CHAPTER 9: COORDINATION CHEMISTRY I: STRUCTURES AND ISOMERS

9.1

Hexagonal:	C_{2v}	C_{2v}	D_{2h}
Hexagonal pyramidal:	C_s	C_s	C_{2v}
Trigonal prismatic:	C_s	C_{2v}	C_2
Trigonal antiprismatic:	C_s	C_2	C_{2h}

The structures with C_2 symmetry would be optically active.

9.2 **a.** dicyanotetrakis(methylisocyano)iron(II) or dicyanotetrakis(methylisocyano)iron(0)

b. rubidium tetrafluoroargentate(III) or rubidium tetrafluoroargentate(1–)

c. *cis*- and *trans*-carbonylchlorobis(triphenylphosphine)iridium(I) or *cis*- and *trans*-carbonylchlorobis(triphenylphospine)iridium(0)

d. pentaammineazidocobalt(III) sulfate or pentaammineazidocobalt(2+) sulfate

e. diamminesilver(I) tetrafluoroborate(III) or diamminesilver(1+) tetrafluoroborate(1–) (The BF_4^- ion is commonly called “tetrafluoroborate.”)

9.3 **a.** tris(oxalato)vanadate(III) or tris(oxalato)vanadate(3–)

b. sodium tetrachloroaluminate(III) or sodium tetrachloroaluminate(1–)

c. carbonatobis(ethylenediamine)cobalt(III) chloride or carbonatobis(ethylenediamine)cobalt(1+) chloride

d. tris(2,2′-bipyridine)nickel(II) nitrate or tris(2,2′-bipyridine)nickel(2+) nitrate (The IUPAC name of the bidentate ligand, 2,2′-bipyridyl may also be used; this ligand is most familiarly called “bipy.”)

e. hexacarbonylmolybdenum(0) (also commonly called “molybdenum hexacarbonyl”). The (0) is often omitted.

9.4 **a.** tetraamminecopper(II) or tetraamminecopper(2+)

b. tetrachloroplatinate(II) or tetrachloroplatinate(2–)

c. tris(dimethyldithiocarbamato)iron(III) or tris(dimethyldithiocarbamato)iron(0)

d. hexacyanomanganate(II) or hexacyanomanganate(4–)

e. nonahydridorhenate(VII) or nonahydridorhenate(2–) (This ion is commonly called “enneahydridorhenate.”)

9.5 **a.** triamminetrichloroplatinum(IV) or triamminetrichloroplatinum(1+)

b. diamminediaquadichlorocobalt(III) or diamminediaquadichlorocobalt(1+)

c. diamminediaquabromochlorocobalt(III) or diamminediaquabromochlorocobalt(1+)

d. triaquabromochloroiodochromium(III) or triaquabromochloroiodochromium(0)

e. dichlorobis(ethylenediamine)platinum(IV) or dichlorobis(ethylenediamine)platinum(2+)
or dichlorobis(1,2-ethanediamine)platinum(IV) or dichlorobis(1,2-ethanediamine)platinum(2+)

f. diamminedichloro(*o*-phenanthroline)chromium(III) or diamminedichloro(*o*-phenanthroline)chromium(1+) or diamminedichloro(1,10-phenanthroline)chromium(III)
or diamminedichloro(1,10-phenanthroline)chromium(1+)

g. bis(2,2′-bipyridine)bromochloroplatinum(IV) or bis(2,2′-bypyridine)bromochloroplatinum(2+)
or bis(2,2′-bipyridyl)bromochloroplatinum(IV) or bis(2,2′-bipyridyl)bromochloroplatinum(2+)

h. dibromo[*o*-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(II) or
dibromo[*o*-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(0) or
dibromo[1,2-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(II) or
dibromo[1,2-phenylene(dimethylarsine)(dimethylphosphine)]rhenium(0)

i. dibromochlorodiethylenetriaminerhenium(III) or
dibromochlorodiethylenetriaminerhenium(0) or dibromochloro(2,2′-
diaminodiethylamine)rhenium(III) or dibromochloro(2,2′-
diaminodiethylamine)rhenium(0)

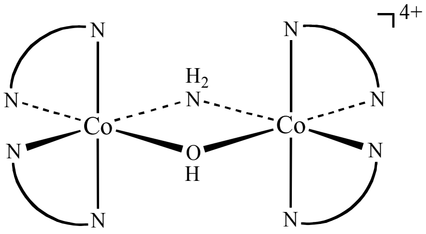
9.6 **a.** dicarbonylbis(dimethyldithiocarbamato)ruthenium(III) or dicarbonylbis(dimethyldithiocarbamato)ruthenium(1+)

b. trisoxalatocobaltate(III) or trisoxalatocobaltate(3–)

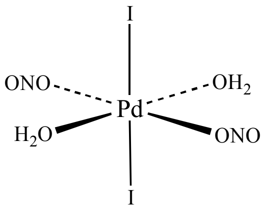
c. tris(ethylenediamine)ruthenium(II) or tris(ethylenediamine)ruthenium(2+)

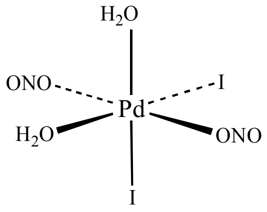
d. bis(2,2′-bipyridine)dichloronickel(II) or bis(2,2′-bipyridine)dichloronickel(2+)

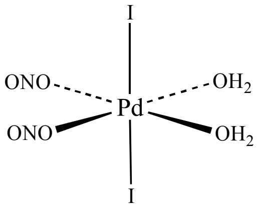
9.7 **a.** Bis(en)Co(III)-μ-amido-μ-hydroxobis(en)Co(III)

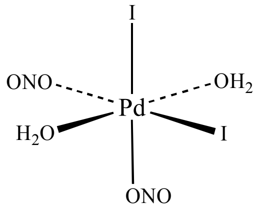


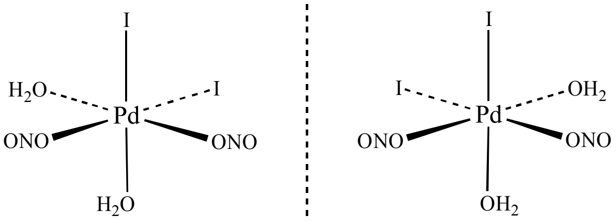
b. Diaquadiiododinitritopalladium(IV)





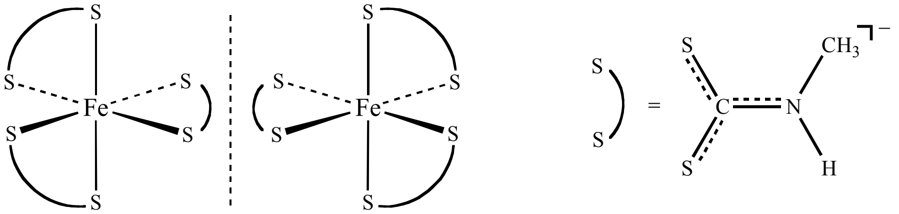






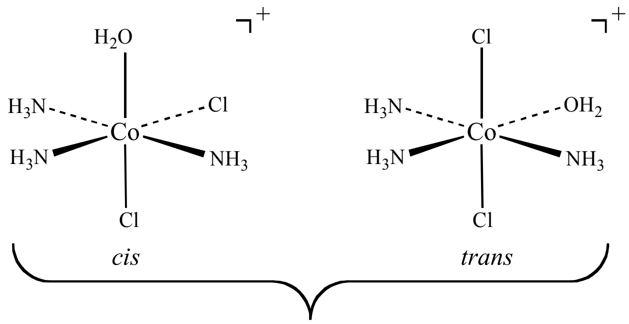
enantiomers

c. Fe(dtc)$_3$



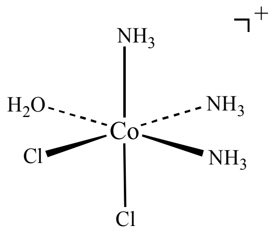
At low temperature, restricted rotation about the C—N bond can lead to additional isomers as a consequence of the different substituents on the nitrogen. These isomers can be observed by NMR.

9.8 **a.** triammineaquadichlorocobalt(III) chloride Isomers are of the cation:



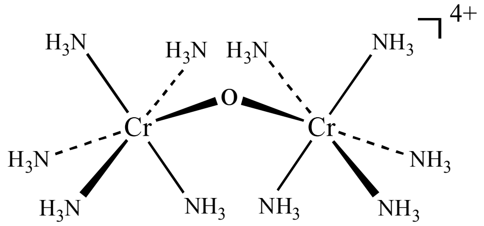
cis *trans*

mer

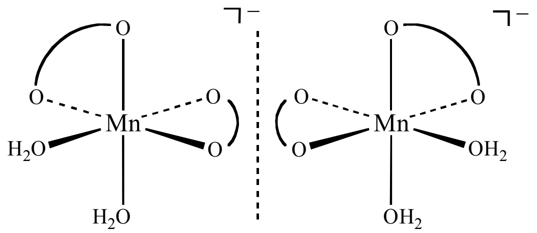


fac

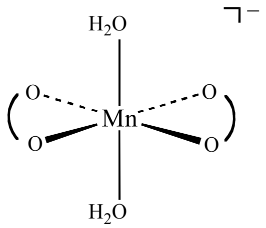
b. μ-oxo-bis(pentammine-chromium(III)) ion



c. potassium diaquabis(oxalato)manganate(III) Isomers are of the anion:

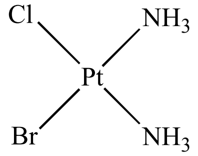


cis enantiomers

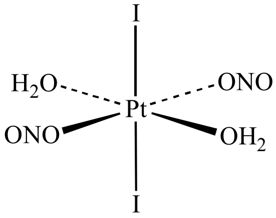


trans

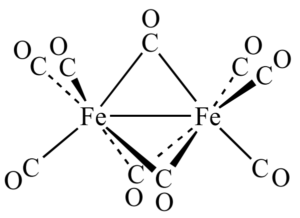
9.9 **a.** *cis*-diamminebromochloroplatinum(II)



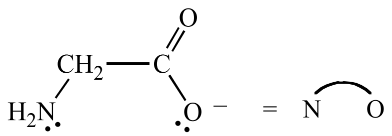
b. diaquadiiododinitritopalladium(IV)

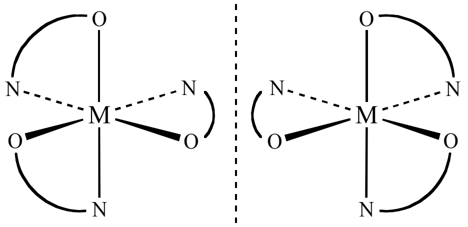


c. tri-μ-carbonylbis(tricarbonyliron(0))

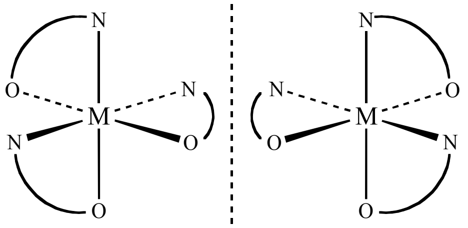


9.10



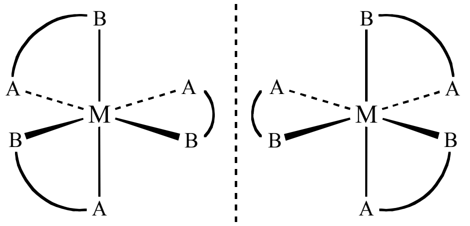


fac

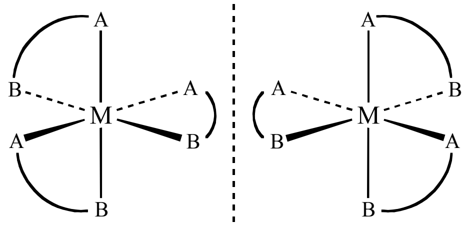


mer

9.11 M(AB)$_3$

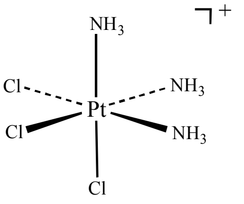


fac

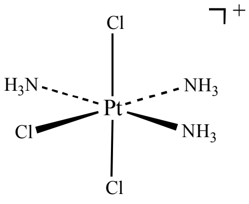


mer

9.12 **a.** $[Pt(NH_3)_3Cl_3]^+$

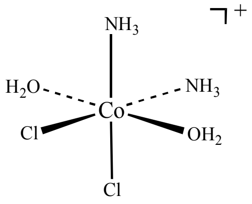


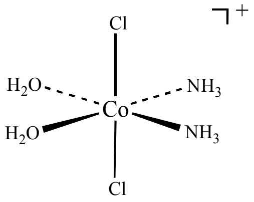
fac

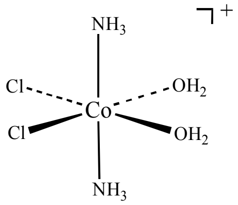


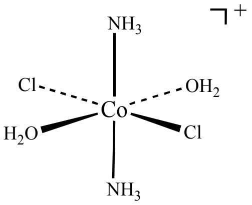
mer

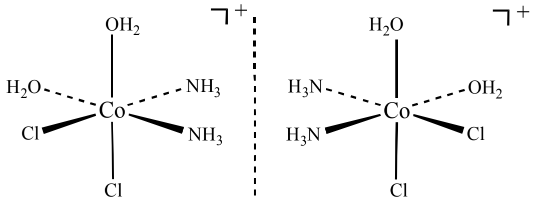
b. $[Co(NH_3)_2(H_2O)_2Cl_2]^+$





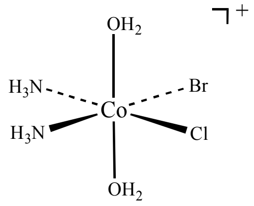


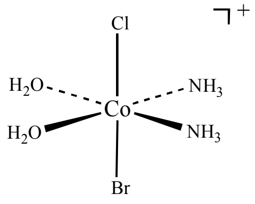


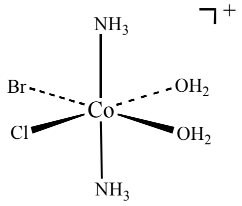


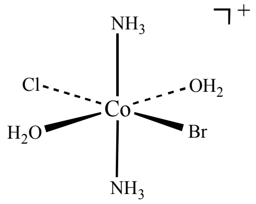
enantiomers

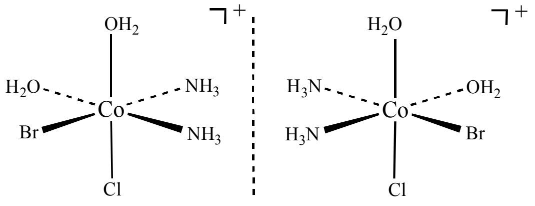
c. $[Co(NH_3)_2(H_2O)_2BrCl]^+$



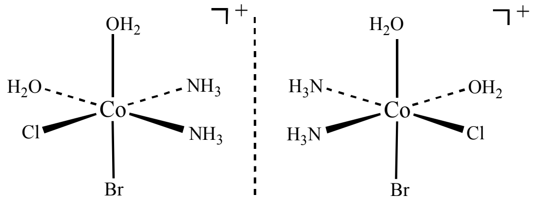






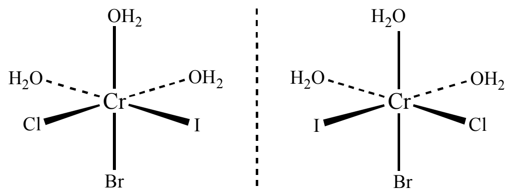


enantiomers

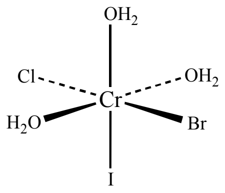


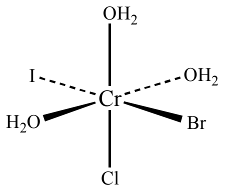
enantiomers

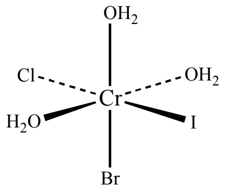
d. $Cr(H_2O)_3BrClI$



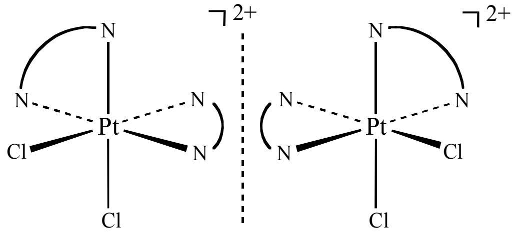
enantiomers



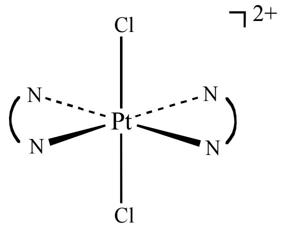




e. $[Pt(en)_2Cl_2]^{2+}$

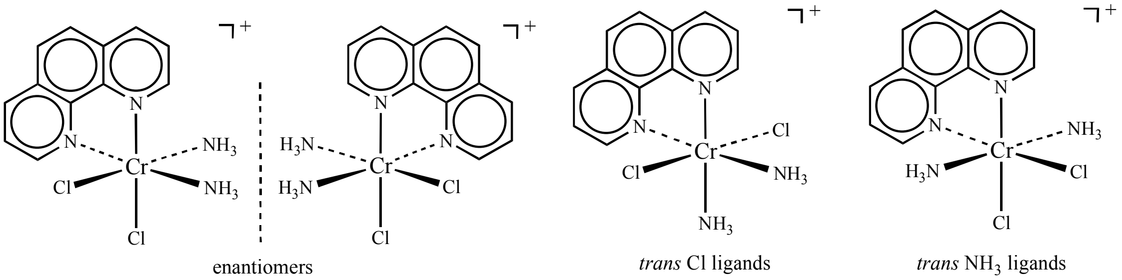


cis enantiomers

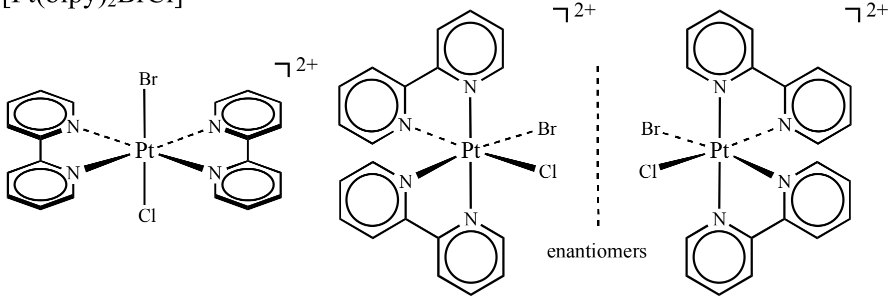


trans

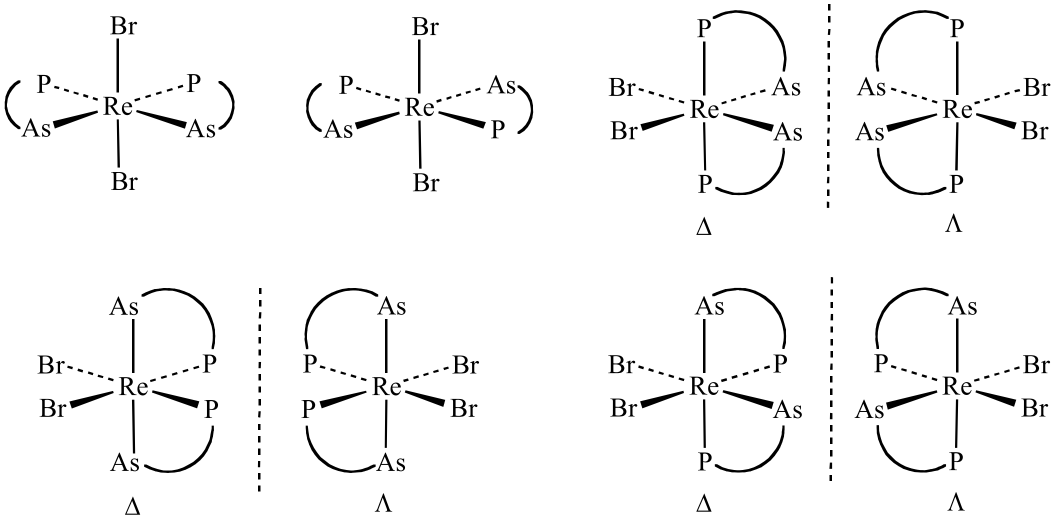
f. $[Cr(o\text{-phen})(NH_3)_2Cl_2]^+$



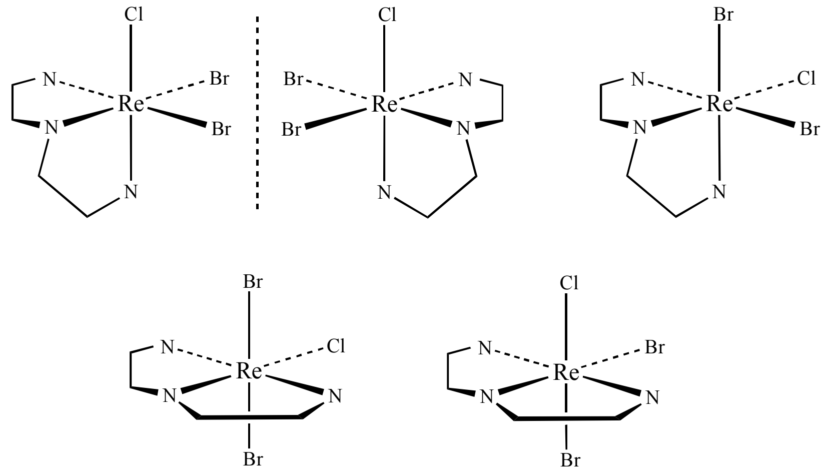
g. $[Pt(bipy)_2BrCl]^{2+}$



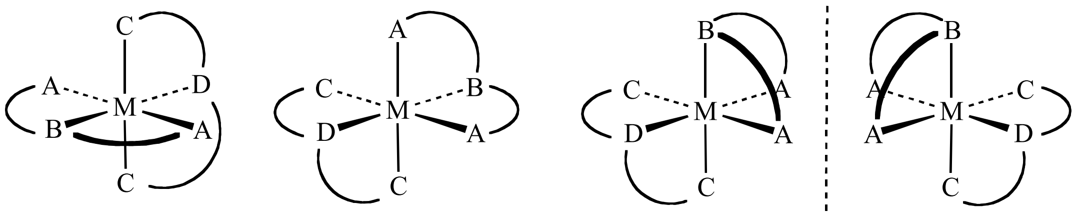
h. $Re(arphos)_2Br_2$ Abbreviating the bidentate ligands As⌒P:



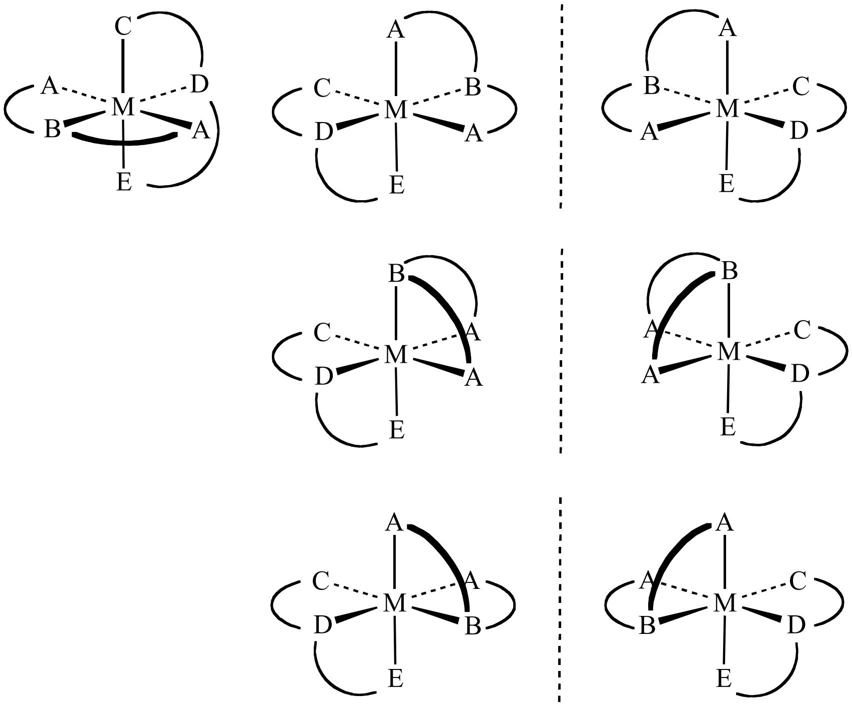
i. Re(dien)Br_2Cl



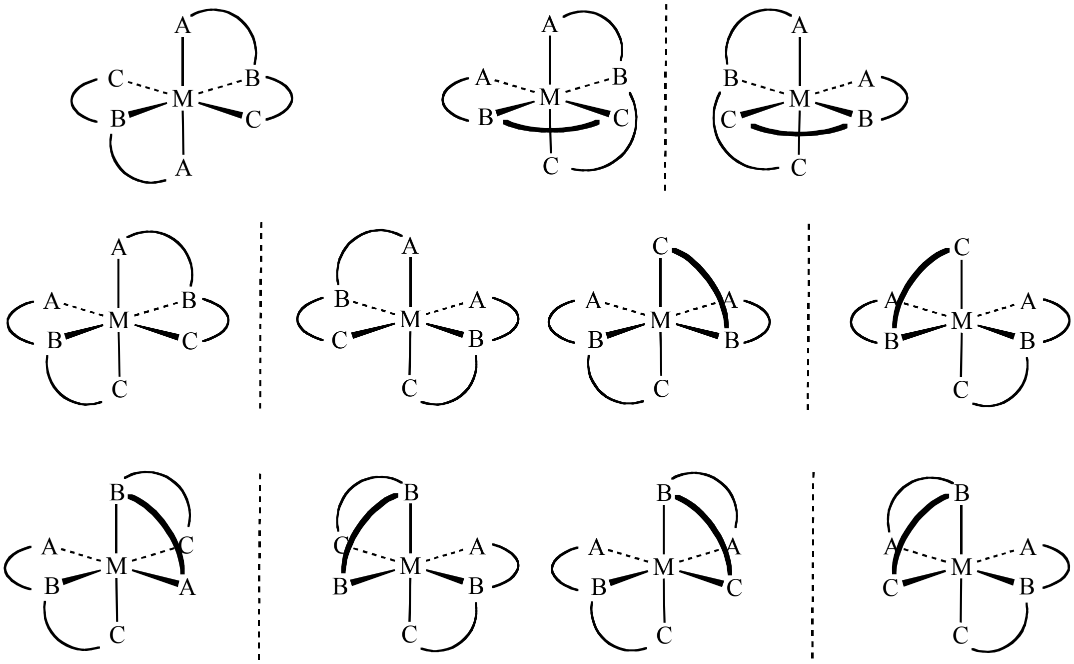
9.13 **a.** M(ABA)(CDC)



b. M(ABA)(CDE)

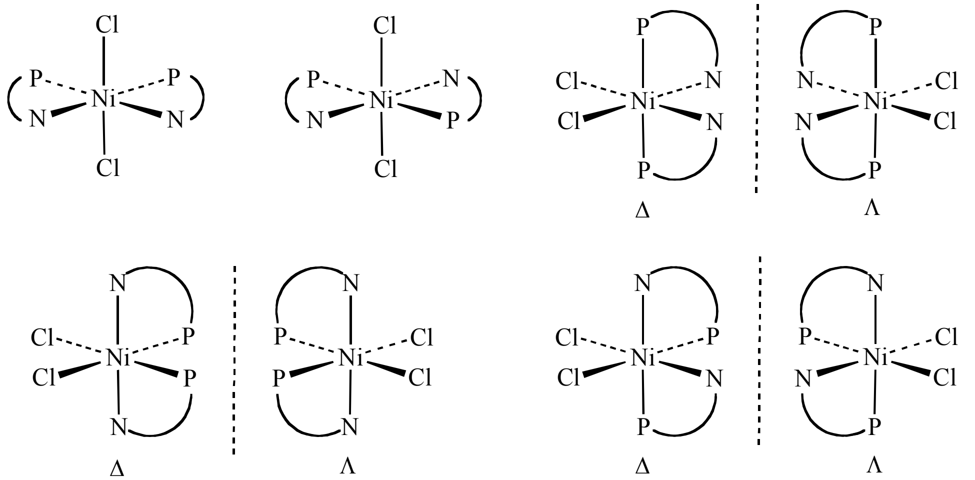


9.14

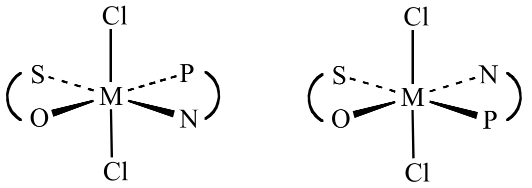


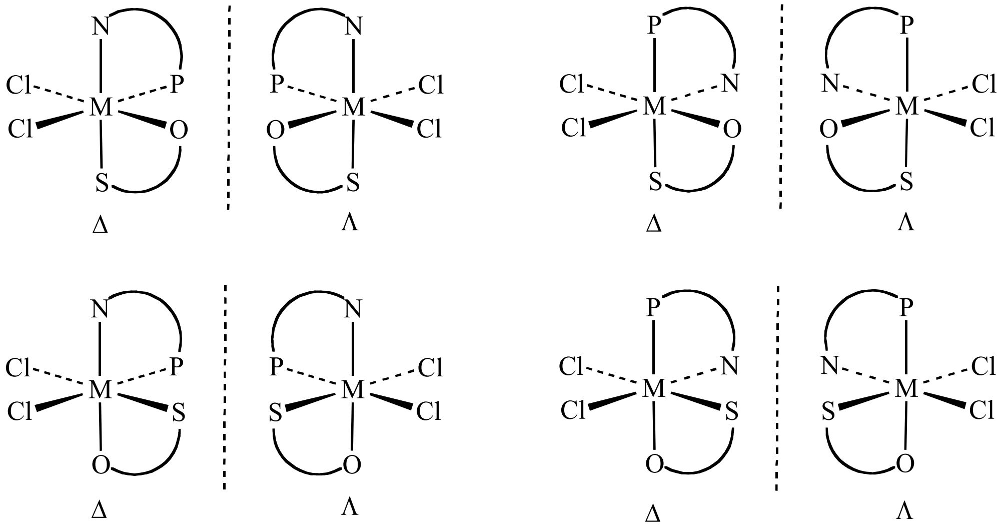
9.15 **a.** The “softer” phosphorus atom bonds preferentially to the soft metal Pd (see Section 6.6.1).

b, c. Abbreviating the bidentate ligands $\overset{\frown}{\mathrm{N\ \ P}}$:

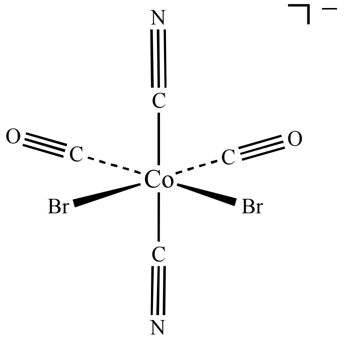


9.16 **a, b.** Abbreviating the bidentate ligands $\overset{\frown}{\text{N P}}$ and $\overset{\frown}{\text{O S}}$:

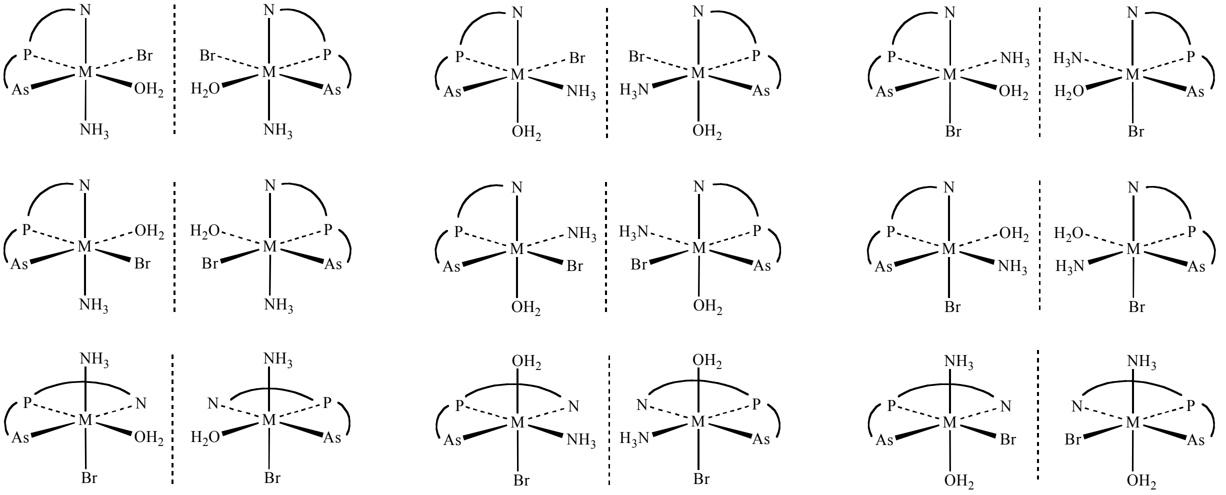




9.17 The single C–N stretching frequency indicates a *trans* structure for the cyanides (the symmetric stretch of the C—N bonds is not IR active), while the two C–O bonds indicate a *cis* structure for the carbonyls (both the symmetric and antisymmetric C–O stretches are IR active). As a result, the bromo ligands are also *cis*.



9.18 There are 18 isomers overall, six with the chelating ligand in a *mer* geometry and 12 with the chelating ligand in a *fac* geometry. All are enantiomers. They are all shown below, with dashed lines separating the enantiomers.

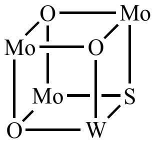


9.19 **a.** Δ **b.** Δ **c.** Λ **d.** Δ

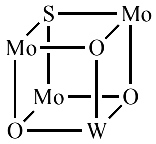
9.20 All are chiral if the ring in **b** does not switch conformations.

9.21 **20b** δ **20c** top ring: δ, bottom ring: λ

9.22 **a, b.** **1.**

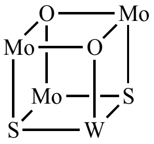


C_s

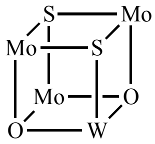


C_{3v}

2.

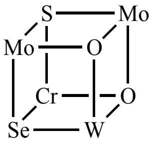


C_s

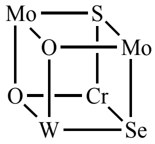


C_s

3.



C_1



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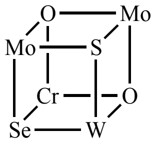

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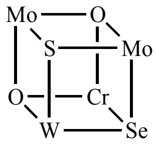

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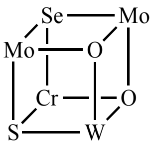

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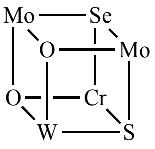
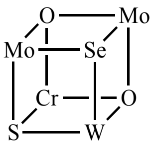


C_1



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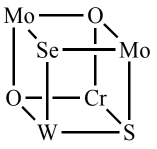
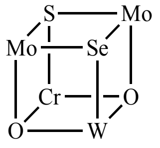
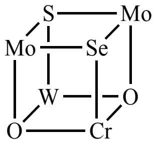


C_1



C_s



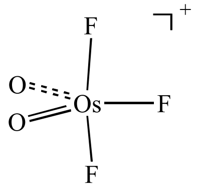
C_s

c. Yes, provided the structure has no symmetry or only C_n axes. Examples are the structures with C_1 symmetry in part **a**.

9.23 The ^{19}F doublet is from the two axial fluorines (split by the equatorial fluorine).

The ^{19}F triplet is from the equatorial fluorine (split by the two axial fluorines).

The two doubly bonded oxygens are equatorial, as expected from VSEPR considerations. Point group: C_{2v}



9.24 Examples include both cations and anions:

$[Cu(CN)_2]^-$, $[Cu_2(CN)_3]^-$, $[Cu_3(CN)_4]^-$, $[Cu_4(CN)_5]^-$, $[Cu_5(CN)_6]^-$
$[Cu_2(CN)]^+$, $[Cu_3(CN)_2]^+$, $[Cu_4(CN)_3]^+$, $[Cu_5(CN)_4]^+$, $[Cu_6(CN)_5]^+$

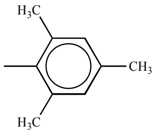
Based primarily on calculations (rather than experimental data), Dance et al. proposed linear structures such as the following:

$[Cu(CN)_2]^-$: NC—Cu—CN
$[Cu_2(CN)_3]^-$: NC—Cu—CN—Cu—CN
$[Cu_3(CN)_4]^-$: NC—Cu—CN—Cu—CN—Cu—CN
$[Cu_2(CN)]^+$: Cu—CN—Cu
$[Cu_3(CN)_2]^+$: Cu—CN—Cu—CN—Cu
$[Cu_4(CN)_3]^+$: Cu—CN—Cu—NC—Cu—CN—Cu

Where 2-coordinate copper appears in these ions, the geometry around the Cu is linear, as expected from VSEPR.

9.25 The bulky mesityl groups cause sufficient crowding that the phosphine ligands can show chirality (C_3 symmetry) and can be considered as similar to left-handed (P_L) and right-handed (P_R) propellers. If two P(mesityl)$_3$ phosphines are attached in a linear arrangement to a gold atom, three isomers are possible:

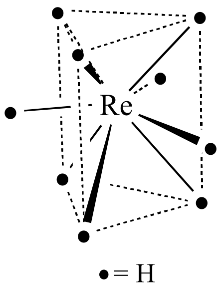
P_L—Au—P_L P_R—Au—P_R P_L—Au—P_R



mesityl

(P_R—Au—P_L is equivalent to P_L—Au—P_R, as can best be seen with models.) NMR data at low temperature support the presence of these isomers, which interconvert at higher temperatures.

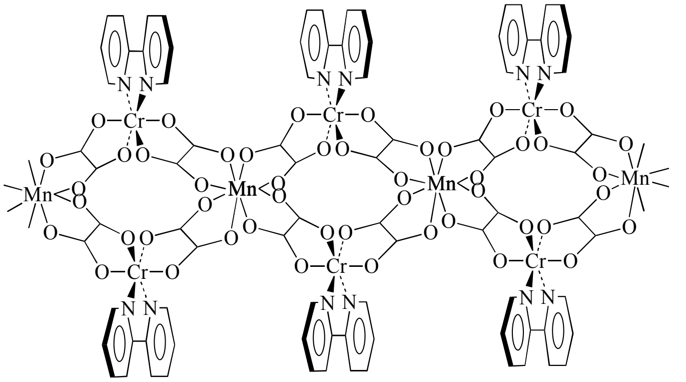
9.26 The point group is D_{3h}. A representation Γ based on the nine 1*s* orbitals of the hydride ligands is:



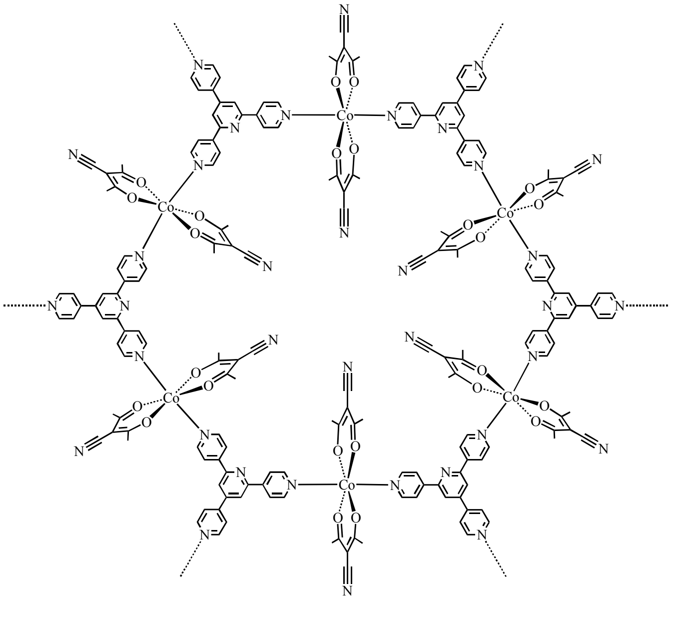
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	9	0	1	3	0	3	
A_1'	1	1	1	1	1	0	z^2
E'	2	–1	0	2	–1	0	(x, y), $(x^2–y^2, xy)$
A_2''	1	1	–1	–1	–1	1	z
E''	2	–1	0	–2	1	0	(xz, yz)

The representation Γ reduces to $2\,A_1' + 2\,E' + A_2'' + E''$. Collectively these representations match all the functions for *s* (totally symmetric, matching A_1'), *p*, and *d* orbitals of Re, so all the *s*, *p*, and *d* orbitals of the metal have suitable symmetry for interaction. (The strength of these interactions will also depend on the match in energies between the rhenium orbitals and the 1*s* orbital of hydrogen.)

9.27



9.28



9.29 **a.** Cu(acacCN)$_2$: D_{2h} tpt: C_{2v}

b. C_6

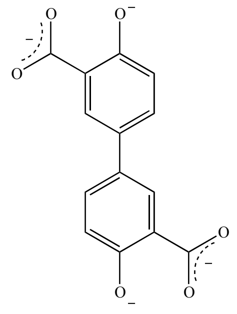
9.30 All four metal-organic frameworks studied (MOF-177, Co(BDP), Cu-BTTri, $\mathrm{Mg_2(dobdc)}$) are significantly more effective at adsorbing carbon dioxide relative to adsorbing hydrogen. This is attributed, in part, to the higher polarizability of $\mathrm{CO_2}$ relative to that of $\mathrm{H_2}$. The formation of an induced dipole in these gases by exposed cations within MOFs is an important prerequisite for adsorption. The two MOF properties that most strongly correlate with $\mathrm{CO_2}$ adsorption capacity are MOF surface area and MOF accessible pore volume. As these values (tabulated below) increase, the $\mathrm{CO_2}$ adsorption capacity increases.

MOF	Surface Area (m^2/g)	Accessible Pore Volume (cm^3/g)
MOF-177	4690	1.59
Co(BDP)	2030	0.93
Cu-BTTri	1750	0.713
$\mathrm{Mg_2(dobdc)}$	1800	0.573

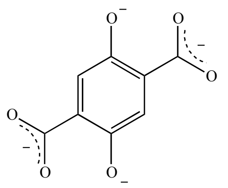
The graphs in Figure 1 of the reference clearly indicate that $\mathrm{Mg_2(dobdc)}$ adsorbs the most $\mathrm{CO_2}$ at 5 bar. The arrangement and concentration of open $\mathrm{Mg^{2+}}$ cation sites on the $\mathrm{Mg_2(dobdc)}$ surface is hypothesized to render this MOF more susceptible to $\mathrm{CO_2}$ adsorption. This MOF, along with Cu-BTTri, which also features exposed metal sites, are identified as the best prospects for $\mathrm{CO_2/H_2}$ separation.

9.31 The synthesis and application of amine-functionalized MOFs for $\mathrm{CO_2}$ adsorption is the general topic of the reference. While the $\mathrm{M_2(dobdc)}$ series of MOFs were proposed as excellent candidates for this functionalization (on the basis of their relatively large concentration of exposed metal cation sites), their amine-functionalization proved difficult. This was attributed to the relatively narrow MOF channels that may hinder amine diffusion into $\mathrm{M_2(dobdc)}$.

One hypothesized solution was to prepare a MOF with the $\mathrm{M_2(dobdc)}$ structure-type, but with larger pores. The wider linker dobpdc (below, along with dobdc for comparison) was used in the hope of obtaining MOFs with larger pores.



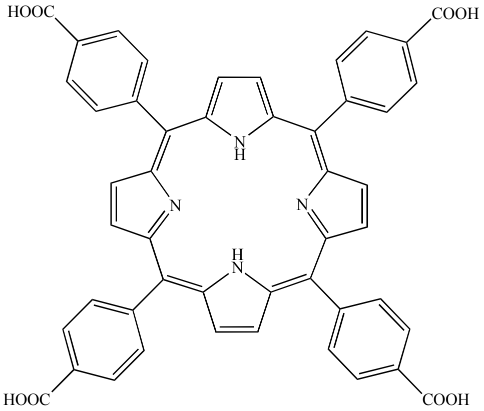
dobpdc



dobdc

Amine-functionalized $Mg_2(dobpdc)$ was prepared by mixing $H_4(dobpdc)$, magnesium bromide, and a small solvent volume (a mixture of *N*,*N*'-diethylformamide and ethanol) in a Pyrex container. The mixture was heated in a microwave reactor, and the $M_2(dobpdc)$ collected by filtration after cooling. Dried samples of $Mg_2(dobpdc)$ were then heated for roughly one hour at 420 °C under dynamic vacuum. After this "activation" step, $Mg_2(dobpdc)$ was stirred with an excess of *N*,*N*'-dimethylethylenediamine (mmen) in hexanes for one day. Subsequent heating under vacuum resulted in removal of residual solvents to afford mmen-functionalized $Mg_2(dobpdc)$. The "activation" step was found necessary to completely remove residual *N*,*N*'-diethylformamide from the Mg^{2+} coordination sites.

9.32 This reference discusses application of porphyrin-containing MOFs where the porphyrin provides a binding site for Fe(III) and Cu(II). The precursor to the porphyrin linker (TCPP) is provided below; the resulting carboxylates of this linker permit its incorporation into the MOF.



The metallation options include premetallation and postmetallation. In premetallation, H_4-TCPP-Cu and H_4-TCPP-FeCl, respectively, are used as reactants for the MOF synthesis. In this case, the porphyrin linker and its bound metal ion are installed simultaneously into the MOF. This general approach afforded MOF-525-Cu, MOF-545-Fe, and MOF-545-Cu. MOF-525-Fe could not be obtained via this strategy. For this MOF, postmetallation was employed, via the reaction of MOF-525 with Fe(III) chloride; Fe(III) ions were introduced into the MOF-525 porphyrin linkers via this method.

In terms of similarities and differences, MOF-545 can be metallated with both Fe(III) and Cu(II) via a premetallation strategy, while MOF-525 requires alternate procedures for incorporation of Cu(II) (premetallation) and Fe(III) (postmetallation), respectively.