

9.3: Nomenclature and Ligands

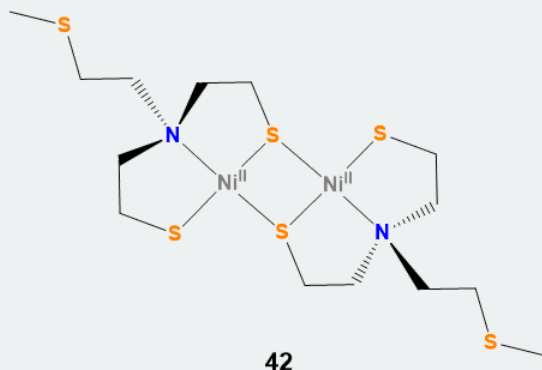
Systems of nomenclature and formulae are intended as tools, to be employed insofar as they are useful

There are well-established rules for both naming and writing the formulae of coordination compounds. The purpose of these rules is to facilitate clear and precise communication among chemists. As with all such rules, some are more burdensome than others to employ, and some serve more crucial roles in the communication process while others are more peripheral - and all are poorly used in the service of pedantic tyranny, especially when used against those who are otherwise doing good work. For this reason, you are urged to approach the rules in a spirit of generosity towards others in

- naming and writing formulas as reasonably accurately as you can so that ligands and metals are where readers expect them and thus can understand what you mean more easily.
- being gracious towards the many professional inorganic chemists who adhere loosely to some of the rules you are about to learn.
- recognizing that in cases when a structure is particularly complex and a picture may make be particularly useful, you should supply one (See the note below).

Note 9.3.1: Sometimes the most helpful name to give a compound is 42.

Even though the IUPAC nomenclature rules permit specification of even the most complex structures, it is often much easier and more effective to supply a numbered structure that can be referred to instead of the IUPAC name. Consider bis{[(μ -2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. Which is easier, to expect readers and hearers to work out the structure from that name or to just refer them to compound **42** in Scheme 9.3.I?



Scheme 9.3.I. Structure of bis{[(μ -2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. The authors of the synthesis of this compound in *Inorganic syntheses*¹ may have had to figure out an IUPAC name for this compound but if you have this scheme in your paper and your instructor is OK with it you can just call it **42**

Coordination Complexes are named as the ligand derivatives of a metal

A variety of systems have been used for naming coordination compounds since the development of the discipline in the time of Alfred Werner. In this section the most common approaches as they are currently used by practicing chemists will be described. Those who need a more thorough and accurate acquaintance with the full IUPAC nomenclature rules are encouraged to consult the [IUPAC brief guide to inorganic nomenclature](#) followed by [complete guidelines, commonly known as the IUPAC red book](#). If those are still not enough a careful read of note 9.3.1 is suggested.

The systems for naming coordination compounds used at present are additive, meaning that they consider coordination compounds as comprising a central metal to which are added ligands. To specify the structure and bonding in this metal-ligand complex then involves:

1. when there are several different ways of attaching the metal and ligands, specifying the structural or stereoisomer
2. systematically listing the ligands in a way that, as necessary, conveys information about how they are linked to the metal and their stereochemistry

- providing the identity of the metal and its oxidation state, or if the oxidation state is unclear, at least the overall charge on the complex
- specifying any counterions present

Since the stereochemistry of coordination compounds forms the subject of the next section, in this section it will be addressed by simply giving the prefixes that designate stereochemistry as if they were self-evident. Do not worry about these for now. They will make sense after you have learned more about stereochemistry in the next section. At that time, you can go back over the examples in that section to solidify your understanding of how to name coordination compounds.

However, in order to name coordination compounds accurately you will need to learn how to think about and name ligands first.

Ligands

Ligands are classified based on whether they bind to the metal center through a single site on the ligand or whether they bind at multiple sites. Ligands that bind through only a single site are called **monodentate** from the Latin word for tooth; in contrast, those which bind through multiple sites are called **chelating** after the Greek $\chi\alpha\lambda\epsilon$ for “claw”. These relationships are summarized in Figure 9.3.1.

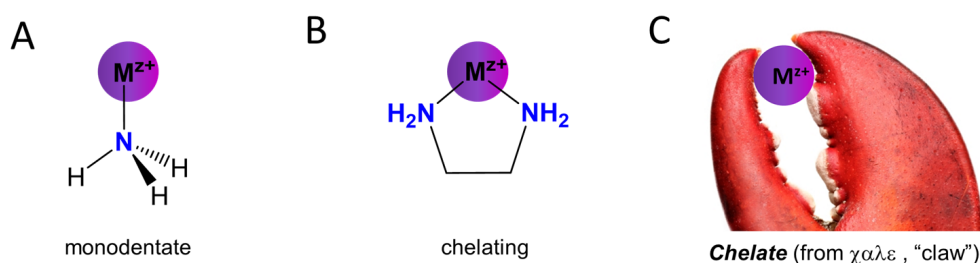
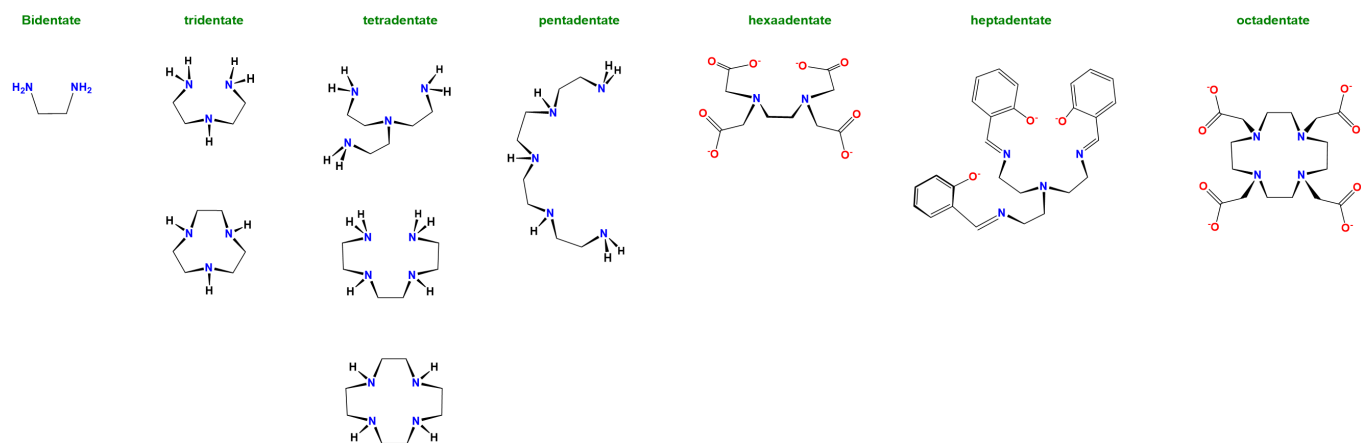


Figure 9.3.1. (A) Ammonia is a monodentate ligand while (B) ethylene diamine is a chelating ligand owing to its capacity to bind metals via its two amine functional groups. (C) Chelating ligands act like a lobster claw in attaching to the metal via multiple sites. The lobster claw image is adapted from <https://www.clipart.email/download/1127636.html>. Otherwise this work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](#).

Following naturally from the classification of non-chelating ligands as monodentate, chelating ligands are further classified according to the number of sites which they can use to bind a metal center. This number of binding sites is called the denticity and ligands are referred to as monodentate (non-chelating), bidentate, tridentate, etc., based on the number of sites available. Ligands with two binding sites have a denticity of two and are said to be bidentate; those with three are tridentate, four tetradentate, and so on. To illustrate this classification system examples of chelating ligands classified according to denticity are given in Scheme 9.3.1.

Scheme 9.3.1. A selection of chelating ligands classified according to denticity.

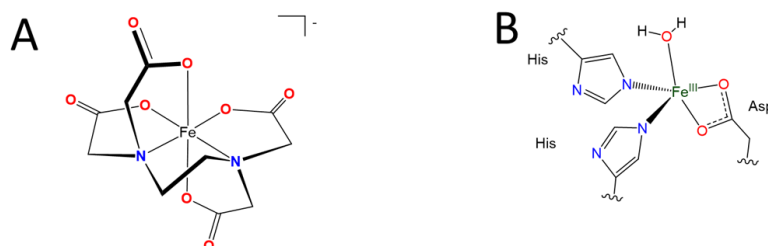


Scheme 9.3.IIA. Because only one oxygen per carboxylate *typically* binds, only one is counted when assigning a ligand's denticity. This work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](#).

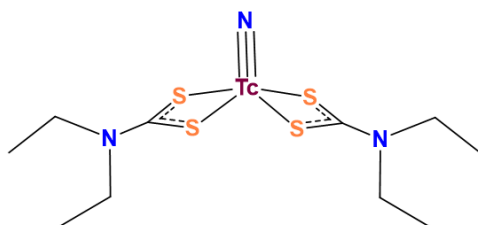
Although only one carboxylate oxygen *usually* binds to a metal, it is still possible for both oxygens to bind to a single metal. As shown in Scheme 9.3.IIB, complexes in which both carboxylates bind to a metal are known, and in fact are common in the

active sites of some enzymes. It is just that the binding of both oxygens gives a strained four-membered ring that is usually unstable.

Scheme 9.3.II. (A) Only one oxygen per carboxylate counts towards the denticity of EDTA since on binding the other oxygen generally points away from the metal center, as in the structure of $\text{Fe}(\text{EDTA})^-$. (B) In some enzyme active sites both oxygens of a carboxylic acid (aspartate or Asp in this example) bind to a metal. The aspartate carboxylic acid group is bidentate while the EDTA carboxylic acid groups in A are monodentate. This work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](#).



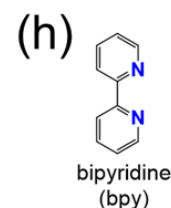
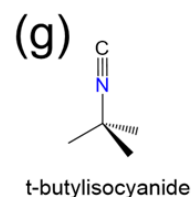
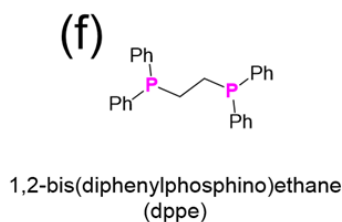
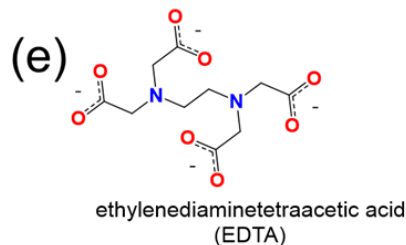
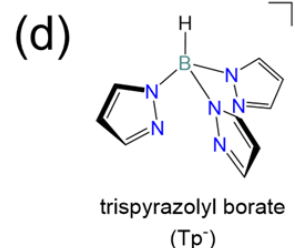
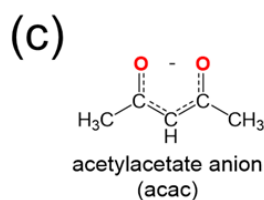
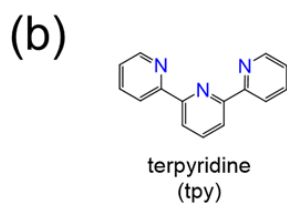
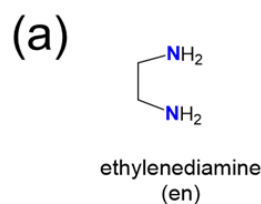
Scheme 9.3.III. As in this complex, dithiocarbamates commonly bind metals through both sulfur atoms. Consequently, dithiocarbamates are classified as bidentate. This work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](#).



Because of these factors it is technically more correct to say that carboxylates *usually act as* monodentate ligands and dithiocarbamates bidentate ones than it is to say that carboxylates *are* monodentate ligands and dithiocarbamates bidentate ones. So in other words the ligand classifications presented here just represent common binding modes.

? Exercise 9.3.1

Determine the denticity of each ligand in the list below and classify them as monodentate, tridentate, etc.



Answer

- (a) bidentate
- (b) tridentate
- (c) bidentate
- (d) tridentate (only the lower N on each ring has a lone pair that can be used to bind the metal)
- (e) hexadentate (remember that each carboxylate only counts as one point of attachment)
- (f) bidentate
- (g) monodentate (through the lone pair on the isocyanide C)
- (h) bidentate

This experimentally-based classification of dithiocarbamates as bidentate and carboxylates as monodentate can be confusing to a beginner. Fortunately, such experimentally based classifications are embedded in the lists of common monodentate ligands as given in Table 9.3.1 and common chelating ligands in Table 9.3.2.

A perusal of the ligands in Table 9.3.1 reveals that several can bind to a metal in multiple ways. For example, thiocyanate, SCN^- can bind metals through its S or N atoms. Such ligands are called **ambidentate ligands**. In naming an ambidentate ligand, the atom through which it attaches to the metal is commonly specified after the ligand name using the italicized element symbol or, more formally, a κ followed by the italicized element symbol. An example is given in Scheme 9.3.1.²

Scheme 9.3.1. Two possible binding modes of nitrite acting as a ligand.³

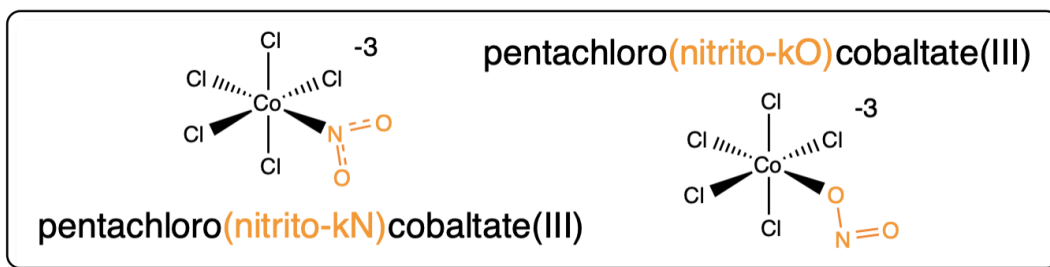




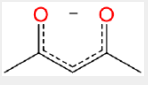
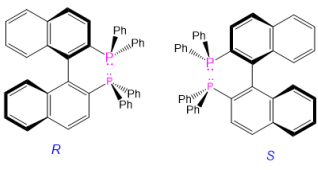
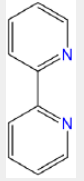

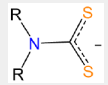
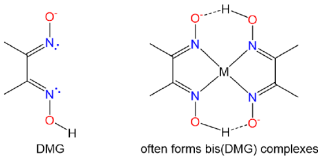
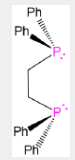


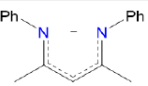



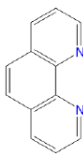
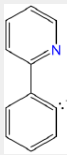
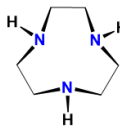
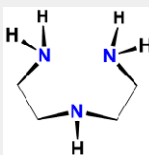
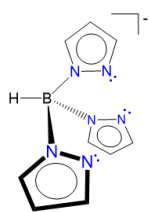
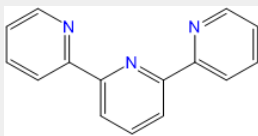
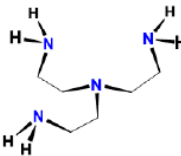
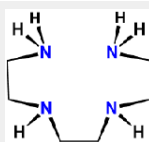
Table 9.3.1. Common monodentate ligands. Most chemists still prefer common names over the IUPAC ones.

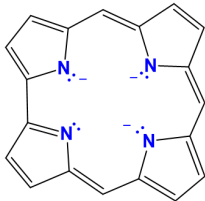
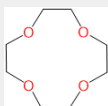
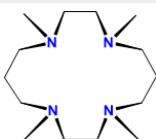
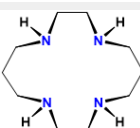

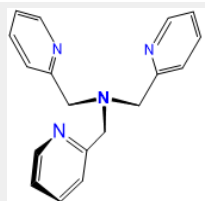
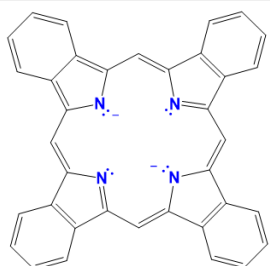
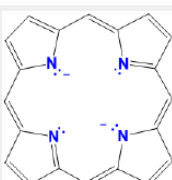
Ligand	Common name	IUPAC name
H ⁻ (H ligands are always considered anions for naming purposes)	hydrido	hydrido
F ⁻	fluoro	fluorido
Cl ⁻	chloro	chlorido
Br ⁻	bromo	bromido
I ⁻	iodo	iodido
CN ⁻ , as M-CN	cyano	cyanido or cyanido- κ C or cyanido-C
CN ⁻ , as M-NC	isocyano	isocyanido or cyanido- κ N or cyanido-N
CH ₃ NC	methylisocyanide	methylisocyanide
N ₃ ⁻	azido	azido
SCN ⁻ , <i>e.g.</i> thiocyanate as M-SCN	thiocyanato	thiocyanato- κ S or thiocyanato-S
NCS ⁻ , <i>e.g.</i> thiocyanate as M-NCS	isothiocyanato	thiocyanato- κ N or thiocyanato-N
CH ₃ CO ₂ ⁻	acetato	ethanoato
N ³⁻	nitrido	nitrido
NH ²⁻	imido	azanediido
NH ₂ ⁻	amido	azanido
NH ₃	ammine	ammine
RNH ₂ , R ₂ NH, R ₃ N	alkylamine, dialkylamine, trialkylamine (<i>e.g.</i> methylamine for CH ₃ NH ₂)	alkylamine, dialkylamine, trialkylamine (<i>e.g.</i> methylamine for CH ₃ NH ₂)
 , piperidine, abbreviated pip	piperidine	piperidine
 , pyridine, abbreviated py	pyridine	pyridine
CH ₃ CN, acetonitrile, abbreviated MeCN	acetonitrile	acetonitrile
P ³⁻	phosphido	phosphido
PH ₃	phosphine	phosphane
PR ₃	trialkylphosphine (<i>e.g.</i> trimethylphosphine for Me ₃ P)	trialkylphosphane (<i>e.g.</i> trimethylphosphane for Me ₃ P)
PAr ₃	triarylphosphine (<i>e.g.</i> triphenylphosphine for Ph ₃ P)	triarylphosphine (<i>e.g.</i> triphenylphosphane for Ph ₃ P)
 , dimethylsulfoxide or DMSO or dmsO	dimethylsulfoxide (sometimes called dimethylsulfoxo but this usage is rare and violates the nomenclature rules for neutral ligands)	(methanesulfinyl)methane or dimethyl(oxido)sulfur
 , thiourea or tu	thiourea	thiourea

Ligand	Common name	IUPAC name
O^{2-}	oxo	oxido
OH^-	hydroxo	hydroxido
H_2O	aqua	aqua
S^{2-}	sulfo	sulfo
HS^-	hydrosulfido	hydrosulfido
RS^-	alkanethiolate (<i>e.g.</i> ethanthiolate for EtS^-)	thioalkanoate
H_2S	hydrogen sulfide	hydrogen sulfide
R_2S	alkylsulfanylalkane (<i>e.g.</i> ethylsulfanylethane for Et_2S)	dialkyl sulfide
O_2	dioxygen	dioxygen
O_2^- , superoxide	superoxido	dioxido(1-) or superoxido
O_2^{2-} , peroxide	peroxido	dioxido(2-) or peroxido
N_2	dinitrogen	dinitrogen
NO (are always considered neutral for naming purposes)	nitrosyl	nitrosyl
CO	carbonyl	carbonyl
CS	thiocarbonyl	thiocarbonyl
SO, as M-SO	sulfinio	sulfur monoxide- κS or sulfur monoxide-S
NO_2 , as M- NO_2	nitryl	nitrogen dioxide- κN or nitrogen dioxide-N
CO_3^{2-}	carbonato	carbonato
NO_2^- , as M- NO_2	nitro or nitrito-N	nitrito- κN or nitrito-N
NO_2^- , as M-ONO	nitrito or nitrito-O	nitrito- κO or nitrito-O
NO_3^-	nitrato	nitrato
SO_3^{2-}	sulfito	sulfito
SO_4^{2-}	sulfato	sulfato
$S_2O_3^{2-}$, as M-S-SO ₂ -O ⁻	thiosulfato-S	thiosulfato- κS or thiosulfato-S
$S_2O_3^{2-}$, as M-O-SO ₂ -S ⁻	thiosulfato-O	thiosulfato- κO or thiosulfato-O

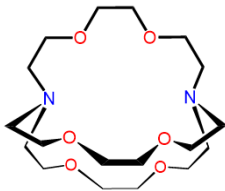
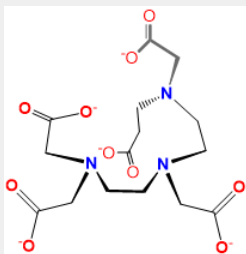
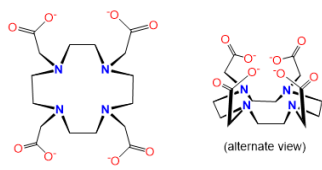
Table 9.3.2. Common chelating ligands organized by denticity. Most chemists use the common names and abbreviations to describe these ligands.

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
<i>bidentate ligands</i>			
acetylacetonato	2,4-pentanediono	acac	
R-BINAP and S-BINAP	R- or S-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl	BINAP	
2,2'-bipyridine	2,2'-bipyridine	bpy or bipy	
cyclooctadiene	1,5-cyclooctadiene	COD	 (binding to the metal occurs through the alkene π cloud)
dialkyldithiocarbamato	dialkylcarbamodithiolato	$R_2NCS_2^-$ or dtc	
dimethylglyoximate	butanedienedioxime	Hdmg or DMG	
diphenylphosphinoethane or (diphenylphosphino)ethane	Ethane-1,2-diylbis(diphenylphosphane)	dppe	
ethylenediamine	Ethane-1,2-diamine	en	
ethylenedithiolato	Ethane-1,2-dithiolato	$C_2H_2S_2^{2-}$	
nacnac	N,N'-diphenyl-2,4-pentandiiminato	nacnac	
oxalato	oxalato	ox	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
1,10-phenanthroline or <i>o</i> -phenanthroline	1,10-phenanthroline	phen or <i>o</i> -phen	
phenylpyridinato	2-phenylpyridinato- C^2,N or 2-phenylpyridinato- $\kappa C^2,N$	ppy	
<i>tridentate ligands</i>			
triazacyclononane	1,4,7-triazacyclononane	tacn	
diethylenetriamine	1,4,7-triazaheptane	dien	
pyrazoylborato (scorpionate)	hydrotris(pyrazo-1-yl)borato	TP	
terpyridine or 2,2';6',2''-terpyridine	1 ² ,2 ² :2 ⁶ ,3 ² -terpyridine or 2,6-bis(2-pyridyl)pyridine, tripyridyl, 2,2':6',2''-terpyridine	tpy or terpy	
<i>tetradentate ligands</i>			
β , β' , β'' -triaminotriethylamine	β , β' , β'' -tris(2-aminoethyl)amine	tren	
triethylenetetramine	1,4,7,10-tetraazadecane	trien	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
corroles	variable and generally not used	cor or Cor	
12-crown-4	1,4,7,10-tetraoxacyclododecane	12-crown-4	
tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC or cyclam	
cyclam	1,4,8,11-tetraazacyclotetradecane	cyclam	
cyclen	1,4,7,10-tetraazacyclododecane	cyclen	
tris(2-pyridylmethyl)amine	1-pyridin-2-yl-N,N-bis(pyridin-2-ylmethyl)methanamine	tpa or TPA	
phthalocyanines	variable and generally not used	variable, usually a modified Pc	
porphyrins	variable and generally not used	variable, usually a modified por, Por, or P (e.g. TPP = tetraphenylporphyrin)	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
salen	2,2'-ethylenebis(nitrilomethylidene) diphenoxido	salen	
<i>pentadentate ligands</i>			
15-crown-5	1,4,7,10,13-Pentaoxacyclopentadecane	15-crown-5	
tetraethylenepentamine	1,4,7,10,13-pentaazatridecane	tepa or TEPA	
<i>hexadentate ligands</i>			
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	18-crown-6	
2,1,1-cryptand	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]icosane	2,1,1-crypt or [2.1.1]-cryptand kryptofix 211 and variations thereof	
ethylenediaminetetraaceto	2,2',2'',2'''-(Ethane-1,2-diyl)dinitrilo)tetraaceto	EDTA, edta, Y ⁴⁻	
<i>heptadentate ligands</i>			
2,2,1-cryptand	4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]icosane	2,2,1-crypt or [2.2.1]-cryptand kryptofix 221 and variations thereof	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or representative/parent structure (shown in the ionization state in which they bind to a metal)
<i>octadentate ligands</i>			
2,2,2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan	2,2,2-crypt or [2.2.2]-cryptand kryptofix 222 and variations thereof	
pentetato acid or diethylenetriaminepentaacetato or DTPA	2-[bis[2-[bis(carboxylatomethyl)amino]ethyl]amino]acetato	DTPA	
DOTA or tetraacetan	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid	Dota, DOTA	

Rules for Naming Coordination Compounds

As explained above, the name of a coordination compound communicates

- as appropriate, information about isomerism
- systematically listing the ligands in a way that as necessary conveys information about their oxidation state and how they are linked to the metal
- the identity of the metal and its oxidation state
- any counterions present

Before going into these rules it is worth pointing out a few things.

1. It is easiest to learn these rules by starting with one or two of the rules, learning how to apply them, and then adding additional rules one at a time. To that end, instructors who wish to use a more programmed approach may find it convenient to first direct their students to [this page which focuses on getting the names of the ligands and metal right, without worrying about isomerism or stereochemistry](#).

2. The rules also assume some familiarity with common coordination geometries and patterns of isomerism in metal complexes. Thus it might be easiest to learn about [common coordination geometries](#) first, followed by [common patterns of isomerism in metal complexes](#) before beginning this section. If you decide to dive right in to this section you might find it helpful to know that when applying nomenclature and formula rules most textbooks *assume*

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I} , or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four are tetrahedral

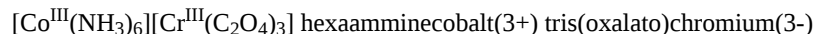
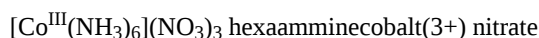
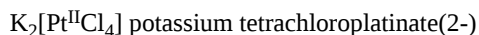
Like all assumptions these don't always work in real life but they should be good enough to get you through your first inorganic chemistry course.

For the pedants among you, note that the complexes given as examples and in exercises on this page have been selected for pedagogical utility. Although many are well-known compounds, others are hypothetical.

Now on to the rules.

Rule 1: If ions are present, name the cation first, followed by the anion.

Examples:

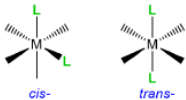
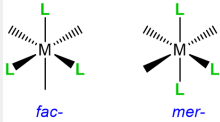
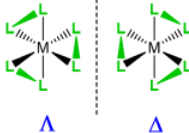


Rule 2: When multiple isomers are possible, designate the particular isomer in *italics* at the front of the name of each complex

If you have not yet learned about isomerism in coordination compounds skip this rule for now and return to it after you have.

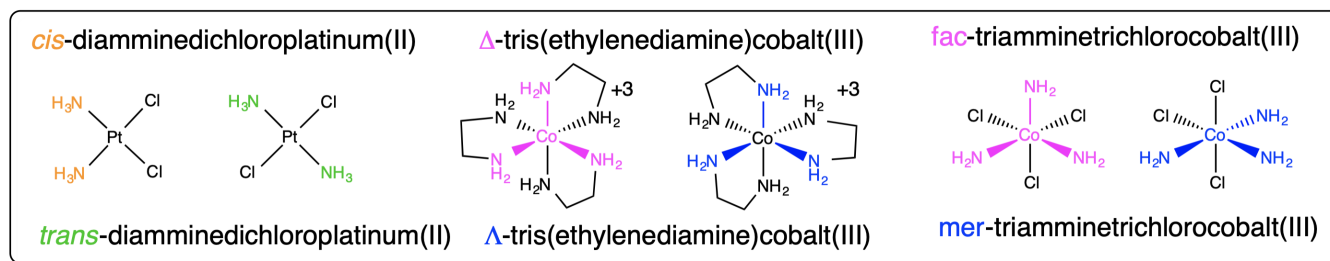
When a complex might exist as one of two stereoisomers, prefixes are commonly used to designate which isomer is present. The most common cases are listed in Table 9.3.3.

Table 9.3.3. Prefixes used to specify isomerism about a metal center when naming and writing coordination compounds' formulae.

Type of isomerism	Graphical reminder	Prefixes
Geometric, <i>cis-</i> , <i>trans-</i>		<i>cis-</i> or <i>trans-</i>
Geometric, <i>fac-</i> / <i>mer-</i>		<i>fac-</i> or <i>mer-</i>
Enantiomers, Δ -, Λ -		Δ - or Λ -

Examples of how isomerism about a metal center is designated are given in Scheme 9.3.II.

Scheme 9.3.II. Application of nomenclature rules for stereoisomerism about a metal.³



There are a number of other cases where it might be advisable to specify the stereochemistry of a complex. These cases involve specifying

- the coordination geometry about a metal center (octahedral, trigonal prismatic, tetrahedral, square planar, etc.)

- the geometry cannot be unambiguously described by a single *cis/trans* or *fac/mer* relationship of ligands

These cases may also be handled by using a designator to specify the coordination geometry and, as necessary, giving the position of ligated atoms in terms of designated numbered positions for that geometry. See the IUPAC red book for details as such cases fall outside the scope of what is normally advisable for an undergraduate course.

Rule 3: Specify the identity, number, and as appropriate, isomerism of the ligands present in alphabetical order by ligand name.

Before specifying the metal, the ligands are written as prefixes of the metal.

In specifying the ligands several rules are followed.

- The ligands are written in alphabetical order by the ligand name only; symbols are not considered and prefixes do not count in determining alphabetical order.

Example: In the name of the complex ion $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, pentamminechlorocobalt(II), the ammine ligand is named before the chloro ligand because the order is alphabetical by the ligand name by virtue of which ammine comes before chloro.

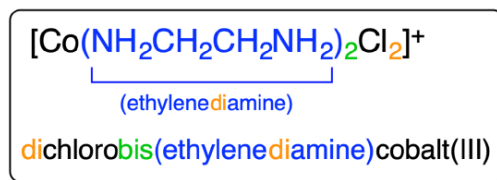
- Prefixes are used to indicate the number of each ligand present. Specifically, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, etc. prefixes are used to indicate multiple ligands of the same type EXCEPT when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc. In that case *bis-*, *tris-*, *tetrakis-*, etc. are used instead. These prefix rules are summarized in Table 9.3.3.

Table 9.3.3. Prefixes used to specify the number of a given ligand present.

Number of identical ligands	prefix used when the ligand name is simple	prefix used when the ligand is polydentate or its name already has a <i>di-</i> , <i>tri-</i> , <i>tetra-</i> etc.
2	di-	bis-
3	tri-	tris-
4	tetra-	tetrakis-
5	penta-	pentakis-
6	hexa-	hexakis-
7	hepta-	heptakis-
8	octa-	octakis-
9	nona-	nonakis-
10	deca-	decakis-

An example of the application of the prefix rule is given in Scheme 9.3.III.

Scheme 9.3.III. Example of the use of prefixes to specify the number of ligands of each type in a complex.³



- Ligand names are based on their charge.

- Neutral and cationic ligand names are the same as the names of their neutral compounds with two caveats:
 - names that involve spaces should either be put in parentheses or the spaces should be eliminated (preferred)

Example: *cis*-dichlorobis(dimethyl sulfoxide)platinum(II) or *cis*-dichlorobis(dimethylsulfoxide)platinum(II)

ii. A few ligands are given common names.

- H_2O = aqua
- NH_3 = ammine (notice that there are two n's)
- CO = carbonyl
- CS = thiocarbonyl
- NO = nitrosyl

- For anionic ligands, the vowel at the end of their anion names is changed to an "-o"

Examples: Cl^- = chloro, NH_2^- = amido, N_3^- = azido

Caveat: some anionic ligands have common names that may also be used

Examples:

I^- = iodo or iodino

CN^- = cyano or cyanido

O^{2-} = oxo or oxido

The IUPAC and common names of many ligands are given in Tables 9.3.1. and 9.3.2.

4. When an ambidentate ligand is present, the atom through which it is bound to the metal is indicated by giving either its element symbol or a κ and its element symbol in italics after the ligand name.

Example:

M-SCN is thiocyanato-S or thiocyanato- κS

M-NCS = thiocyanato-N or thiocyanato- κN

The use of κ and an element symbol to indicate how a ligand and metal are linked is called a **k-term**. More complex k-terms might also involve specifying the atoms by number, though their use is outside the scope of this text.

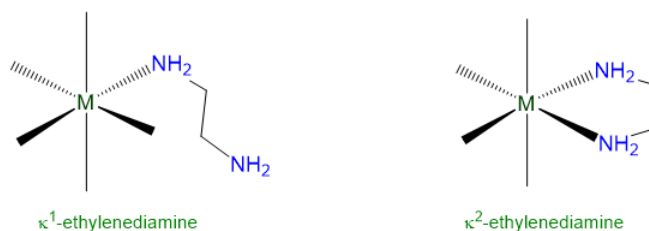
5. As appropriate, additional information about the way a ligand is bound to the metal center and/or its stereochemistry is specified using a prefix. The prefixes to provide linkage and stereochemistry for ligands are given in Table 9.3.4.

Table 9.3.4. Prefixes used to specify ligands' isomerism when naming and writing coordination compounds' formulae. Some of these types of isomerism will be discussed in later pages.

Type of isomerism	Graphical reminder	Prefixes
when a multidentate ligand binds through less than the full number of atoms		κ^n where n is the number of attached atoms; used when the attached atoms are not directly connected by a chemical bond. The metal-ligand bonding usually involves σ -type coordination.
hapticity		η^n where n is the number of attached atoms; used when the coordinated atoms are all connected by bonds. Usually the metal-ligand bonding involves π -type coordination. In speech, η^1 =monohapto; η^2 =dihapto; η^3 =trihapto, etc.
bridging ligands		μ_n where n is the number of atoms bridged. The number n is usually omitted when n = 2.
chelating ligand ring twist		λ - or δ -

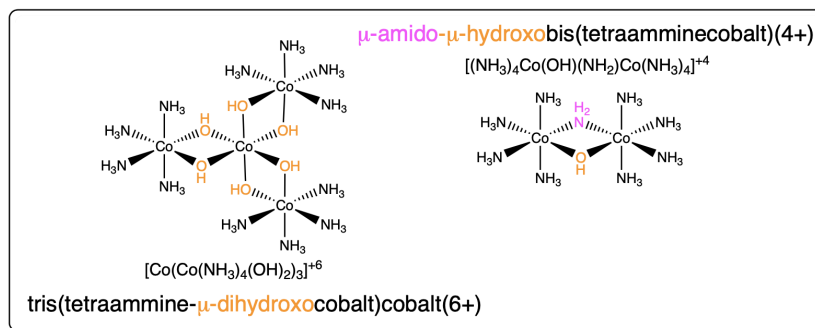
A example showing how the nomenclature rule is applied to a ligand that can have two coordination modes is given in Scheme 9.3.IV.

Scheme 9.3.IV. Use of the κ notation to specify the number of attached groups in a multidentate ligand.



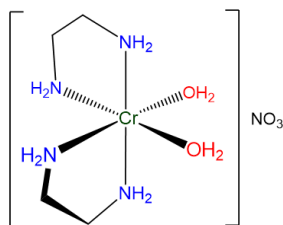
Scheme 9.3.V. The names of the complexes follow the rules described in 9.2.6: [multinuclear coordination complexes](#).

Scheme 9.3.V. Use of the μ notation to specify bridging ligands in metal complexes.³



6. If desired, parentheses *may* be used to delineate a ligand name to make it easier to identify in the name of the complex. This can be particularly helpful when the entire name contains a lot of information to keep track of. An example is given in Scheme 9.3.VI.

Scheme 9.3.VI. When naming the complex shown, *cis*-diaquabis(ethylenediamine)chromium(III) nitrate is easier to read than *cis*-diaquabisethylenediaminechromium(III) nitrate.



Rule 4: Specify the identity of the metal

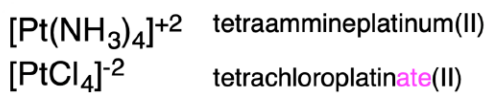
- In neutral and cationic complexes the metal's name is used directly
- *e.g.* as in hexammineruthenium(III) for $[\text{Ru}(\text{NH}_3)_6]^{3+}$
- In anionic complexes, *-ate* replaces *-ium*, *-en*, or *-ese* or adds to the metal name,
e.g., as in hexachloromanganate(IV) for MnCl_6^{2-}
- In anionic complexes of some metals a Latin-derived name is used instead of the element's English name. These names are given in Table 9.3.5.

Table 9.3.5. Latin terms for select metal Ions. Redrawn from this page describing the [nomenclature of coordination complexes](#).

Transition Metal	Latin
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

An example of the application of the metal naming rules is given in Scheme \sf{\PageIndex{VII}}).

Scheme 9.3.VII. Example of the application of the metal specification rules to a cationic and an anionic platinum complex.³

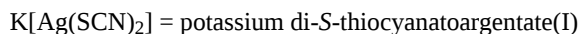
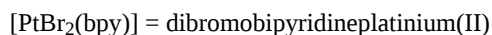
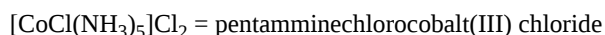


Rule 5: Specify the oxidation state of the metal.

Two different systems are used to specify the oxidation state of the metal.

- In the **Stock system** the metal's oxidation state is indicated in Roman numerals after the metal name.

Examples:



- In the **Ewing-Bassett system** the charge on the complex is specified in Arabic numerals after the complex name. This provides a way of specifying a complex even when the oxidation state of the metal isn't known and, in cases where it is known, the value

of the metal's oxidation state may be inferred from the complex ion's charge.

$[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ = pentamminechlorocobalt(2+) chloride

$[\text{PtBr}_2(\text{bpy})]$ = dibromobipyridineplatinum(0)

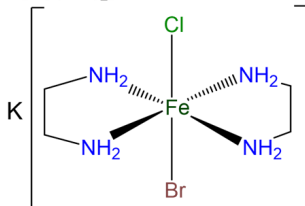
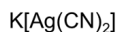
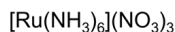
$\text{K}[\text{Ag}(\text{SCN})_2]$ = potassium di-S-thiocyanatoargentate(1-)

Summary of rules for naming coordination complexes.

A graphical summary of the **rules for naming complexes** along with a few examples that you can use to review the nomenclature rules is given in Figure 9.3.1. This work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

stereochemical prefix-	Specify Ligands	Indicate Metal	Charge on the complex or metal oxidation state
As appropriate use <i>cis-</i> , <i>trans-</i> , <i>fac-</i> , <i>mer-</i> , Λ -, Δ -, to indicate stereochemistry.	<p>What ligands and how many?</p> <ul style="list-style-type: none"> List alphabetically by ligand name <ul style="list-style-type: none"> Neutral – ligand name Cationic – ligand name Anionic – change last vowel to "o" Indicate # by di-, tri-, tetra-, etc. (or bis-, tris-, tetrakis-, etc. if there is a di-, tri-, tetra-, etc. in the ligand name) <p>As appropriate, how are the ligands arranged?</p> <ul style="list-style-type: none"> Ambidentate – indicate linkage point by κ & italicized element symbol other structure – use κ^n, η^n, μ_n, λ-, δ- <p>For clarity, parentheses may be used to delineate ligands</p>	<p>Neutral, cationic: English name</p> <p>Anionic – change ending to "ate"</p> <ul style="list-style-type: none"> Latin names for Ag, Au, Cu, Fe, Pb, Sn; English for others 	<p>Stock system: Metal Oxidation state in capital Roman numerals</p> <p>Ewing-Bassett system: Complex's charge in Arabic numerals</p>

Examples:



hexamineruthenium(3+) nitrate

or

hexamineruthenium(III) nitrate

potassium tetrachloroplatinate(2-)

or

potassium tetrachloroplatinate(II)

potassium dicyanoargentate(1-)

or

potassium dicyanoargentate(I)

potassium *trans*-bromochlorobis(ethylenediamine)iron(1+) (Ewing-Bassett)

-or-

potassium *trans*-bromochlorobis(ethylenediamine)iron(III) (Stock)

Figure 9.3.1. Summary of nomenclature rules for coordination complexes along with a few examples of their application.

When learning chemical nomenclature, practice makes perfect. The following examples and exercises are provided to give you this practice. Additional examples and exercises on the <https://chem.libretexts.org/> site include [a set of simple examples with explained solutions](#), [a set of simple exercises with solutions](#), and [a set of more challenging exercises without solutions](#).

? Exercise 9.3.2. Assigning metal oxidation states in a complex

In order to name a complex in the Stock system it is necessary to assign a formal oxidation state to the metal. For this reason it is important to be able to assign the oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state the ligands can be treated as having an oxidation state equal to their charge - *i.e.*, the charge they possess in the form in which they coordinate the metal, so if they need to lose a proton to bind, don't forget to account for that.

Given the above, assign the oxidation state of the metal in the following real and hypothetical complexes.

a. $\text{K}_3[\text{Fe}(\text{CN})_6]$

- b. $[\text{CoCl}(\text{NH}_3)_5](\text{NO}_3)_2$
- c. $\text{K}_2[\text{PtCl}_4]$
- d. $[\text{MnCl}(\text{por})]$
- e. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$
- f. $[\text{PdCl}_2(\text{dppe})]$
- g. $[\text{Mn}(\text{en})_2(\text{SCN})_2]$

Answer for $\text{K}_3[\text{Fe}(\text{CN})_6]^{3-}$.

This contains $[\text{Fe}(\text{CN})_6]^{3-}$; so $\text{O.S.}_{\text{Fe}} + 6 \times (-1)$ (for CN^-) = -3 (the complex's charge) so $\text{O.S.}_{\text{Fe}} = +3$ or Fe^{3+} .

Answer for $[\text{CoCl}(\text{NH}_3)_5](\text{NO}_3)_2$.

This contains $[\text{CoCl}(\text{NH}_3)_5]^{2+}$; so $\text{O.S.}_{\text{Co}} + 1 \times (-1)$ (for Cl^-) + 0×5 (for NH_3) = +2 (the complex's charge) so $\text{O.S.}_{\text{Co}} = +3$ or Co^{3+} .

Answer for $\text{K}_2[\text{PtCl}_4]$.

This contains 2K^+ and $[\text{PtCl}_4]^{2-}$; so $\text{O.S.}_{\text{Pt}} + 4 \times (-1)$ (for Cl^-) = -2 (the complex's charge) so $\text{O.S.}_{\text{Pt}} = +2$ or Pt^{2+} .

Answer for $[\text{MnCl}(\text{por})]$.

$\text{O.S.}_{\text{Pt}} + 1 \times (-2)$ (for por; see [table 9.2.2](#)) + $1 \times (-1)$ (for Cl^-) = +0 (the complex's charge) so $\text{O.S.}_{\text{Mn}} = +3$ or Mn^{3+} .

Answer $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$.

The complex is $[\text{Ru}(\text{bpy})_3]^{2+}$ so $\text{O.S.}_{\text{Ru}} + 0 \times 3$ (for bpy) = +2 (the complex's charge) so $\text{O.S.}_{\text{Ru}} = +2$ or Ru^{2+} .

Answer $[\text{PdCl}_2(\text{dppe})]$.

$\text{O.S.}_{\text{Pd}} + 2 \times (-1)$ (for Cl^-) + 0×3 (for dppe) = +0 (the complex's charge) so $\text{O.S.}_{\text{Pd}} = +2$ or Pd^{2+} .

Answer $[\text{Mn}(\text{en})_2(\text{SCN})_2]$.

$\text{O.S.}_{\text{Mn}} + (2 \times 0)$ (for en) + $2 \times (-1)$ (for SCN^-) = +0 (the complex's charge) so $\text{O.S.}_{\text{Mn}} = +2$ or Mn^{2+} .

? Exercise 9.3.3: Simple Nomenclature Problems.

Name the following compounds in both the Stock and Ewing-Bassett systems:

- a. $[\text{Ru}(\text{NH}_3)_6](\text{NO}_3)_3$
- b. $\text{K}_2[\text{PtCl}_4]$
- c. $\text{K}[\text{Ag}(\text{CN})_2]$
- d. $\text{Cs}[\text{CuBrCl}_2\text{F}]$
- e. $[\text{Cu}(\text{acac})_2]$

Answer

	Complex	Stock system name	Ewing-Bassett System name
a	$[\text{Ru}(\text{NH}_3)_6](\text{NO}_3)_3$	hexammineruthenium(III) nitrate	hexammineruthenium(3+) nitrate
b	$\text{K}_2[\text{PtCl}_4]$	potassium tetrachloroplatinate(II)	potassium tetrachloroplatinate(2-)
c	$\text{K}[\text{Ag}(\text{CN})_2]$	potassium dicyanoargentate(I)	potassium dicyanoargentate(1-)
d	$\text{Cs}_2[\text{CuBrCl}_2\text{F}]$	cesium bromodichlorofluorocuprate(I)	cesium bromodichlorofluorocuprate(2-)
e	$[\text{Cu}(\text{acac})_2]$	bis(acetylacetonato)copper(II)	bis(acetylacetonato)copper(0)

? Exercise 9.3.4: More simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems.

- $\text{Cu}(\text{OH})_4^-$
- $[\text{AuXe}_4]^{2+}$
- AuCl_4^-
- $\text{Fe}(\text{CN})_6^{3-}$
- $\text{K}_4[\text{Fe}(\text{CN})_6]$
- trans*- $[\text{Cu}(\text{en})_2(\text{NO}_2)_2]$ (the N is bound to Cu)
- cis*- $\text{IrCl}_2(\text{CO})(\text{PPh}_3)$ (ignore stereochemistry)
- $\text{IrCl}(\text{PPh}_3)_3$

Answer

	Compound	Stock System Name	Ewing-Bassett System Name
a	$\text{Cu}(\text{OH})_4^-$	tetrahydroxidocuprate(III) or tetrahydroxidocuprate(III)	tetrahydroxidocuprate(1-) or tetrahydroxidocuprate(1-)
b	$[\text{AuXe}_4]^{2+}$	tetraxenongold(II)	tetraxenongold(2+)
c	AuCl_4^-	tetrachloroaurate(III)	tetrachloroaurate(1-)
d	$\text{Fe}(\text{CN})_6^{3-}$	hexacyanoferrate(III) or hexacyanidoferrate(III)	hexacyanoferrate(3-) or hexacyanidoferrate(3-)
e	$\text{K}_4[\text{Fe}(\text{CN})_6]$	potassium hexacyanoferrate(II) or potassium hexacyanidoferrate(II)	potassium hexacyanoferrate(4-) or potassium hexacyanidoferrate(4-)
f	<i>trans</i> - $[\text{Cu}(\text{en})_2(\text{NO}_2)_2]$ (the N is bound to Cu)	bis(ethylenediamine)bisnitro copper(II) or bis(ethylenediamine)bis(nitrito- κ N)copper(II)	bis(ethylenediamine)bisnitro copper(0) or bis(ethylenediamine)bis(nitrito- κ N)copper(0)
g	<i>cis</i> - $\text{IrCl}_2(\text{CO})(\text{PPh}_3)$	<i>cis</i> -dichlorocarbonyltriphenylphosphineiridium(I) or <i>cis</i> -dichloro(carbonyl)(triphenylphosphine)iridium(I)	<i>cis</i> -dichlorocarbonyltriphenylphosphineiridium(0) or <i>cis</i> -dichloro(carbonyl)(triphenylphosphine)iridium(0)
h	$\text{IrCl}(\text{PPh}_3)_3$	chlorotris(triphenylphosphine)iridium(I)	chlorotris(triphenylphosphine)iridium(0)

? Exercise 9.3.5: Even more simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

- $\text{Fe}(\text{acac})_3$
- $\text{K}_2[\text{CuBr}_4]$
- ReH_9
- $[\text{Ag}(\text{NH}_3)_2]\text{BF}_4$
- $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$
- $[\text{Ni}(\text{CN})_4]^{2-}$
- $[\text{Co}(\text{N}_3)(\text{NH}_3)_5]\text{SO}_4$
- $[\text{CoBrCl}(\text{H}_2\text{O})(\text{NH}_3)]\text{I}$ (ignore stereochemistry)

Sample Answers

	Complex	Stock system name	Ewing-Bassett System name
a	$\text{Fe}(\text{acac})_3$	tris(acetoacetato)iron(III)	tris(acetoacetato)iron(0)
b	$\text{Na}_2[\text{CuBr}_4]$	sodium tetrabromocuprate(II)	sodium tetrabromocuprate(2-)
c	$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{ox})_3]$	hexamminecobalt(III) tris(oxalato)cobalt(III)	hexamminecobalt(3+) tris(oxalato)cobalt(3-)
d	$[\text{Ag}(\text{NH}_3)_2]\text{BF}_4$	diamminesilver(I) tetrafluoroborate	diamminesilver(1+) tetrafluoroborate
e	$[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$	diamminesilver(I) dicyanoargentate(I) or diamminesilver(I) dicyanidoargentate(I)	diamminesilver(1+) dicyanoargentate(1-) or diamminesilver(1+) dicyanidoargentate(1-)
f	$[\text{Ni}(\text{CN})_4]^{2-}$	tetracyanonickelate(II) or tetracyanonickelate(II) ion	tetracyanonickelate(2-) or tetracyanonickelate(2-) ion
g	$[\text{Co}(\text{N}_3)(\text{NH}_3)_5]\text{SO}_4$	pentammineazidocobalt(III) sulfate	pentammineazidocobalt(2+) sulfate
h	$[\text{CoBrCl}(\text{H}_2\text{O})(\text{NH}_3)]\text{I}$ (ignore stereochemistry)	ammineaquabromochlorocobalt(III) iodide	ammineaquabromochlorocobalt(1+) iodide

? Exercise 9.3.6: Nomenclature problems, some of which involve consideration of isomerism.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

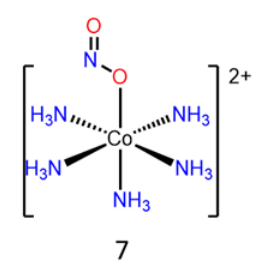
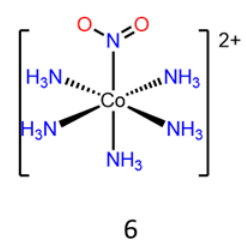
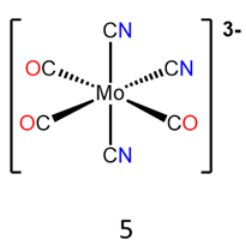
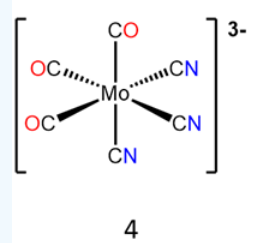
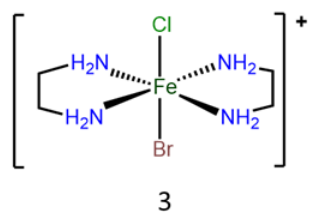
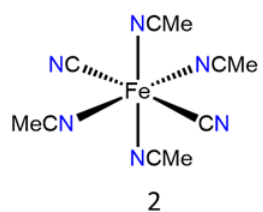
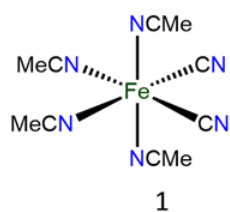
- $\text{trans}-[\text{Cu}(\text{dppe})_2(\text{NO}_2)_2]$ (the N is bound to Cu)
- $[\text{Pd}(\text{en})_2(\text{SCN})_2]$, with the thiocyanates bound Pd-SCN
- $[\text{Mn}(\text{CO})_6]\text{BPh}_4$ (BPh_4 = tetraphenylborate)
- $\text{Rb}[\text{AgF}_4]$
- K_2ReH_9
- K_3CrCl_6
- $[\text{Ru}(\text{H}_2\text{O})_6]\text{Cl}_2$
- $[\text{cis}-\text{Fe}(\text{CO})_4\text{I}_2]$
- $\text{K}_2[\text{trans}-\text{Fe}(\text{CN})_4(\text{CO})_2]$
- $[\text{cis}-\text{MnCl}(\text{H}_2\text{O})_4(\text{NH}_3)](\text{NO}_3)$
- $\text{K}_3[\text{fac}-\text{RuCl}_3(\text{PMe}_3)_3]$

Answer

	Complex	Stock system name	Ewing-Bassett System name
a	$\text{trans-[Cu(dppe)}_2\text{(NO}_2\text{)}_2\text{]}$	<i>trans</i> -bis(diphenylphosphinoethane)bisnitrocopper(II) or <i>trans</i> -bis(diphenylphosphinoethane)bis(nitrito- κ N)copper(II)	<i>trans</i> -bis(diphenylphosphinoethane)bisnitrocopper(0) or <i>trans</i> -bis(diphenylphosphino)ethane bis(nitrito- κ N)copper(0)
b	$[\text{Pd(en)}_2\text{(SCN)}_2]$, with the thiocyanates bound Pd-SCN	bis(ethylenediamine)bisthiocyanatopalladium(II) or bis(ethylenediamine)bis(thiocyanato-S)palladium(II) or bis(ethylenediamine)bis(thiocyanato- κ S)palladium(II)	bis(ethylenediamine)bisthiocyanatopalladium(0) or bis(ethylenediamine)bis(thiocyanato-S)palladium(0) or bis(ethylenediamine)bis(thiocyanato- κ S)palladium(0)
c	$[\text{Mn(CO)}_6]\text{BPh}_4$	hexacarbonylmanganese(I) tetraphenylborate	hexacarbonylmanganese(1+) tetraphenylborate
d	$\text{Rb[AgF}_4\text{]}$	rubidium tetrafluoroargentate(III)	rubidium tetrafluoroargentate(1-)
e	K_2ReH_9	potassium nonahydridorhenium(VII)	potassium nonahydridorhenium(2-)
f	K_3CrCl_6 or $\text{K}_3[\text{CrCl}_6]$	potassium hexachlorochromium(III) or potassium hexachloridochromium(III)	potassium hexachlorochromium(3-) or potassium hexachloridochromium(3-)
g	$[\text{Ru(H}_2\text{O)}_6]\text{Cl}_2$	hexaaquaruthenium(II) chloride	hexaaquaruthenium(2+) chloride
h	$[\text{cis-Fe(CO)}_4\text{I}_2]$	<i>cis</i> -tetracarbonyldiiodoiron(II)	<i>cis</i> -tetracarbonyldiiodoiron(0)
i	$\text{K}_2[\text{trans-Fe(CN)}_4\text{(CO)}_2]$	potassium <i>trans</i> -dicarbonyltetracyanoferrate(II)	potassium <i>trans</i> -dicarbonyltetracyanoferrate(2-)
j	$[\text{cis-MnCl(H}_2\text{O)}_4\text{(NH}_3\text{)}](\text{NO}_3)$	<i>cis</i> -amminetetraaquachloromanganese(0) nitrate	<i>cis</i> -amminetetraaquachloromanganese(1+) nitrate
k	$\text{K[fac-RuCl}_3\text{(PMe}_3\text{)}_3\text{]}$	potassium <i>fac</i> -trichlorotris(triphenylphosphine)ruthenium(II)	potassium <i>fac</i> -trichlorotris(triphenylphosphine)ruthenium(1-)

? Exercise 9.3.7

Name the compounds and ions below using both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.



Answer

#	Structure	Stock system name	Ewing-Bassett system name
1		<i>cis</i> -tetraacetonitriledicyanoiron(II) or <i>cis</i> -tetraacetonitriledicyanidoiron(II)	<i>cis</i> -tetraacetonitriledicyanoiron(0) or <i>cis</i> -tetraacetonitriledicyanidoiron(0)
2		<i>trans</i> -tetraacetonitriledicyanoiron(II) or <i>trans</i> -tetraacetonitriledicyanidoiron(II)	<i>trans</i> -tetraacetonitriledicyanoiron(0) or <i>trans</i> -tetraacetonitriledicyanidoiron(0)
3		<i>trans</i> -bromochlorobis(ethylenediamine)iron(III) or <i>trans</i> -bromidochloridobis(ethylenediamine)iron(III)	<i>trans</i> -bromochlorobis(ethylenediamine)iron(1+) or <i>trans</i> -bromidochloridobis(ethylenediamine)iron(1+)
4		<i>fac</i> -tricarbonyltricyanomolybdate(0) or <i>fac</i> -tricarbonyltricyanomolybdate(0)	<i>fac</i> -tricarbonyltricyanomolybdate(3-) or <i>fac</i> -tricarbonyltricyanomolybdate(3-)
5		<i>mer</i> -tricarbonyltricyanomolybdate(0) or <i>mer</i> -tricarbonyltricyanomolybdate(0)	<i>mer</i> -tricarbonyltricyanomolybdate(3-) or <i>mer</i> -tricarbonyltricyanomolybdate(3-)
6		pentamminenitrito- <i>N</i> -cobalt(III), pentamminenitrito- κ <i>N</i> -cobalt(III), or pentamminenitrocobalt(III)	pentamminenitrito- <i>N</i> -cobalt(2+), pentamminenitrito- κ <i>N</i> -cobalt(2+), or pentamminenitrocobalt(2+)
7		pentamminenitrito- <i>O</i> -cobalt(2+), pentamminenitrito- κ <i>O</i> -cobalt(2+), or pentamminenitritocobalt(2+)	pentamminenitrito- <i>O</i> -cobalt(2+), pentamminenitrito- κ <i>O</i> -cobalt(2+), or pentamminenitritocobalt(2+)

? Exercise 9.3.8

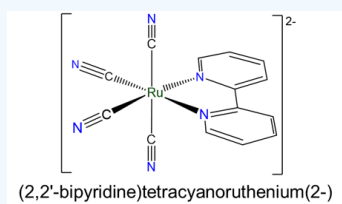
Draw structural formulae for the following compounds and ions. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal

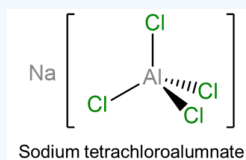
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I} , or Ir^{I} have a coordination number of four are square planar
 - other complexes in which the metal has a coordination number of four will be tetrahedral
- (2,2'-bipyridine)tetracyanoruthenium(2-)
 - sodium tetrachloroaluminate (note that since Al is a main group metal with a generally fixed oxidation state no oxidation state is given)
 - pentaamminechlorocobalt(2+) sulfate
 - carbonylhydridotris(triphenylphosphine)rhodium(I) (the ligands in this complex occupy sterically preferred positions)
 - bromotrichlorocobaltate(III)
 - hexaaquacopper(2+) sulfate
 - sodium tris(oxalato)cobalt(III)
 - fac*-(1,10-phenanthroline)tricarbonylchlororhenium(I)
 - mer*-triaquatrichlorochromium(III)
 - trans*-dichlorobis(ethylenediamine)platinum(IV)

Answers

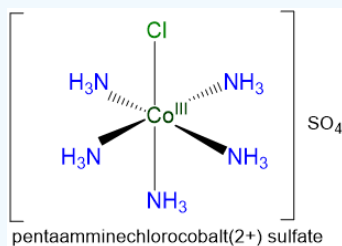
a



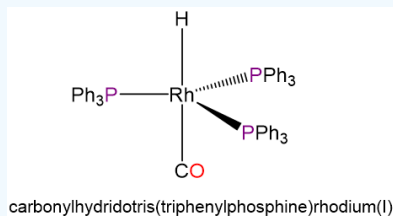
b



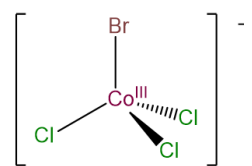
c



d

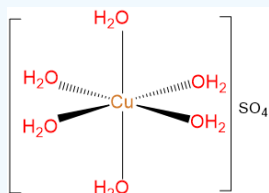


e



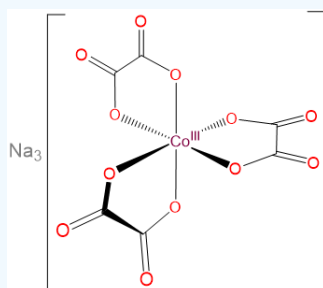
bromotrichlorocobaltate(III)

f



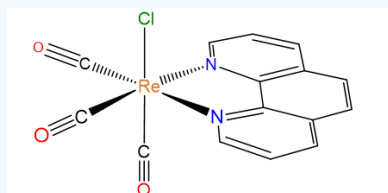
hexaaquacopper(2+) sulfate

g



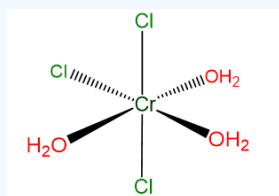
sodium tris(oxalato)cobalt(III)
Δ-enantiomer shown

h



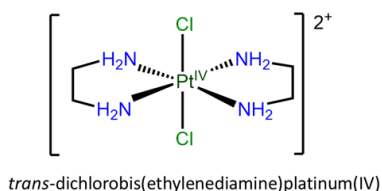
fac-(1,10-phenanthroline)tricarbonylchlororhenium(I)

i



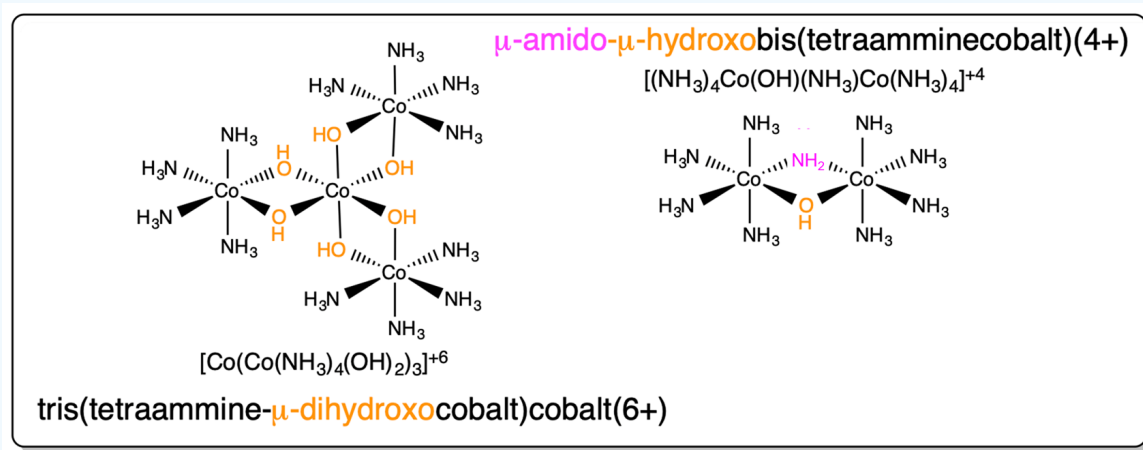
mer-triaquatrichlorochromium(III)

j



? Exercise 9.3.9.

The name of the structure named tris(tetraammine- μ -dihydroxocobalt)cobalt(6+) in Scheme 9.3.III (reproduced below) is incomplete. Give the complete name of the structure in both the Stock and Ewing-Basset systems.



Answer

Δ -tris(tetraammine- μ -dihydroxocobalt)cobalt(6+) or Δ -tris(tetraammine- μ -dihydroxocobalt(III)cobalt(III)

📌 Note: Rules for Writing the Formulae of Coordination Copounds

Rules for writing the formulae of coordination compounds

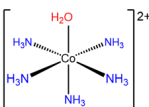
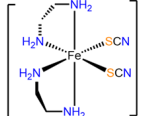
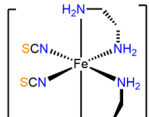
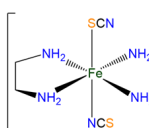
As organized predictable formulae can be easier to read and understand than haphazardly written ones, the rules for writing the formulae of coordination compounds have value. To support those who wish to employ them they are given in this section. The rules as given here are adapted from a [summary by Robert Lancashire](#).

The rules for writing the formulae of coordination compounds follow the same convention used to specify their names.

1. If there are multiple ions present list the cations before anions.
2. Enclose all the constituents of each complex ion in square brackets.
3. For each complex ion,
 - Give the **central metal** atom first.
 - Then **ligands** next, listed in alphabetical order, ignoring prefixes according to the first letters in the ligand's symbol as written. This is true regardless of whether the symbol is an element symbol (like C, N, O, etc.) or a symbol for the ligand name (bpy, en, MeCN, etc.). Contrary to widely-circulated myths, the ligand's charge does not matter.⁴
 - The formulae or abbreviations (e.g. en) for all polyatomic ligands should be enclosed in ordinary parentheses.
 - As appropriate, use italicized atom symbols to indicate linkage isomerism and prefixes such as *cis*-, *trans*-, *fac*-, *mer*-, Δ -, Δ -, κ^n , η^n , μ_n , λ -, or δ - to indicate stereochemistry.

- When a ligand is bound to a metal through a particular atom, preferably place that atom closest to the metal - e.g., $[\text{Fe}(\text{CN})_6]^{3-}$ not $[\text{Fe}(\text{NC})_6]^{3-}$ (Note: this rule is used primarily for ambidentate ligands; although IUPAC recommends that aqua ligands be written as OH_2 when the O would be closest to its coordinated metal, they are still usually written as H_2O).

These rules are graphically summarized in Figure 9.3.2.

<p>prefix- [Metal(oxidation state)(ligands)] charge\pm</p> <p>- or -</p> <p>prefix- [Metal oxidation state (ligands)] charge\pm</p> <p>- or -</p> <p>prefix- [Metal (ligands)] charge\pm</p>				<p>Examples:</p> <div style="display: flex; align-items: center;">  <div style="margin-left: 10px;"> $[\text{Co}(\text{II})(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$, $[\text{Co}^{\text{II}}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$, $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$, $[\text{Co}(\text{II})(\text{NH}_3)_5(\text{OH}_2)]^{2+}$, $[\text{Co}^{\text{II}}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$, or $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{2+}$ </div> </div> <div style="display: flex; align-items: center;">  <div style="margin-left: 10px;"> $\Delta\text{-cis-}[\text{Fe}(\text{II})(\text{en})_2(\text{SCN})_2]$, $\Delta\text{-cis-}[\text{Fe}^{\text{II}}(\text{en})_2(\text{SCN})_2]$, or $\Delta\text{-cis-}[\text{Fe}(\text{en})_2(\text{SCN})_2]$ </div> </div> <div style="display: flex; align-items: center;">  <div style="margin-left: 10px;"> $\Delta\text{-cis-}[\text{Fe}(\text{II})(\text{en})_2(\text{NCS})_2]$, $\Delta\text{-cis-}[\text{Fe}^{\text{II}}(\text{en})_2(\text{NCS})_2]$, or $\Delta\text{-cis-}[\text{Fe}(\text{en})_2(\text{NCS})_2]$ </div> </div> <div style="display: flex; align-items: center;">  <div style="margin-left: 10px;"> $\text{trans-}[\text{Fe}(\text{II})(\text{en})_2(\text{NCS})(\text{SCN})]$, $\text{trans-}[\text{Fe}^{\text{II}}(\text{en})_2(\text{NCS})(\text{SCN})]$, or $\text{trans-}[\text{Fe}(\text{en})_2(\text{NCS})(\text{SCN})]$ </div> </div>	
<p>As appropriate use <i>cis-</i>, <i>trans-</i>, <i>fac-</i>, <i>mer-</i>, Λ-, Δ-, etc.</p> <p>Usually goes before the brackets but may be placed inside to avoid ambiguity</p>	<p>Chemical symbol</p>	<p>Optional but use the stock system</p>	<p>Alphabetical by chemical symbol or abbreviation irrespective of ligand charge</p> <p>Preferably place attached atoms nearest the metal</p> <p>As appropriate, use κ^1, η^1, μ_2, λ-, δ-, to indicate structure</p>		

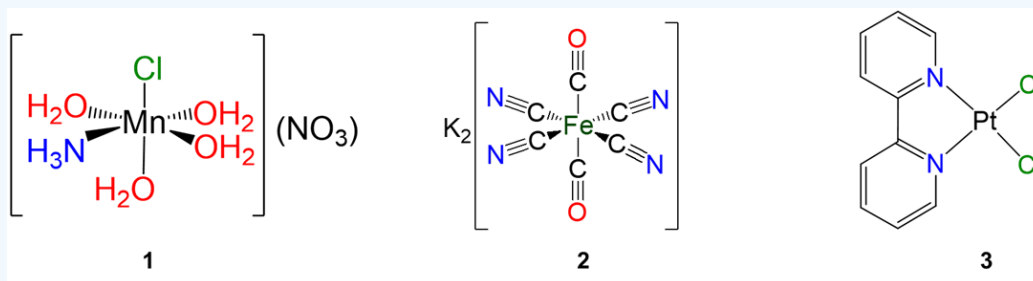
Multimetallic complexes:

- Place bridging ligands after others of the same type in order of bridging multiplicity (μ_4 then μ_3 then μ_2 , etc.)
- May write ligands and metals in a way that indicates structure (e.g. $[(\text{NH}_3)_5\text{Co}^{\text{III}}-\mu-(\text{OH})-\text{Cr}^{\text{II}}\text{Cl}_5]$ instead of $[\text{CoCrCl}_5(\text{NH}_3)_5-\mu-\text{OH}]$)

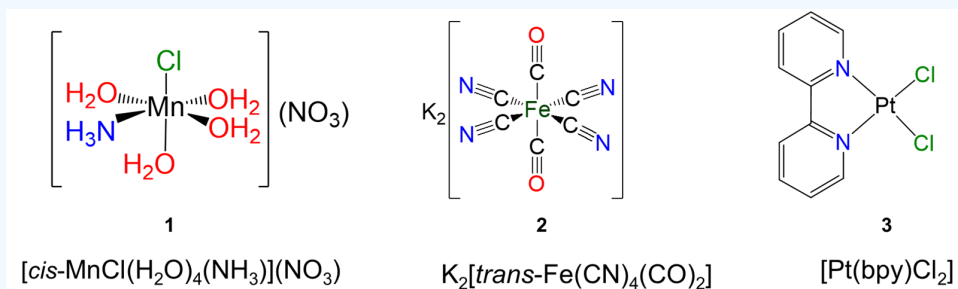
Figure 9.3.2. Summary of the rules for writing the formula of a coordination complexes along with a few examples of their application. This work by Stephen Contakes is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

? Exercise 9.3.10

Give the formulae of the following complexes.



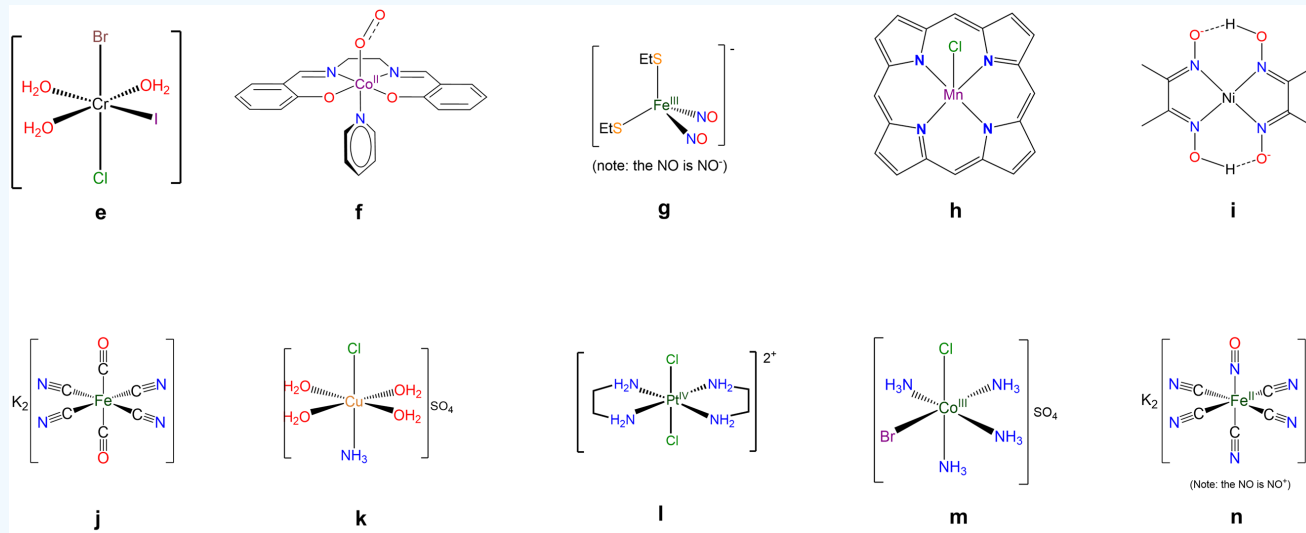
Answer



? Exercise 9.3.11

Write formulae for each of the following compounds and ions. When multidentate ligands are present use suitable abbreviations.

- pentaamminechlorocobalt(2+) sulfate
- Δ -diamminebis(oxalato)manganate(III)
- trans*-tetraacetonitriledicyanoiron(II)
- tricarbonyldichlorobis(triphenylphosphine)molybdenum



Answers

- $[\text{CoCl}(\text{NH}_3)_5](\text{SO}_4)$
- $\Delta\text{-}[\text{Mn}(\text{NH}_3)_2(\text{ox})_2]^-$
- trans*- $[\text{Fe}(\text{CN})_2(\text{NCMe})_4]$
- $[\text{MoCl}_2(\text{CO})_3(\text{PPh}_3)]$ or $\text{MoCl}_2(\text{CO})_3(\text{PPh}_3)$
- mer*- $[\text{CrBrCl}(\text{H}_2\text{O})_3\text{I}]$
- $[\text{Co}(\text{O}_2)\text{py}(\text{salen})]$
- $[\text{Fe}(\text{NO})_2(\text{SEt})_2]^-$
- $[\text{MnCl}(\text{por})]^-$ or $[\text{MnCl}(\text{porphyrin})]^-$

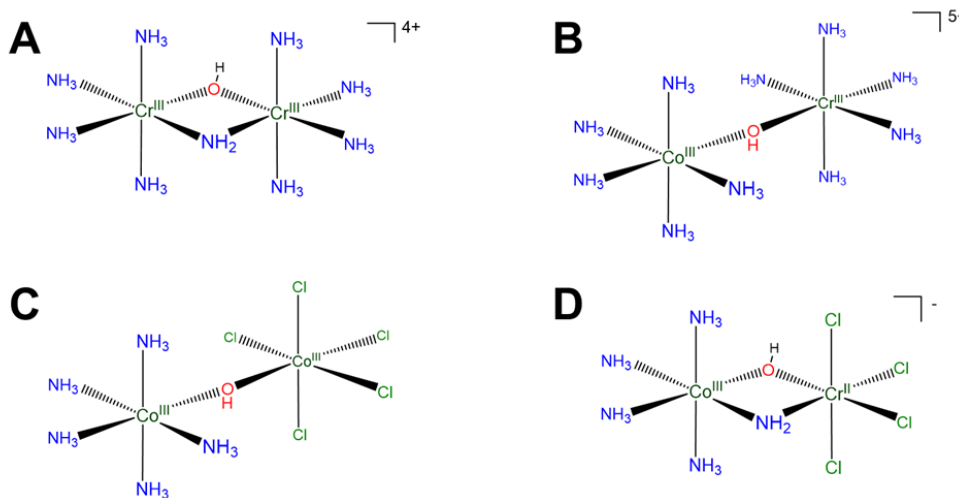
- i.
[Ni(DMG)₂] or [Ni(Hdmg)₂]
- j.
potassium *trans*-[Fe(CN)₂(CO)₄]
- k.
trans-[CuCl(H₂O)₄(NH₃)]SO₄
- l.
trans-[PtCl₂(en)₂]²⁺
- m.
cis-[CoBrCl(NH₃)₄]SO₄
- n.
K₂[Fe(CN)₅NO]

Multinuclear coordination complexes

Multinuclear coordination complexes contain multiple metals connected by one or more bridging ligands. The structures of bridging complexes can usually be inferred from their μ -tagged ligands in their names and formulae. For the benefit of instructors who wish to have their students name multinuclear complexes, the rules are presented below.

Multinuclear complexes are named differently depending on whether the groups on either side of the bridging ligands are identical or different, as shown in Scheme 9.3.VIII.

Scheme 9.3.VIII. Multinuclear coordination complexes may be named differently depending on whether the groups on either side of the bridging ligands are the same or different. The groups are the same if the metal, ligands, and ligand arrangement are identical. This is true in A but in B the metals differ, in C the ligands differ, and in D both the metal and ligands differ.



Naming multinuclear complexes

Let's look at the rules for naming symmetric and asymmetric multinuclear complexes.

Application of the IUPAC system and variants thereof to symmetric complexes

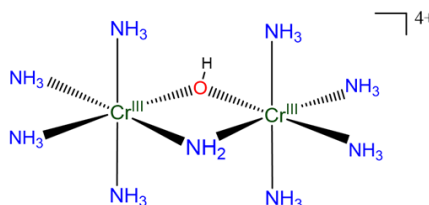
The IUPAC naming system helpfully avoids the sort of ambiguities and *ad hoc* choices involved in most textbook-level nomenclature systems for multimetallic complexes. Unfortunately, it is correspondingly difficult for beginners to employ. Thus it

will only be applied in depth to the case of symmetric complexes. Symmetric complexes are particularly easy to name in the IUPAC system and several of its variants that find common use. In these

1. The ligands are given in alphabetical order. When there are bridging and non-bridging ligands of the same type the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.*, μ_4^- , μ_3^- , μ_2^-), the bridging ligands are specified in decreasing order of bridging multiplicity, *e.g.*, μ_3 -sulfido-di- μ -sulfido.
2. The groups bridged are given afterwards using names that follow the ordinary rules. Generally this involves either
 - a. naming all the ligands followed by all the metals, in both cases using prefixes to indicate the number of each, or
 - b. naming each group of atoms individually as in the less formal naming system, using prefixes to indicate the number of ligands (this is an unofficial variant of the IUPAC system that some textbook authors seem to prefer).

These two rules are sufficient to describe simple symmetric bridging complexes.

Example: The compound in Scheme 9.3.VIIIA



may be named

[μ -amido- μ -hydroxo-octaamminedichromium(4+)] ion

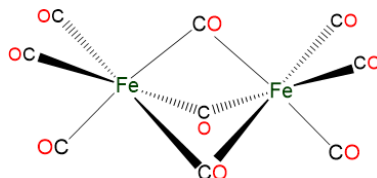
or

[μ -amido- μ -hydroxo-bis(tetraamminechromium(III))] ion

or

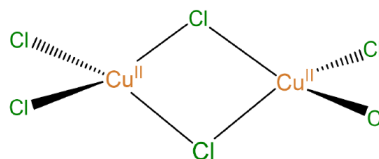
[μ -amido- μ -hydroxo-bis(tetraamminechromium)(4+)] ion

Example: The complex⁵



may be named [tri- μ -carbonyl-bis(tricarbonyliron)(0)], [tri- μ -carbonyl-bis(tricarbonyliron(0))], or [tri- μ -carbonyl-hexacarbonyldiiron(0)]

Example: The complex



may be named di- μ -chlorido-tetrachloridodicopper(II), di- μ -chlorido-bis(dichlorocopper(II)), or di- μ -chlorido-bis(dichlorocopper)(0)

A note on the application of the IUPAC system and variants thereof to asymmetric complexes

For a symmetrical complex like the $[\text{Cu}_2\text{Cl}_4(\mu\text{-Cl})_2]$ considered above it is enough to specify the existence of the two bridging and four terminal chloro ligands; there is no need to number the chloro ligands or to specify exactly which ones are involved in

bridging or to clarify that the bridging involves κ^2 coordination of the chloro ligands. In cases where the two metal centers or the chloro ligands differ it is necessary to specify the exact ligands and metals involved and how they are connected.

For example, a more extensive IUPAC name for $[\text{Cu}_2\text{Cl}_4(\mu\text{-Cl})_2]$ in which the chloro ligands are individually and more completely specified would read di- μ_2 -chlorido-tetrachlorido-1 κ^2 Cl,2 κ^2 Cl-dicopper(II).

Even more extensive systems would involve numbering the metals and specifying how they are connected together too. The details of how this is done are typically beyond the level of most undergraduate and graduate courses in inorganic chemistry. Those who want to know the details should consult [the red book](#). In many cases it is sufficient to reserve the use of formal IUPAC names for use in publications and to employ a convenient shorthand naming system for everyday use. An example of one type of system that is sometimes employed is given next.

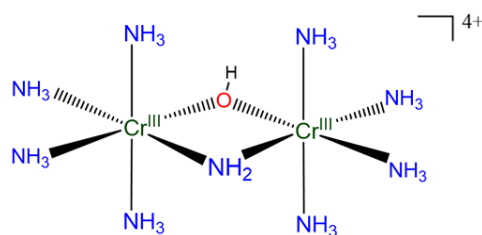
Unofficial but commonly used methods applicable to complexes in which the groups bridged are identical or different.

It can be quite complicated to use the IUPAC system to name asymmetric multinuclear coordination complexes. Fortunately it is rarely necessary and there are a variety of simpler somewhat *ad hoc* methods that work well for such cases. Since these methods are commonly used by textbooks and inorganic instructors it is likely worth your while to learn about their general features. In these methods

1. A multinuclear complex is named as a derivative of one of the metal centers and the other metal centers and their ligands are treated as ligands to the prioritized metal center.
2. Unfortunately, most of the time the choice of which metals are part of the ligands and which one is central is made haphazardly. In other words, there is no agreed upon system for assigning which metal center is the central metal and which should be regarded as part of the ligands around it. One way to be more systematic about the selection of the central and ligand-embedded metals is to assign the central metal as the metal of highest priority in the IUPAC priority rules. In the IUPAC priority rules, the central metal is the highest priority metal alphabetically by name; then if there is a tie the ligands on each tied metal center are ranked alphabetically and the tied metal center with the highest priority (or most highest priority) ligands wins.
3. The metal centers not chosen as the primary metal center and all ligands around them, including those bridging to the winning metal center, are then treated as a single ligand that coordinates the winning metal center.
4. When naming the ligands and the overall complex, again there is much that is haphazard. However, in the best systems each coordination sphere is named using the same rules as for mononuclear complexes - *i.e.*, the ligands are given in alphabetical order, etc.
 - This is true of any metal center-containing ligands.
 - When there is a bridging and non-bridging ligand of the same type, the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.* μ_4^- , μ_3^- , μ_2^-), the ligands are specified in decreasing order of bridging multiplicity, *e.g.* μ_3 -sulfido-di- μ -sulfido.

Let's apply these rules to the examples in Scheme 9.3.VIII.

Compound A:



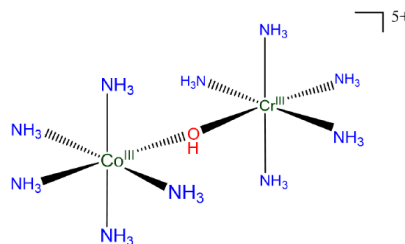
Using hydroxo for the OH^- , it may be named

$[(\mu\text{-amido-tetraammine-}\mu\text{-hydroxochromium(III)})\text{tetraamminechromium(III)}]$ ion

or

$[(\mu\text{-amido-tetraammine-}\mu\text{-hydroxochromium})\text{chromium(4+)}]$ ion

Compound B:



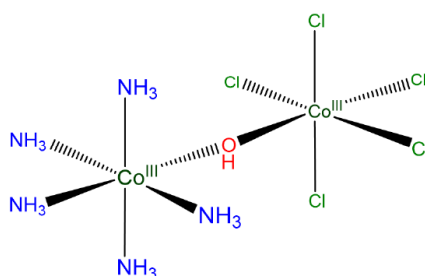
Using hydroxo for the OH^- , it may be named

[(pentaammine- μ -hydroxocobalt(III))tetraamminechromium(III)] ion

or

[(pentaammine- μ -hydroxocobalt)tetraamminechromium(5+)] ion

Compound C:



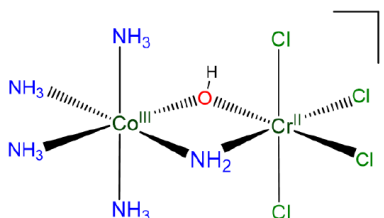
Using hydroxo for OH^- , it may be named

[pentaammine(pentachloro- μ -hydroxocobalt(III))cobalt(III)]

or

[pentaammine(pentachloro- μ -hydroxocobalt)cobalt](0)]

Compound D:



Using hydroxo for OH^- and chloro for Cl^- , it may be named

[pentaammine(pentachloro- μ -hydroxocobalt(III))chromate(III)] ion

or

[(tetrammine- μ -ammine- μ -hydroxocobalt)tetrachlorochromate](1-)] ion

As can be seen from the examples above this system gives serviceable names for multimetallic complexes but those names are not the IUPAC names and so should not be used to describe complexes outside of pedagogical and informal settings.

Writing and interpreting formulae for multinuclear complexes

The rules for writing formulae for multinuclear complexes are the same as for mononuclear ones with two added details:

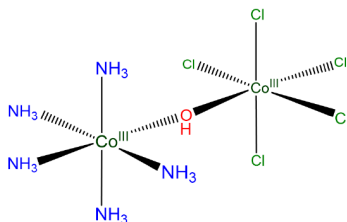
1. Write bridging ligands after nonbridging ligands of the same type. For example, Cu_2Cl_6 should be written as $[\text{Cu}_2\text{Cl}_4(\mu\text{-Cl})_2]$

2. However, you may ignore that and other rules if you find it helpful to keep groups of metals and ligands together in a way that better conveys how the atoms are connected. Just as the structure of ethane may be more clearly conveyed as H_3CCH_3 instead of CH_3CH_3 , the complex $[\text{Cu}_2\text{Cl}_4(\mu\text{-Cl})_2]$ may be written as $[(\text{Cl}_2\text{Cu})(\mu\text{-Cl})_2(\text{CuCl}_2)]$.

Other Examples:

For dichromate write, $[\text{Cr}_2\text{O}_6(\mu\text{-O})]^{2-}$ or $[\text{O}_5\text{Cr}-\mu\text{-O}-\text{CrO}_5]^{2-}$

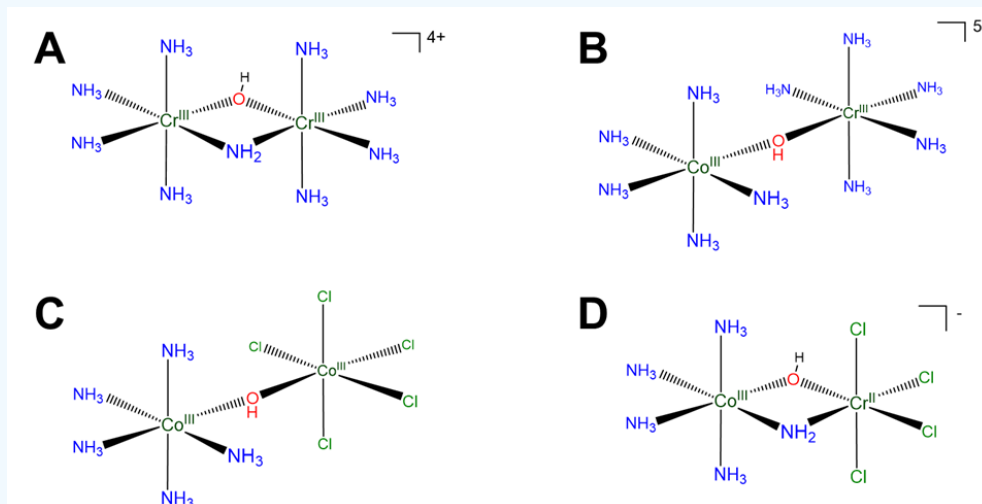
For compound C of Scheme 9.3.VIII.



write $[\text{Co}_2\text{Cl}_5(\text{NH}_3)_5(\mu\text{-OH})]$ or, even better, $[(\text{H}_3\text{N})_5\text{Co}(\mu\text{-OH})\text{CoCl}_5]$.

? Exercise 9.3.10

Write reasonable formulae for complexes A, B, and D in Scheme 9.3.VIII, which for convenience is reproduced below.



Sample answers for A

$[\text{Cr}_2(\text{NH}_3)_8-\mu(\text{NH}_2)-\mu(\text{OH})]^{4+}$ or $[(\text{H}_3\text{N})_4\text{Cr}^{\text{III}}-\mu(\text{NH}_2)-\mu(\text{OH})-\text{Cr}^{\text{II}}(\text{NH}_3)_4]$ and variants thereof involving writing the H_3N as NH_3 , μ as μ_2 , etc.

Sample answers for B

$[\text{CoCr}(\text{NH}_3)_{10}-\mu(\text{OH})]^{5+}$ or, better, $[(\text{H}_3\text{N})_5\text{Co}^{\text{III}}-\mu(\text{OH})-\text{Cr}^{\text{III}}(\text{NH}_3)_5]^{5+}$

Sample answers for C

This was already done as an example above, $[\text{Co}_2\text{Cl}_5(\text{NH}_3)_5-\mu(\text{OH})]$ or, better, $[(\text{NH}_3)_5\text{Co}^{\text{III}}-\mu(\text{OH})-\text{Co}^{\text{III}}\text{Cl}_5]$ and variants thereof

Sample answers for D

$[\text{CoCrCl}_4(\text{NH}_3)_4-\mu(\text{NH}_2)-\mu(\text{OH})]$ or, better, $[(\text{H}_3\text{N})_4\text{Co}^{\text{III}}-\mu(\text{NH}_2)-\mu(\text{OH})-\text{Cr}^{\text{II}}\text{Cl}_4]$

References

1. International Union of Pure and Applied Chemistry *Nomenclature of Inorganic Chemistry* Cambridge, UK, 2005.
2. The structure and name is taken from Choudhury, S. B.; Allan, C. B.; Maroney, M.; Wodward, A. D.; Lucas, C. R. *Inorg. Synth.* **1998**, 32, 98-107.

3. Haas, K. Naming Transition Metal Complexes.

[https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bioinorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-](https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bioinorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes)

[Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes](https://chem.libretexts.org/Courses/Saint_Mary's_College%2C_Notre_Dame%2C_IN/CHEM_342%3A_Bioinorganic_Chemistry/Readings/Week_2%3A_Introduction_to_Metal-Ligand_Interactions_and_Biomolecules/2.1_Transition_metal_complexes/2.1.6%3A_Naming_Transition_Metal_Complexes)

4. There is a widely-circulated myth that anionic ligands should be named before neutral ones. This myth is false. According to the IUPAC red book (bolding mine):

IR-2.15.3.4: Ordering ligands in formulae and names in formulae of coordination compounds,

The formulae or abbreviations representing the ligands **are cited in alphabetical order as the general rule**. Bridging ligands are cited immediately after terminal ligands of the same kind, if any, and in increasing order of bridging multiplicity. (See also Sections IR-9.2.3 and IR-9.2.5.)

IR-9.2.3.1 Sequence of symbols within the coordination formula

(i) The central atom symbol(s) is (are) listed first.

(ii) The **ligand symbols (line formulae, abbreviations or acronyms) are then listed in alphabetical order** (see Section IR-4.4.2.2).⁵ Thus, CH₃CN, MeCN and NCMe would be ordered under C, M and N respectively, and CO precedes Cl because single letter symbols precede two letter symbols. **The placement of the ligand in the list does not depend on the charge of the ligand.**

(iii) More information is conveyed by formulae that show ligands with the donor atom nearest the central atom; this procedure is recommended wherever possible, even for coordinated water.

5. Technically organometallic complexes are named according to slightly different rules but the coordination compound naming system works here. Note that this complex was once thought to possess an Fe-Fe bond, in accordance with the predictions of the 18-electron rule. Consequently, older sources often give an [Fe-Fe] after the name to reflect the presence of that bond. However, as the complex is no longer thought to possess an Fe-Fe bond it is omitted here.

Contributors and Attributions

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with some examples taken from [Naming Transition Metal Complexes](#) by Kathryn Haas.

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