Če	Pr	Ñd	Pm	Sm	Eu	Ğd	Τ̈́b	Ďy	Ho	ἕr	Τ̈́m	Ϋ́b	Lu	
	Actin	ides**	Åc	<sub>5</sub> %	Pa	92 <b>U</b>	Np	₽u	Am	c <sub>m</sub>	Bk	Cf	es Es	Fm	Md	No	Lr	

### **MARKS DISTRIBUTUION**

$$70 + 30$$

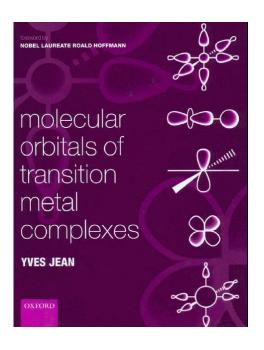
$$MID SEM(20) + END SEM (25)$$

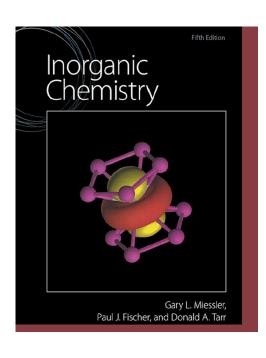
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3 Class Tests (each 20 Marks)

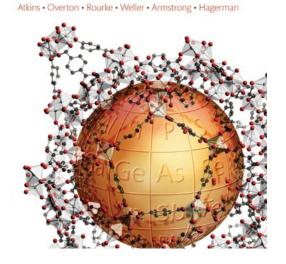
(Best two: 40 scaled down to (25)

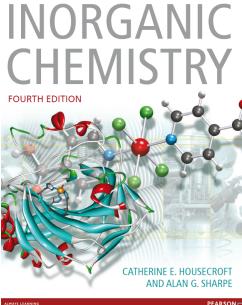
### **BOOKS**

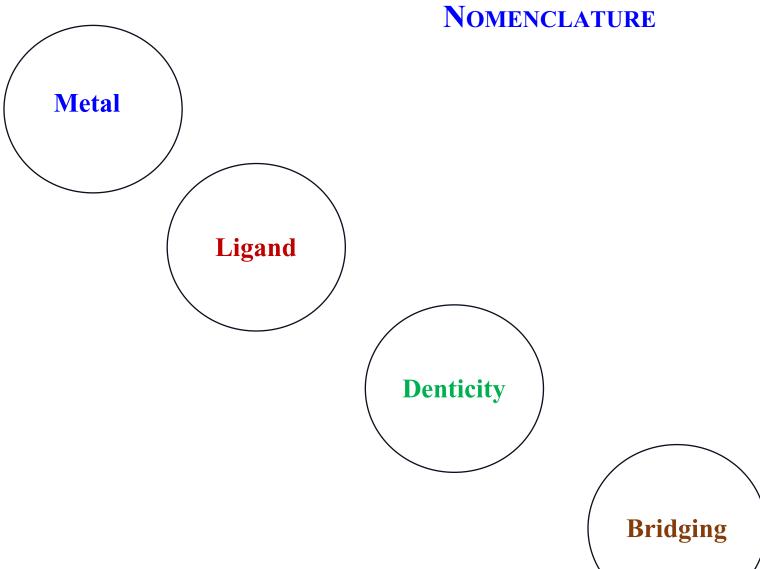




### Shriver & Atkins' **Inorganic Chemistry**







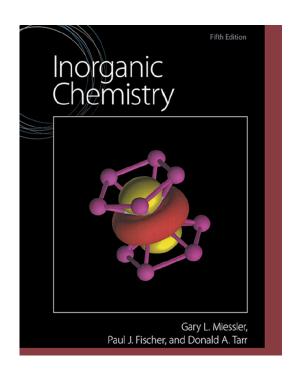


Table 7.7 Names and structures of selected ligands.

Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Water		Monodentate	н о н
Ammonia		Monodentate	$H \stackrel{N}{{{}{}{}{}{}{\stackrel$
Tetrahydrofuran	THF	Monodentate	o
Pyridine	ру	Monodentate	N
1,2-Ethanediamine <sup>†</sup>	en	Bidentate	H <sub>2</sub> N NH <sub>2</sub>
Dimethylsulfoxide	DMSO	Monodentate	Me Me Me Me Me O O

Acetylacetonate ion	[acac] <sup>-</sup>	Bidentate	0 0
Oxalate or ethanedioate ion	[ox] <sup>2-</sup>	Bidentate	0 0 -
2,2'-Bipyridine	bpy or bipy	Bidentate	$\left\langle \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \right\rangle$
1,10-Phenanthroline	phen	Bidentate	N N
1,4,7-Triazaheptane <sup>†</sup>	dien	Tridentate	H <sub>2</sub> N N NH <sub>2</sub>
$1,4,7,10$ -Tetraazadecane $^{\dagger}$	trien	Tetradentate	$H_2N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$
$N,N,N',N'$ -Ethylenediaminetetraacetate ion $^{\ddagger}$	[EDTA] <sup>4-</sup>	Hexadentate	See eq. 7.75

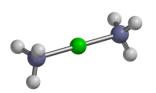
Table 2.1 Naming of different numbers of donor groups bound to a single metal ion, with examples of typical simple linear ligands of each class.

No. bound donors	Ligand denticity	Examples of ligands (donor atoms highlighted in bold)
One	Monodentate	NH <sub>3</sub> OH <sub>2</sub> F <sup>-</sup>
Two	Didentate	$H_2N$ — $CH_2$ — $CH_2$ — $NH_2$ $H_2N$ — $CH_2$ — $CO$ — $O$
Three	Tridentate	$H_2N$ — $CH_2$ — $CH_2$ — $NH$ — $CH_2$ — $CH_2$ — $NH_2$
		-OCOCH <sub>2</sub> NHCH <sub>2</sub> COO-
		$H_2N$ — $CH_2$ — $CH_2$ — $CO$ — $CH_2$ — $P(CH_3)_2$
Four	Tetradentate	H <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>
		-O-CO-CH <sub>2</sub> -NCO-CH <sub>2</sub> -NCO-CH <sub>2</sub> -NH <sub>2</sub>
Five	Pentadentate	$H_2N$ — $CH_2$ — $CH_2$ — $NH$ — $CH_2$ — $CH_2$ — $NH$ — $CH_2$ — $CH_2$ — $NH$ —
		CH <sub>2</sub> —CH <sub>2</sub> —NH <sub>2</sub>
		O-CO-CH2-NH-CH2-CH2-S-CH2-CH2-NH-
		$CH_2$ — $CH_2$ — $O^-$
Six	Hexadentate	O-CO-CH2-NH-CH2-CH2-NH-CH2-CH2-NH-
		$CH_2$ — $CH_2$ — $NH$ — $CH_2$ — $CO$ — $O$

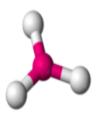
# A polydentate ligand is a *chelating agent*, complexes containing polydentate ligands:

Ethylenediaminetetraacetate ion: hexadentate ligand

### Basic Structure of Metal – Ligand Complex Monodentate Ligand



Coordination # 2 = linear Rare for most metals: common for  $d^{10}$  metal ions. especially: Cu+, Ag+, Au+, and Hg<sup>2+</sup>



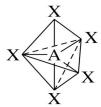
Coordination #3 Encountered with  $d^{10}$  metal ions e.g.Cu<sup>+</sup> & Hg<sup>2+</sup>

Coordination # 4 Two common structures: tetrahedral & square planar

Tetrahedral: 4-coordinate all complexes of non-transition metals and  $d^{10}$  ions and first-row transition metals.



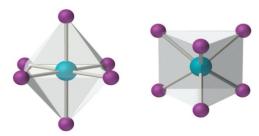
Coordination # 5 trigonal planar structure



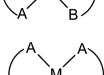
Trigonal bipyramidal



Coordination # 6 Most common: six ligands at vertices of an octahedron or a distorted octahedron.



Square planar: 4-coordinate complexes of 2<sup>nd</sup> & 3<sup>rd</sup> row transition metals with d<sup>8</sup> e<sup>-</sup> configurations, e.g. Rh<sup>+</sup>, Pt<sup>2+</sup> and Pd<sup>2+</sup>, also encountered in some Ni2+ & Cu<sup>2+</sup> complexes

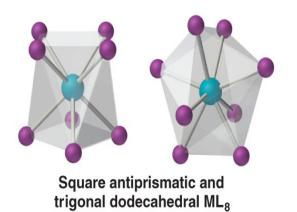


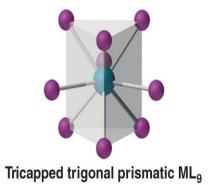


### ... and 2<sup>nd</sup> & 3<sup>rd</sup> row transition metals

7, 8 & 9 coordination #'s, give other geometries





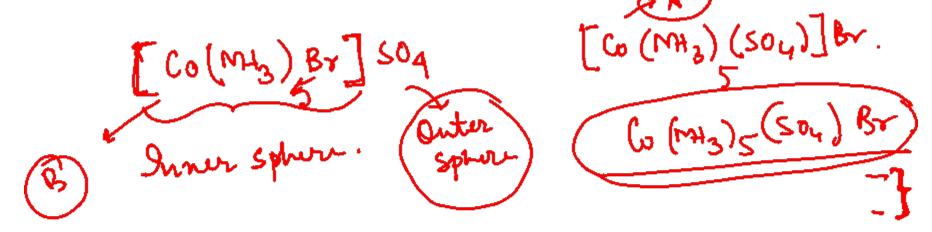


### **ISOMERISM**

#### Structural isomerism

1. Ionization isomers: Interchange of an anionic ligand within the first coordination sphere with an anion

outside the coordination sphere.



2. Hydration isomers: Hydration isomers result from the interchange of H2O and another ligand between the first coordination sphere and the ligands outside it.

Structural isomerism continues....

3. Coordination isomerism: Coordination isomers are possible only for salts in which both cation and anion are complex ions

(Coordination position isomerism: In some of the polynuclear complexes, interchange of the ligands between the two metal nuclei takes place, which is give to rice to coordination position isomerism

 $(M_3)_{4}^{Co} \qquad (M_3)_{2}^{Cl} \qquad (M_3)_{2}^{Cl} \qquad (Co(NH_3)_6][Cr(CN)_6] \text{ and } [Cr(NH_3)_6][Co(CN)_6]; \\ (Co(NH_3)_6][Co(NO_2)_6] \text{ and } \\ (Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]; \\ (Pt^{II}(NH_3)_4][Pt^{IV}Cl_6] \text{ and } [Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4].$ 

4. Linkage isomers Linkage isomers may arise when one or more of the ligands can coordinate to the metal ion in more than one way, e.g. in [SCN] both the N and S atoms are potential donor sites. Such a ligand is ambidentate.

M-NCS? dinker M-NON-0} NO, M-SCN) 5. Polymerization Isomer: The empirical formula obtained from elemental analysis identifies the ratio of components, not their actual number. Thus an empirical formula MA2B2 could be considered as any of  $[MA_2]_n$  (for n=1, 2, 3, . . .), a series of compounds with the same empirical formula, and with the molecular formula of each some multiple of the simplest formula

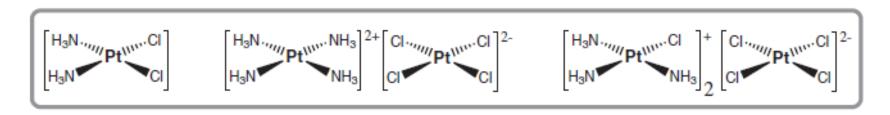
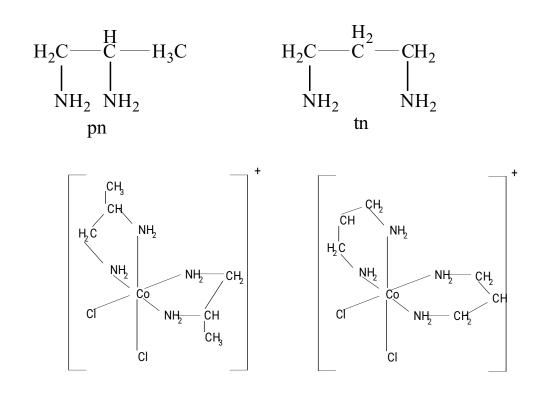


Figure 4.27
Polymerization isomers: the complexes exemplified have identical empirical formulae but differ in the number of replications of the empirical formula, {Pt Cl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>}<sub>n</sub>.

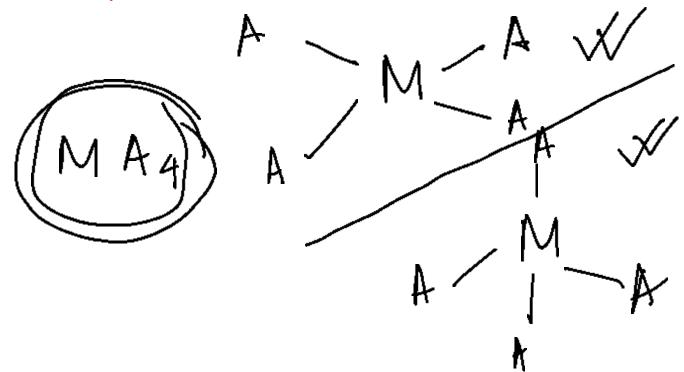
6. Ligand isomerism: Some of the ligands themselves are capable of existing as isomers, e.g. diaminopropane can exist isomers as 1, 2-diaminopropane (pn) and 1, 3-diaminopropane (tn).



 $[Co(pn)_2Cl_2]^+$  and  $[Co(tn)_2Cl_2]^+$ 

### Stereoisomerism: diastereoisomers

Stereoisomers are molecules of the same empirical formula that have identical coordination number and basic shape, and display the same atom-to-atom bonding sequence throughout, but in which the ligand atoms differ in their locations in space.



*Diastereomers* are the general class of stereoisomers, and includes geometric isomers (such as *cis*, *trans isomeric forms*) *as a sub-c<del>lass.</del>* 

Any particular diastereomer may have an enantiomer, which is a stereoisomer that is a non-superimposable mirror image of the original diastereomer

Not all compounds will exist as two mirror image forms (the enantiomers), as it is a property related to the symmetry of the compound; consequently, diastereomers are not the same thing as enantiomers.

For complexes to have enantiomers, they must be either asymmetric (that is be a molecule totally lacking in symmetry apart from the identity operation) or dissymmetric (that is lacking an Sn axis, which is a rotation-reflection axis – without an Sn axis, it can have neither a plane of symmetry nor a centre of symmetry; however, a dissymmetric molecule can have a proper axis of rotation, Cn (n 1)).

A molecule that is asymmetric or dissymmetric (and therefore not superimposable on its mirror image) is called a *chiral compound; this means* that all enantioners are chiral.

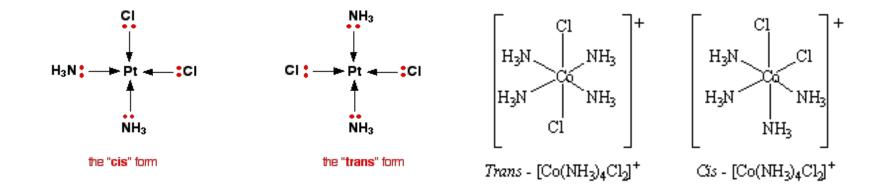
Such a compound will display *optical activity as an individual enantiomer*, *which is the* ability to rotate the plane of plane-polarized light (measured using a polarimeter), which is one way that we can detect the presence of an enantiomer and define its optical purity.

Whereas diastereomers usually differ appreciably in their chemical and physical properties, enantiomers differ only in their ability to rotate polarized light and related optical properties

## Metal complexes that differ only in which ligands are adjacent to one another (cis)

or

directly across from one another (trans).



### Geometrical isomers

### Square planar complexes:

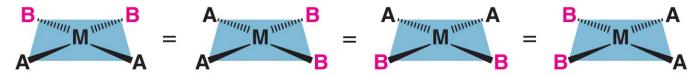
all vertices of a square are equivalent, it does not matter which vertex is occupied by ligand B

in a square planar MA<sub>3</sub>B complex.

Only one geometrical isomer is possible

MA<sub>3</sub>B square planar complex

### With two, there are other possible arrangements

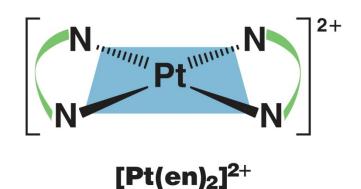


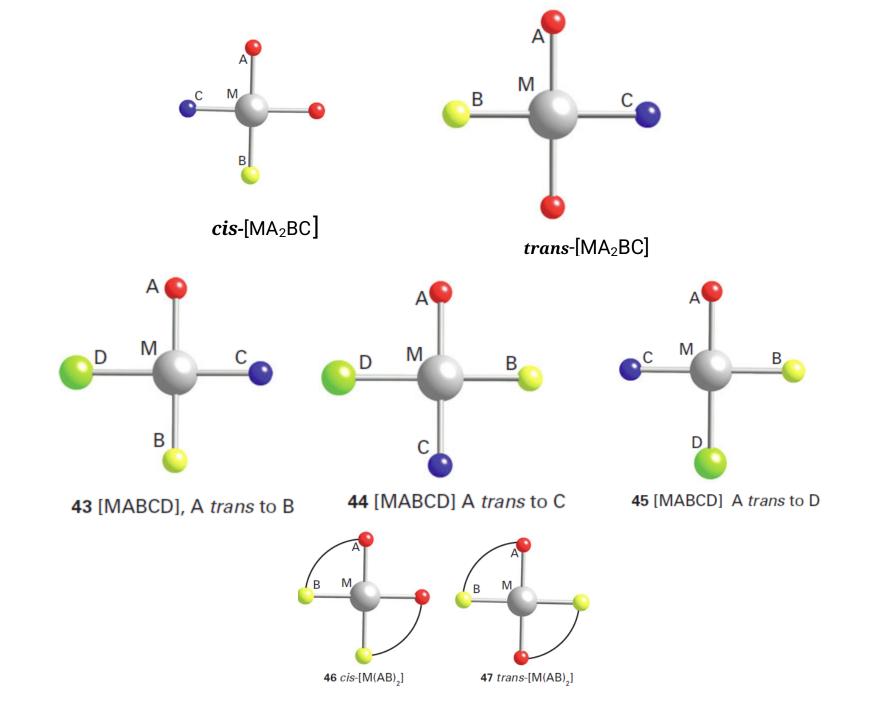
MA<sub>2</sub>B<sub>2</sub> square planar complex, cis isomer

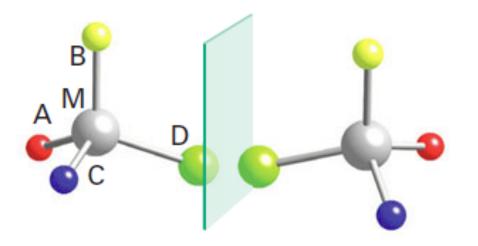


MA<sub>2</sub>B<sub>2</sub> square planar complex, trans isomer

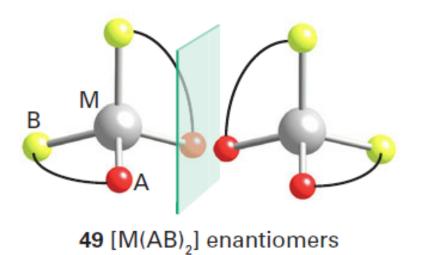
Symmetrical bidentate ligands also only have one structure

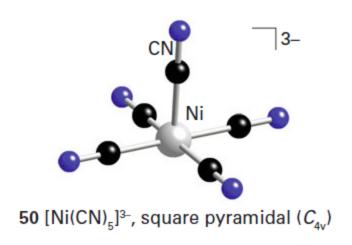


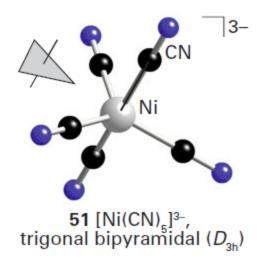




48 [MABCD] enantiomers







The energies of the various geometries of five-coordinate complexes often differ little from one another. The delicacy of this balance is underlined by the fact that  $[Ni(CN)_6]^{3-}$  can exist as both square-pyramidal and trigonal-bipyramidal conformations in the same crystal. In solution, trigonal-bipyramidal complexes with monodentate ligands are often highly fluxional (that is, able to twist into different shapes), so a ligand that is axial at one moment becomes equatorial at the next moment: the conversion from one stereochemistry to another may occur by a Berry pseudorotation. Thus, although isomers of five-coordinate complexes do exist, they are commonly not separable.

55 trans-[ $MA_4B_2$ ]  $\mathbf{54} \ cis\text{-}[\mathsf{MA}_{\scriptscriptstyle{4}}\mathsf{B}_{\scriptscriptstyle{2}}]$ 

