Chem 253 A/B Materials
TuTh 2:00 - 3:30 pm, 433 Latimer Hall

253 A, Monday 2/23/15 to Friday, 4/3/15

2/24, 2/26	Molecular chemical structure from chemical formula
3/3, 3/5	Topology in chemistry
3/10,	Topology in chemistry
3/12	Important 0-D, 1-D, 2-D and 3D chemical structure motifs
3/17, 3/19	Important 0-D, 1-D, 2-D and 3D chemical structure motifs
3/24, 3/26	Spring Break
3/31,	Metal-organic frameworks and related materials
4/2	Quiz

253 B, Monday 4/13/15 to Friday, 5/8/15

4/14, 4/16	Crystal structure modeling lab
4/21, 4/23	Special x-ray crystallography (structure from diffuse scattering)
4/28, 4/30	Special x-ray crystallography (structure from diffuse scattering)
5/5	Carbon capture and other applications of porous crystals
5/7	Quiz

Consider these:

H_2SO_4

P_4, S_8

P2O5, P4O10

C(diamond)

Cu2O

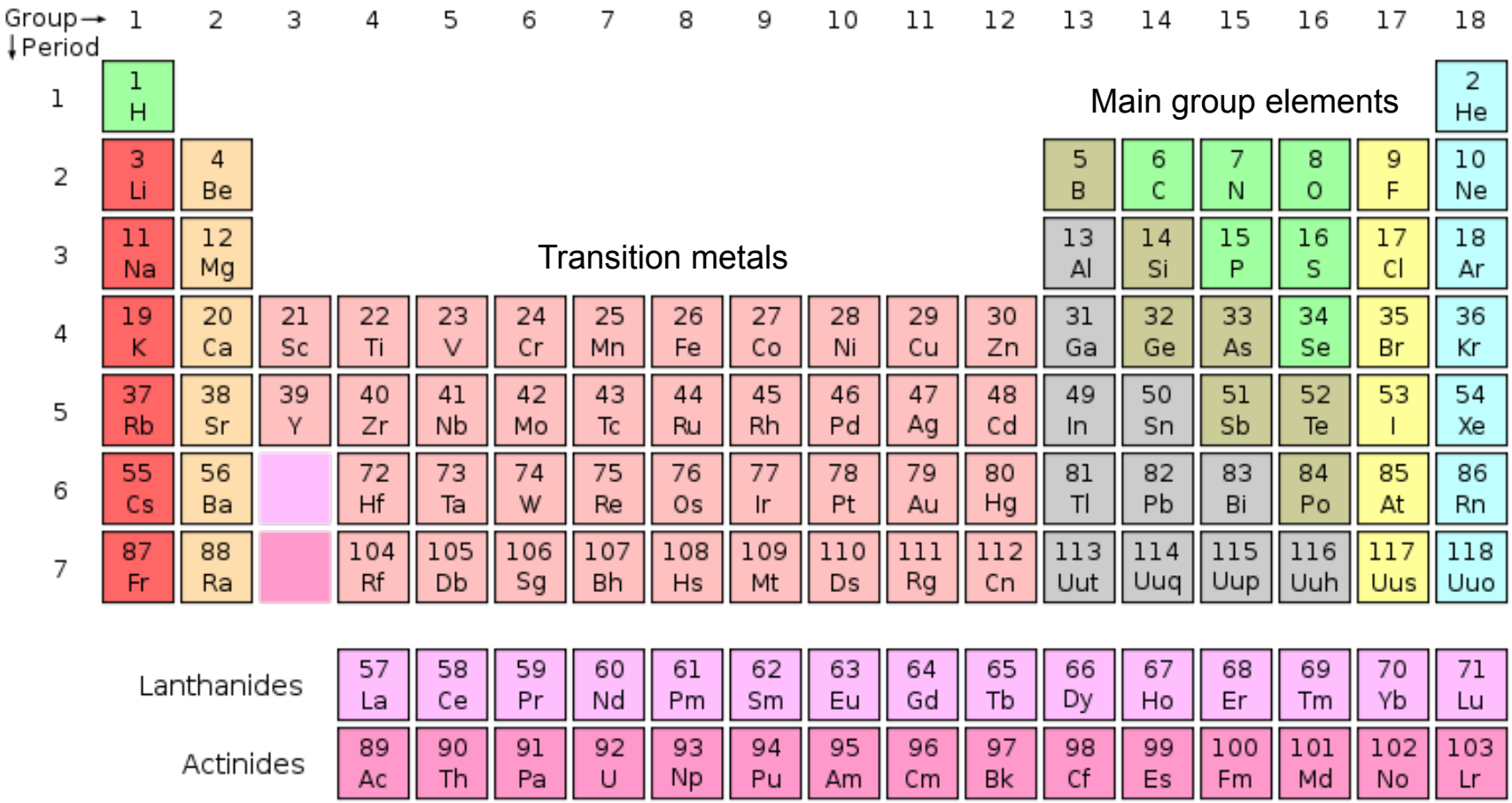
Cu(CN)2

PtS

Li4(CH3)4

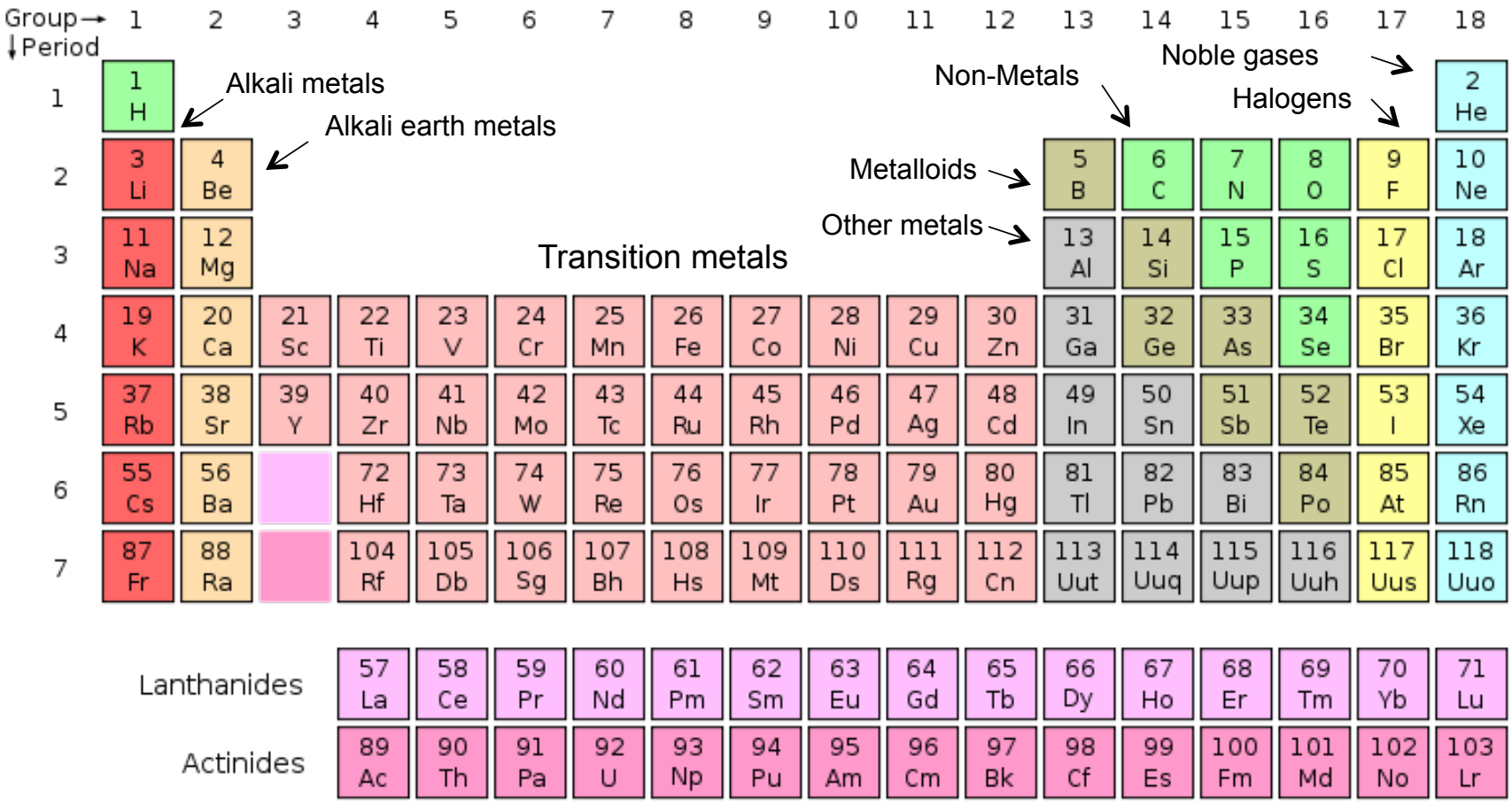
Co(NH3)4Cl2.3H2O`

Periodic table of the elements



http://en.wikipedia.org/wiki/File:Periodic_table.svg

Periodic table of the elements

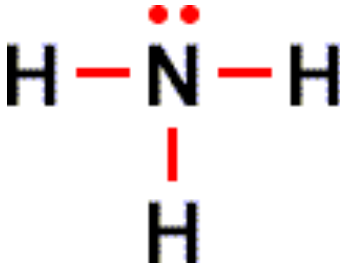


http://en.wikipedia.org/wiki/File:Periodic_table.svg

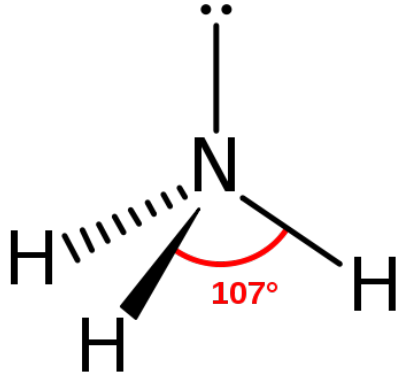
Chemical formula, structural formula, geometry, and shape of a molecule (e.g. ammonia)

NH_3

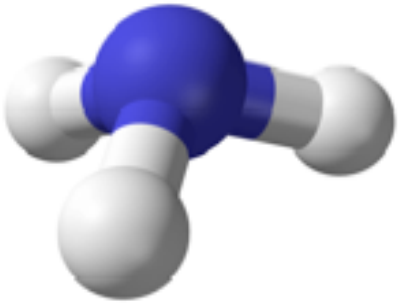
Chemical formula



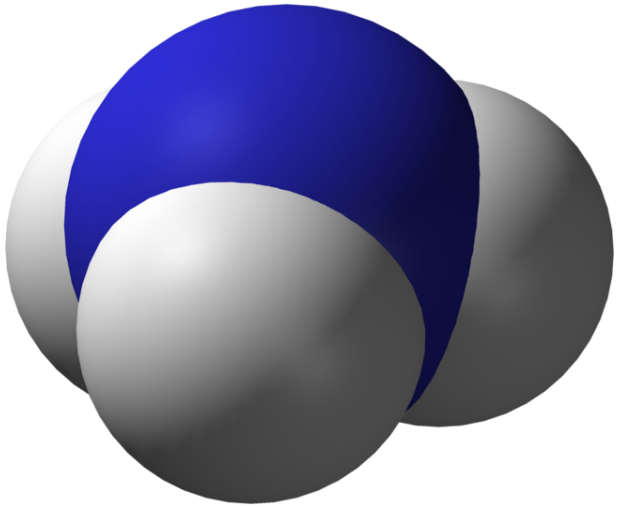
Lewis structure



Electron domain geometry (tetrahedral)

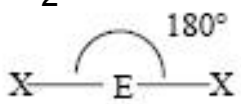
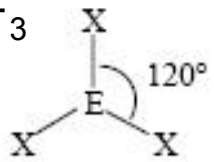
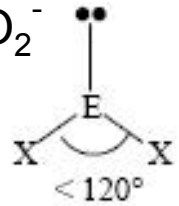
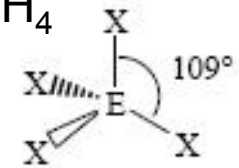
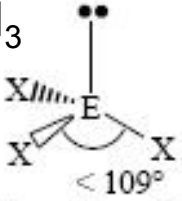
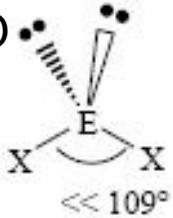
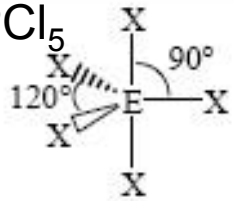
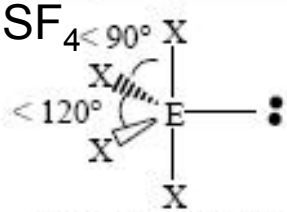
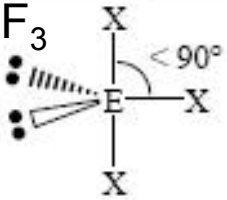
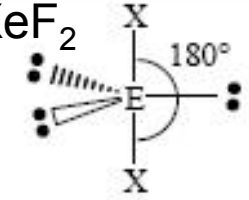
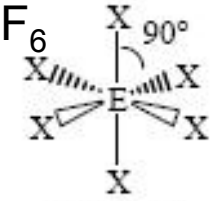
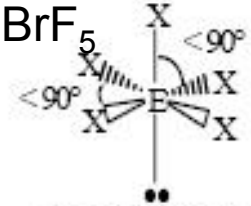
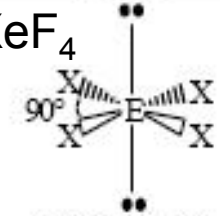
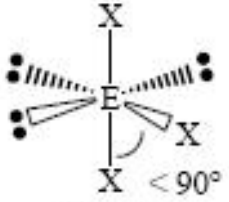
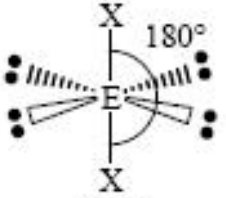


Ball-and-stick model of shape (trigonal pyramidal)



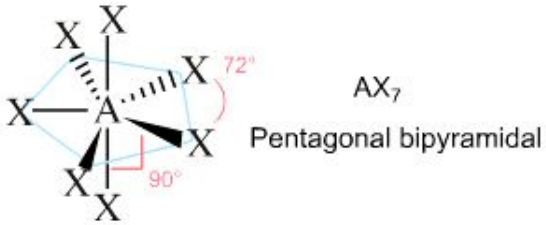
Space-filling model of shape

VSEPR Geometries

No: e^- pair	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	CO_2  Linear				
3	BF_3  Trigonal Planar	NO_2^-  Bent or Angular			
4	CH_4  Tetrahedral	NH_3  Trigonal Pyramid	H_2O  Bent or Angular		
5	PCl_5  Trigonal Bipyramid	SF_4  Sawhorse or Seesaw	ClF_3  T-shape	XeF_2  Linear	
6	SF_6  Octahedral	BrF_5  Square Pyramid	XeF_4  Square Planar	 T-shape	 Linear

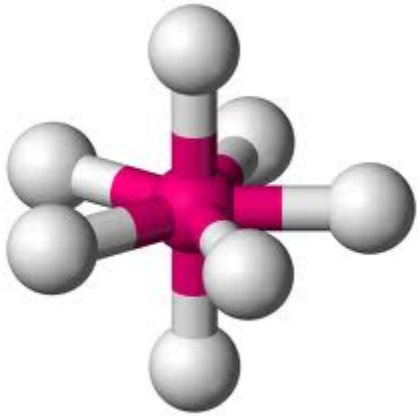
Seven electron pairs

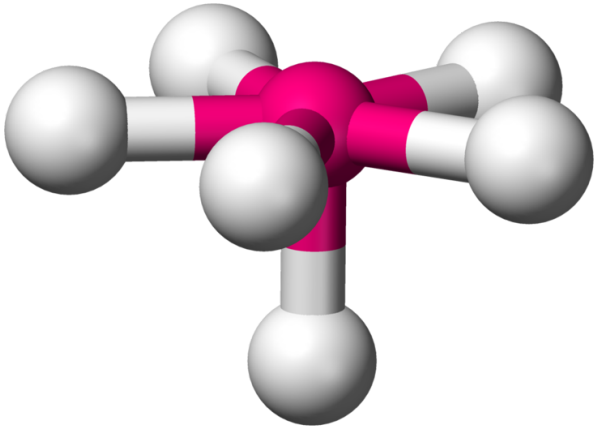
IF_7



IOF_5^{2-}

$XeOF_5^-$



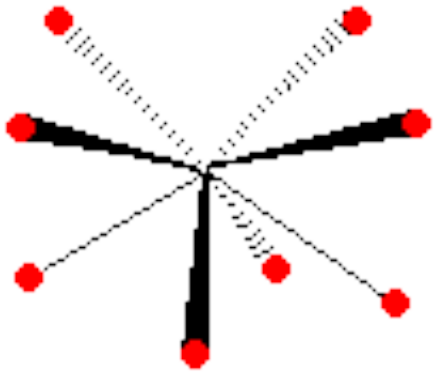


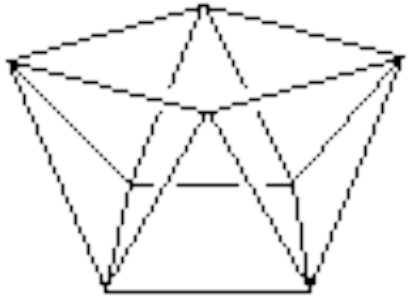
Pentagonal bipyramid

Pentagonal pyramid

8 electron pairs

XeF_8^{2-}





Square antiprism

Deriving structures of main group molecules where resonance and formal charge are important

e.g.

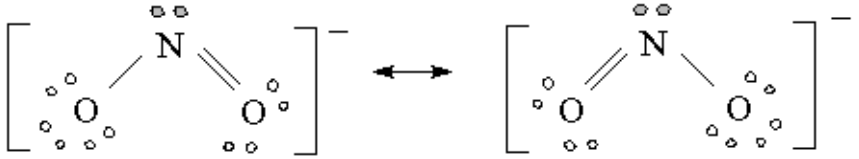
NO_2^-

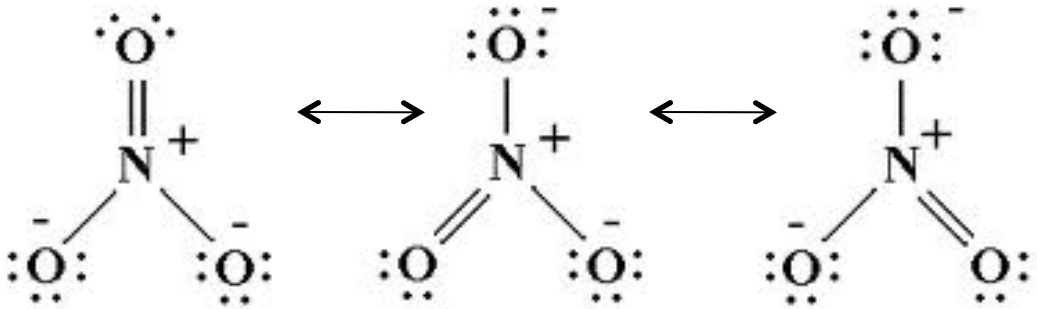
NO_3^-

PO_4^{3-}

SO_4^{2-}

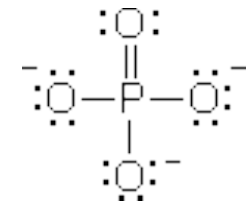
Examples of deriving structures of main group molecules with resonance and formal charge considerations

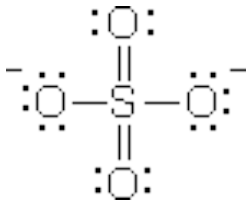




Best structures for phosphate and sulfate: usefulness of formal charge considerations

Formal charge = normal valency – (1/2 bonding electrons + number of lone electron)

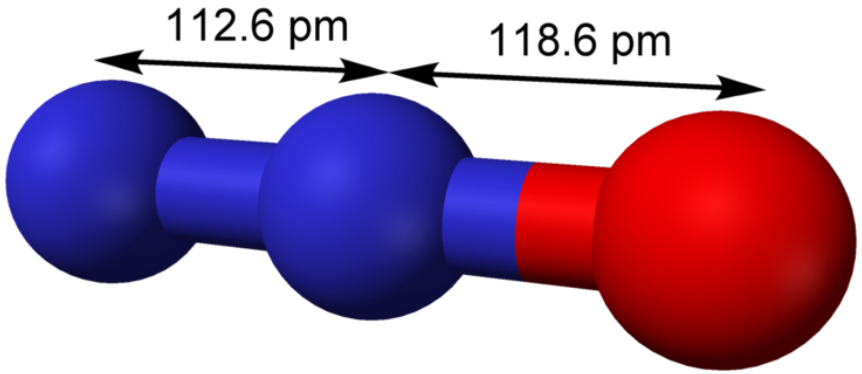




In deciding the best structure aim for:

1. Few charges on the molecule or ion
2. Zero or low charges on atoms
3. Negative and positive charges are distributed
4. Negative charges on the more electronegative atom and positive charges on the less electronegative one

Exercise: What is the most likely structure for N_2O?



Some Guidelines for deriving the geometries and shapes of ‘simple’ molecules

1)Count the number of valence electrons
2)Place the least electronegative atom in the center
3)Place other atoms around the central atom as far apart as possible to minimize repulsions, and choose the most symmetric structures
4)Distribute valence electron so that octet is obeyed (with some exceptions, see examples).
5)Determine the number of electron domains and the geometry
6)Determine the shape without lone pairs
7)Confirm you have the most likely structure by determining formal charges

Coordination geometry of transition metal complexes

- Coordination number (C.N.) is the number of ligands around the transition metal

- To recognize the structure of a coordination compound, one needs to know:
  - the metal, its oxidaton state and C.N.
  - the ligand composition, donor atoms, and chelation number (if applicable)
  - Electron counting (18 electron rule)

Coordination number 1

Complexes with coordination number 1 were erroneously claimed for copper and silver, but a genuine metal complex with CN= 1 (M = Indium) was recently reported by P. Power (S. T. Haubrich, P. Power, JACS **1998**, 120, 2202-2203):

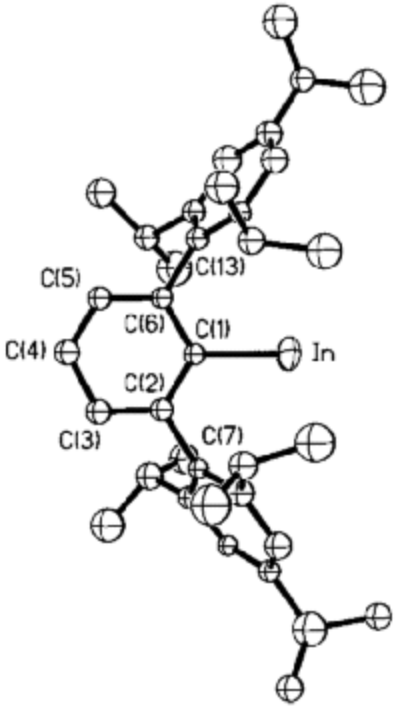
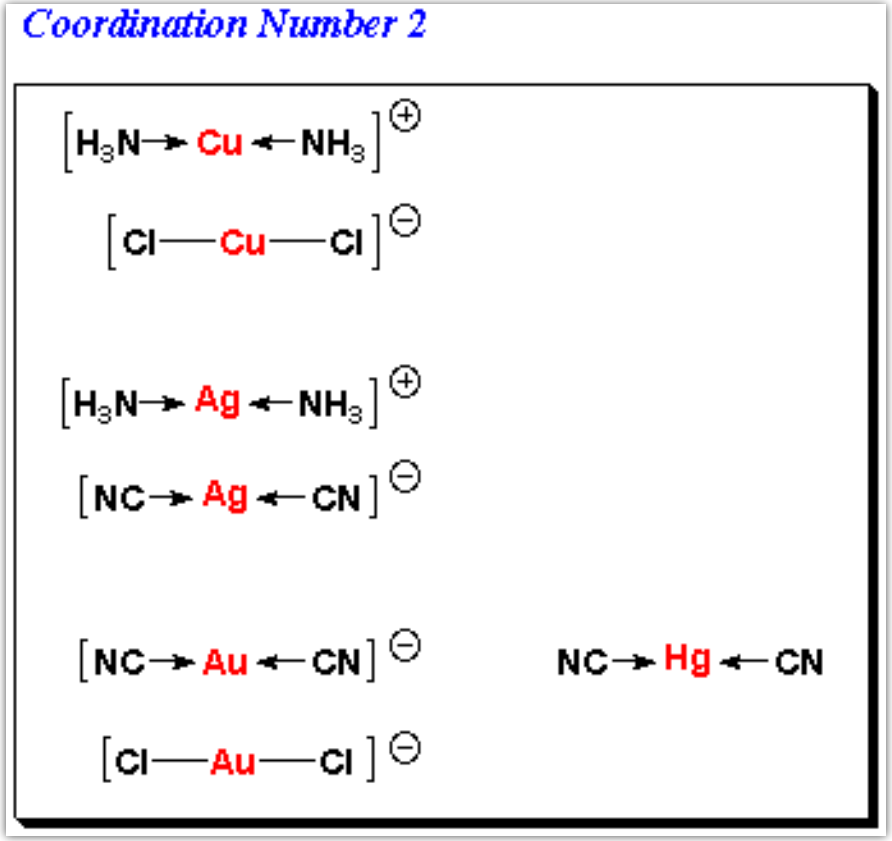
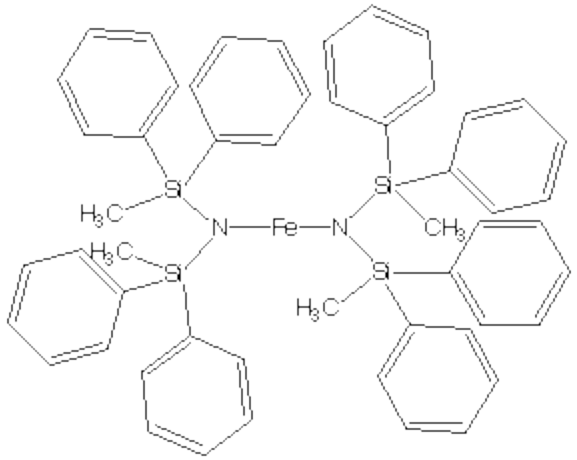


Figure 1. Computer-generated drawing of **1** with H atoms not shown. Selected bond distances (Å) and angles (deg): In−C(1) = 2.260(7), C(1)−C(2) = 1.39(2), C(2)−C(3) = 1.42(2), C(3)−C(4) = 1.44(2), C(4)−C(5) = 1.35(2), C(5)−C(6) = 1.39(2), C(1)−C(6) = 1.42(2), In−C(1)−C(2) = 121.9(14), In−C(1)−C(6) = 120.2(14), C(2)−C(1)−C(6) = 117.5-(6), C(1)−C(2)−C(7) = 115(2), C(1)−C(6)−C(13) = 118(2).

Coordination number 2

Uncommon but known for Ag(I), Au(I) and Hg(II); also, known for metal surrounded by very bulky ligands (e.g. Fe complex)

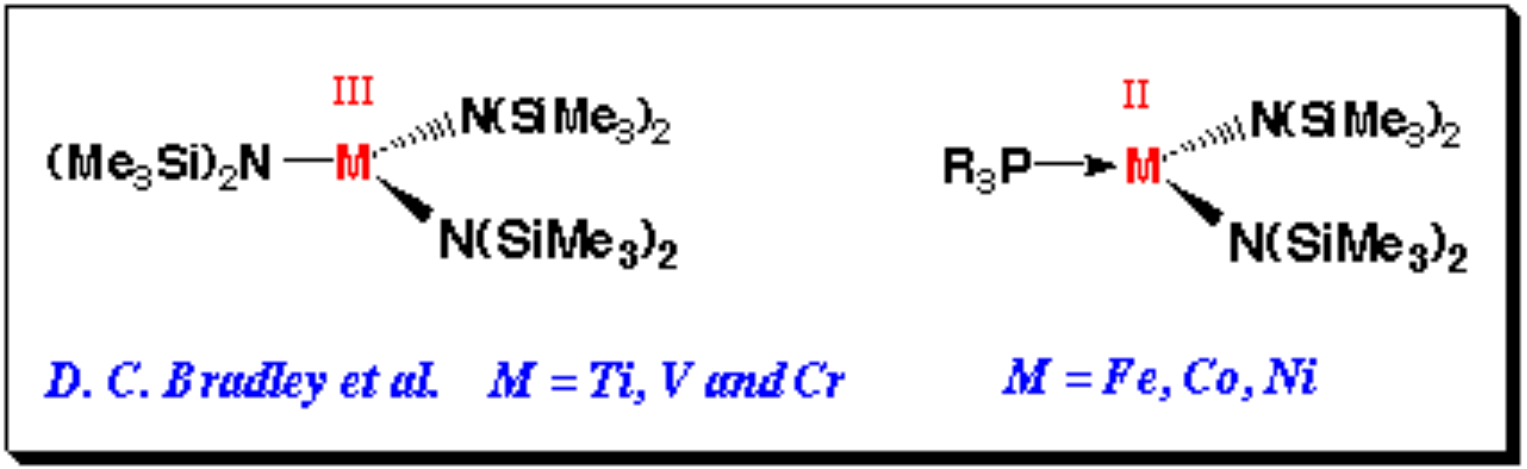




Coordination number 3

Rare but accessible by use of very bulky ligands

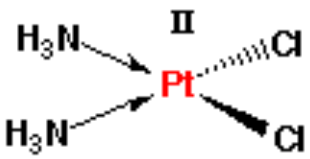
Coordination Number 3



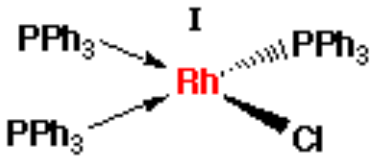
Coordination number 4: square

Well-known for d^8 complexes

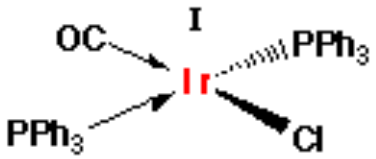
Important square planar d^8-complexes



"Cis-Platin"



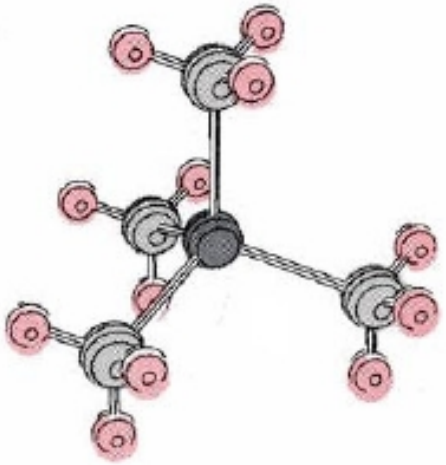
Wilkinson's Catalyst



Vaska's Catalyst

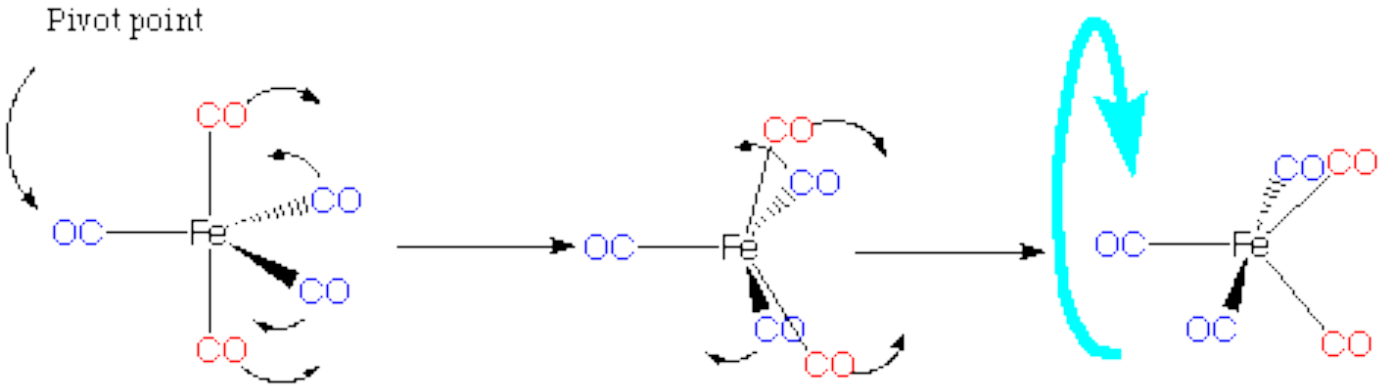
Coordination number 4: Square vs. tetrahedron

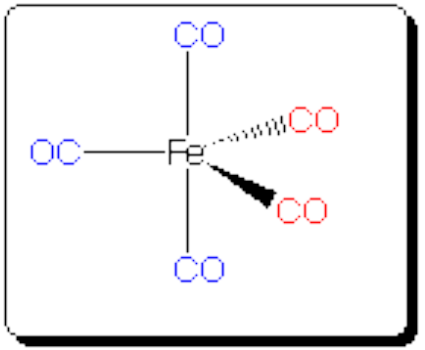
$Pt(NH_3)_4^{2+}$



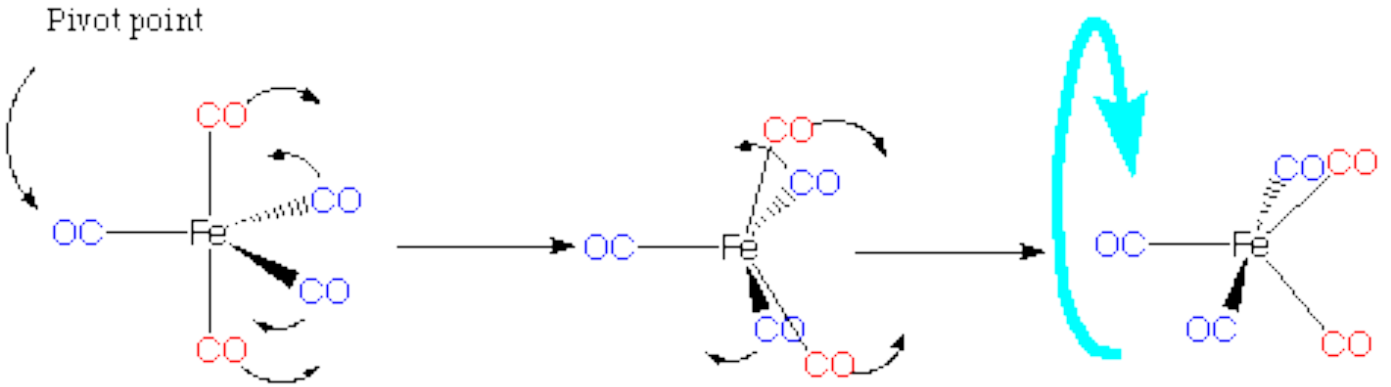
$Zn(NH_3)_4^{2+}$

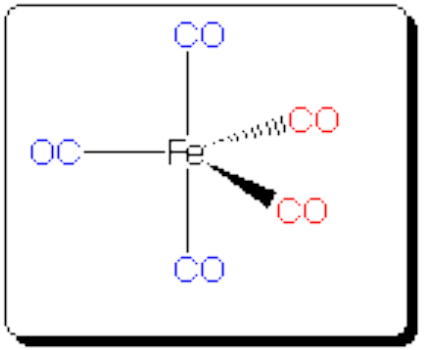
Coordination number 5: trigonal bipyramid and square pyramidal





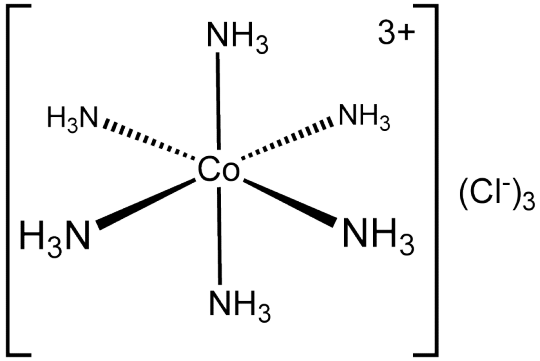
Coordination number 5: trigonal bipyramid and square pyramid



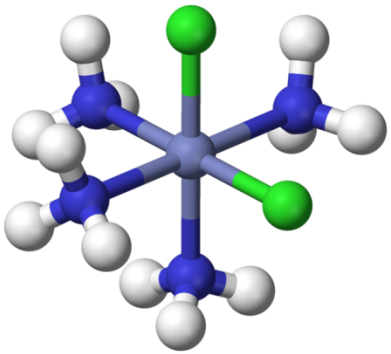


Also $Ni(CN)_5^{3-}$ depending on the cation, it can be isolated in both geometries

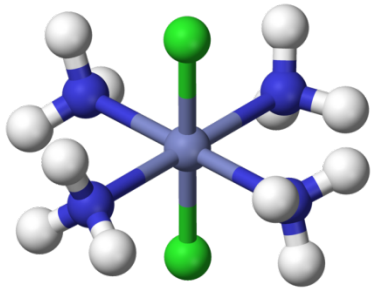
Coordination number 6: Octahedron



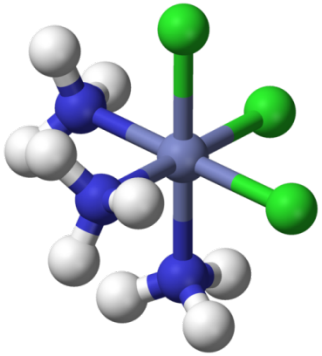
$[Co(NH_3)_6]Cl_3$



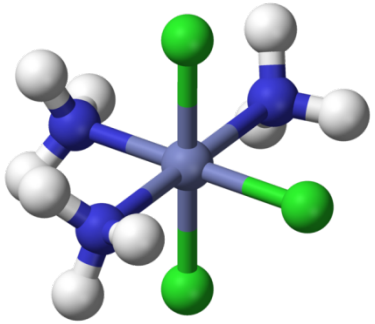
cis-$[CoCl_2(NH_3)_4]^+$



trans-$[CoCl_2(NH_3)_4]^+$



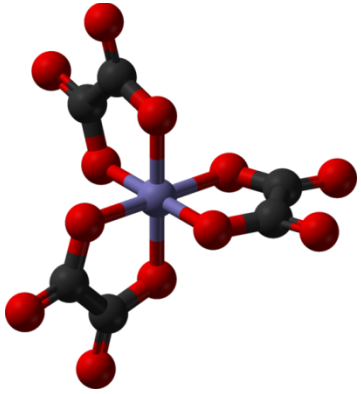
fac-$[CoCl_3(NH_3)_3]$



mer-$[CoCl_3(NH_3)_3]$

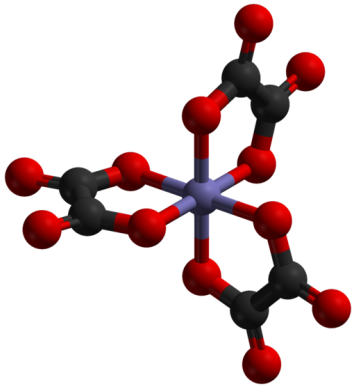
facial isomer (*fac*) where the three identical ligands are mutually cis, and a **meridional** isomer (*mer*) where the three ligands are coplanar.

Chirality in octahedral complexes



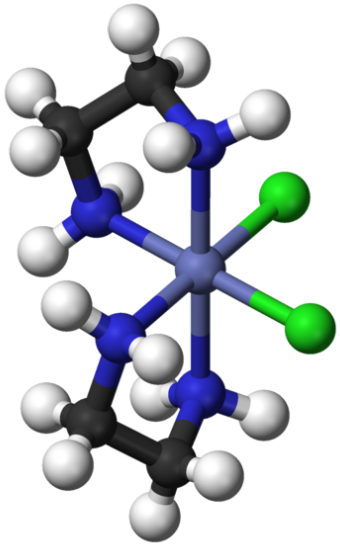
Λ-$[Fe(ox)_3]^{3-}$

left

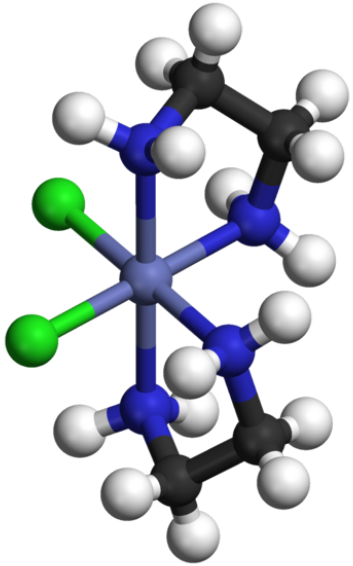


Δ-$[Fe(ox)_3]^{3-}$

right

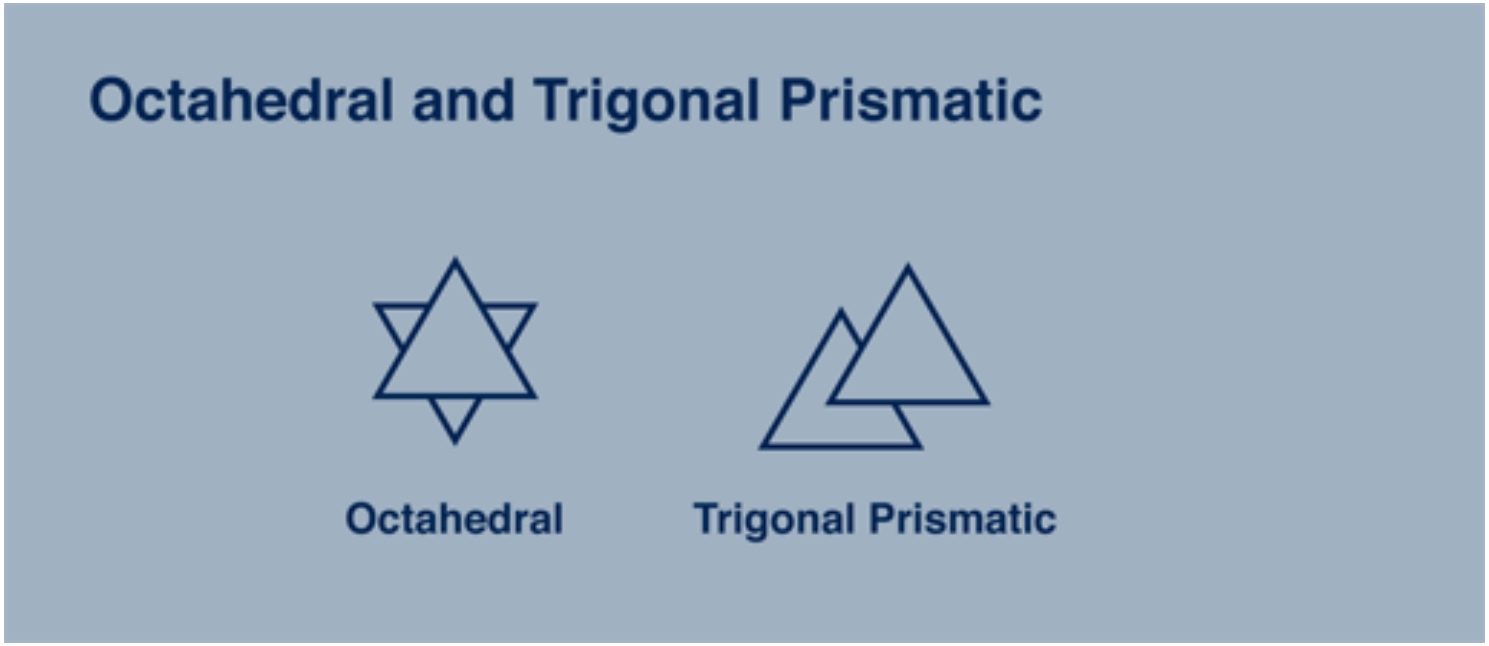


Λ-*cis*-$[CoCl_2(en)_2]^+$

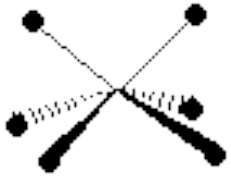


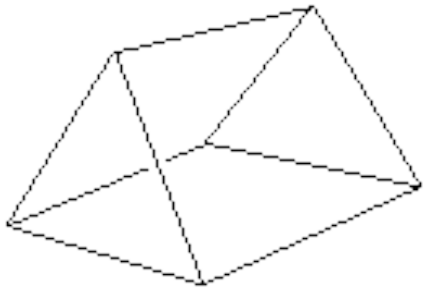
Δ-*cis*-$[CoCl_2(en)_2]^+$

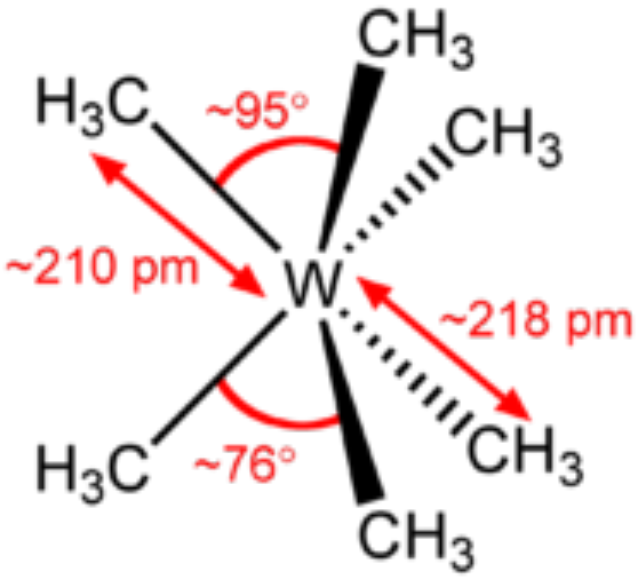
Coordination number 6: Trigonal Prism

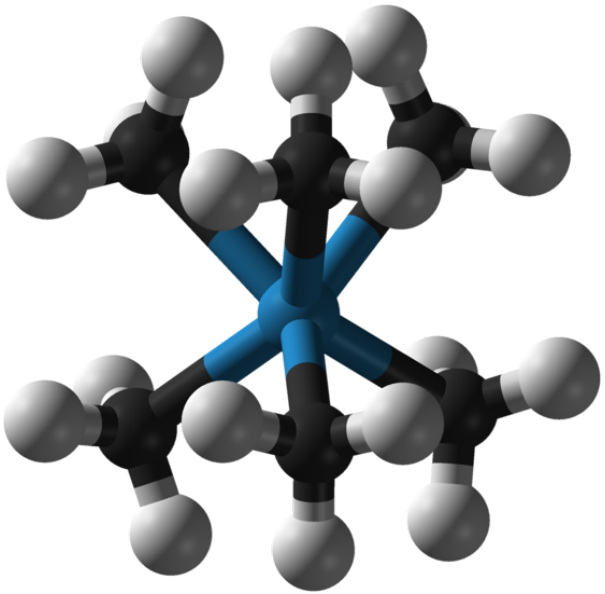


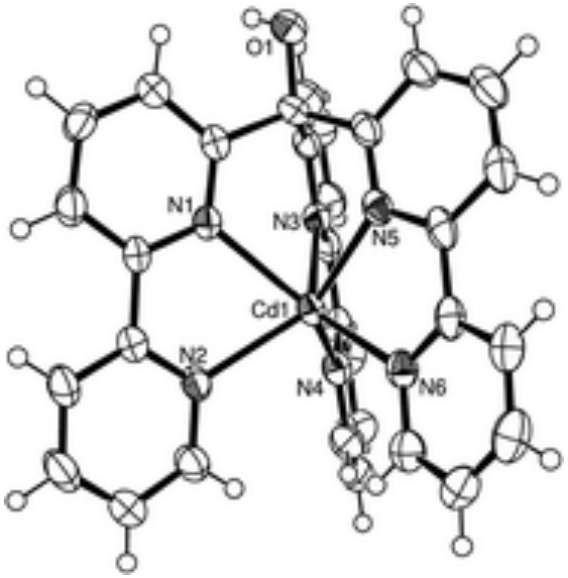
Coordination number 6: Trigonal Prism





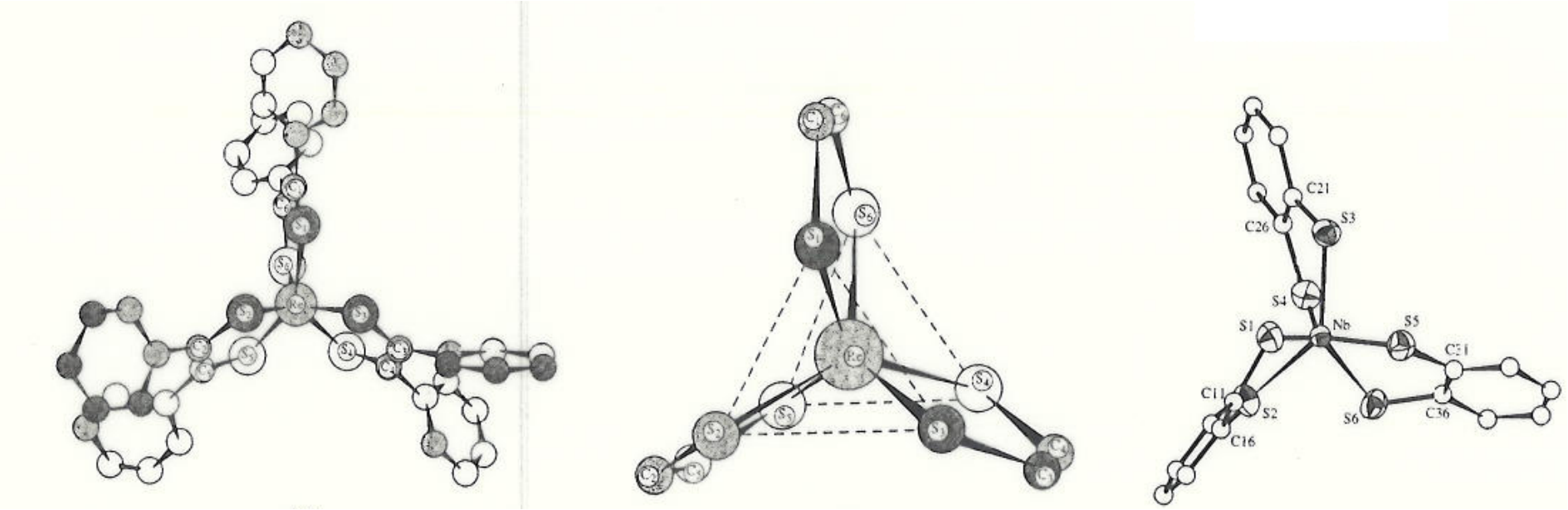






Also $[Zr(CH_3)_6]^{2-}$

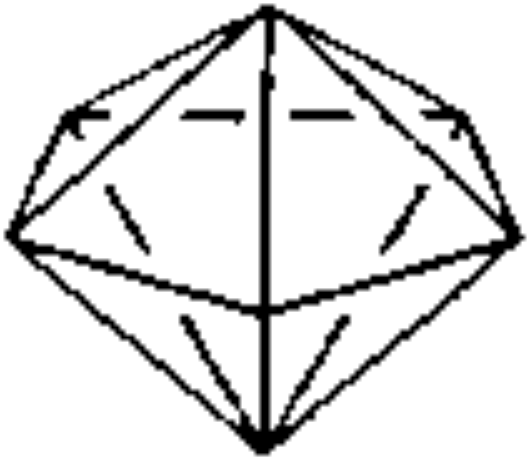
C.N. 6, trigonal prism, Rhenium and Niobium dithiolate complexes



Geometries observed for coordination number 7

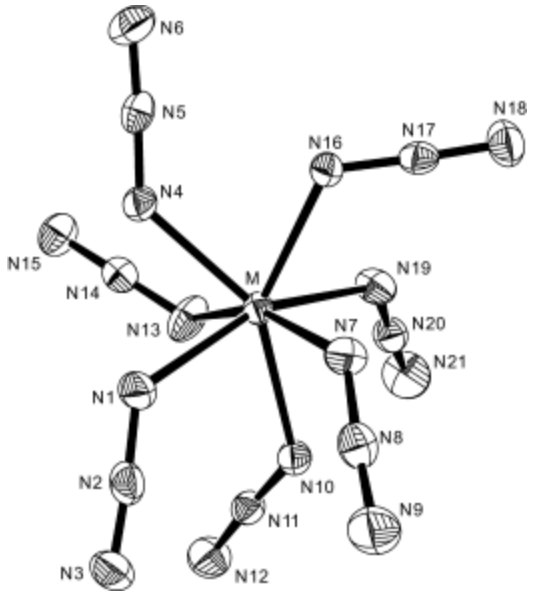
monocapped octahedron (C_3v)

monocapped trigonal prism (C_2v)



Pentagonal Bipyramid (D_5h)

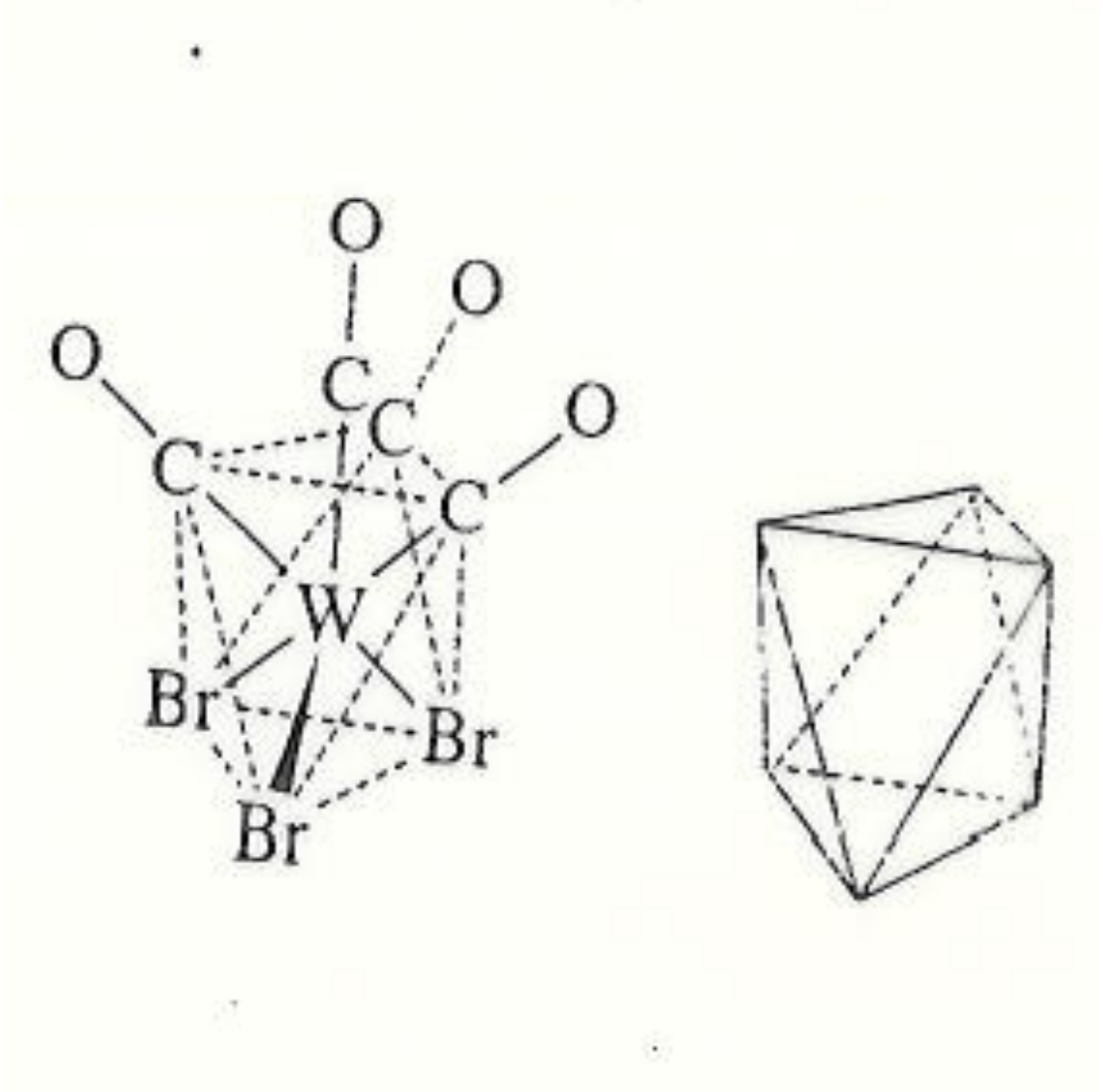
coordination number 7: monocapped trigonal prism



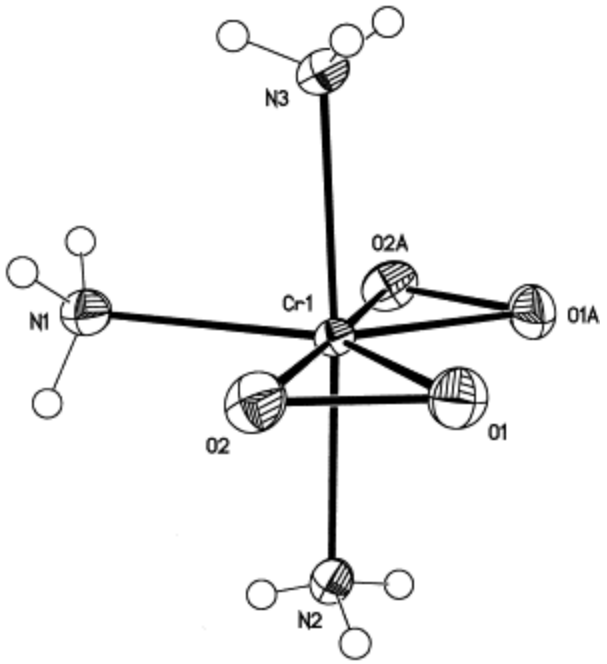
Monocapped Trigonal-Prismatic Transition-Metal Heptaazides: Syntheses, Properties, and Structures of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$

Also NbF_7^{2-}

C.N. 7, monocapped octahedron

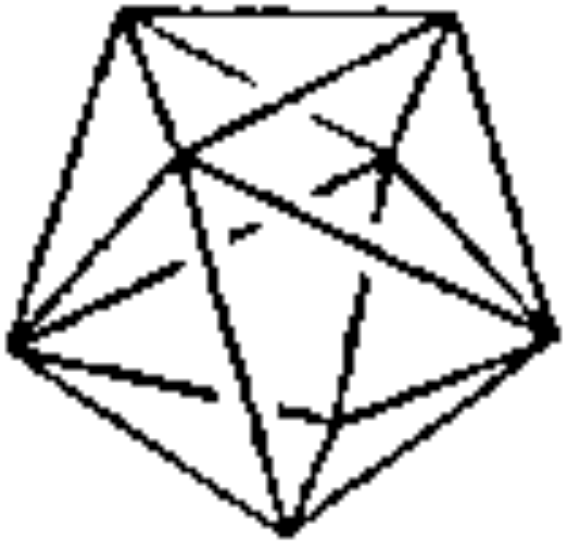


C.N. 7, pentagonal bipyramid

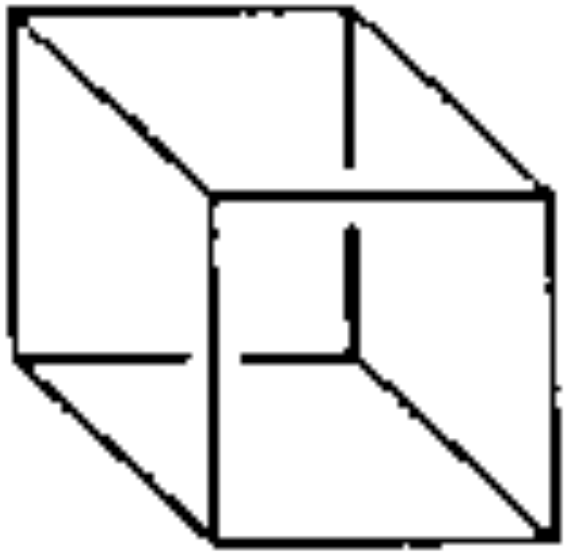


Triaminodiperoxychromate complex $Cr(NH_3)_3(O_2)_2$.

Geometries observed for coordination number 8



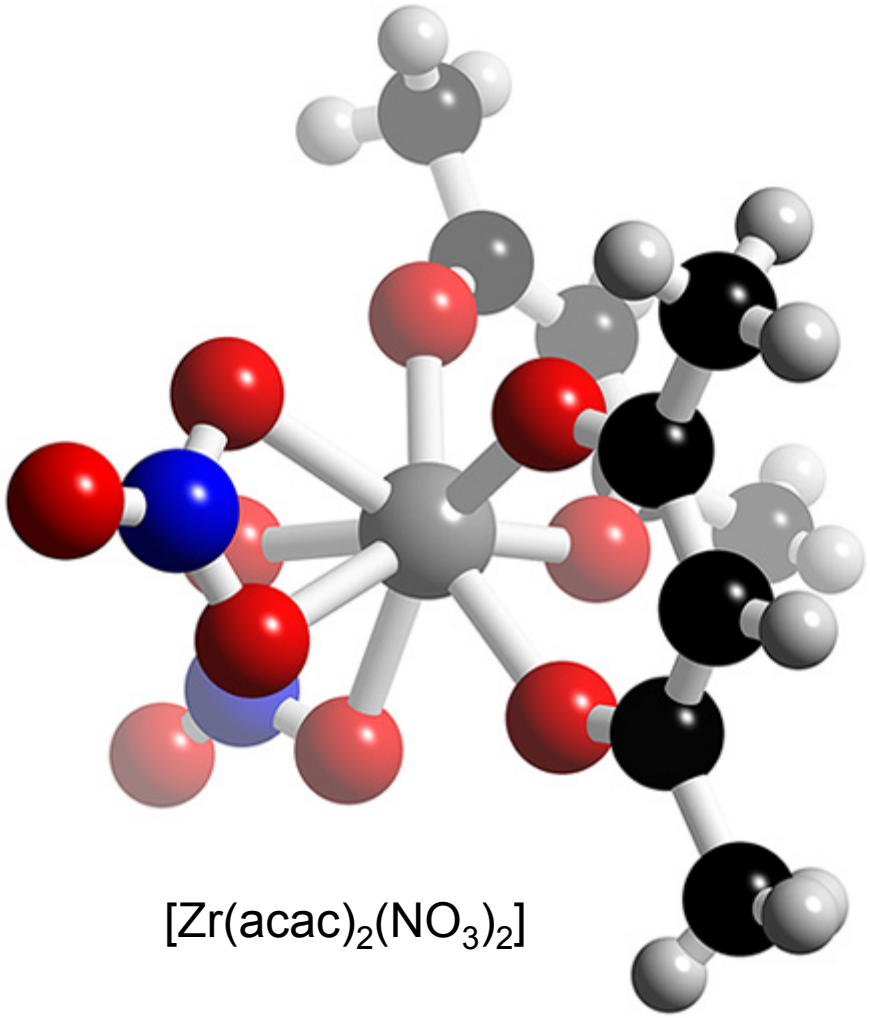
Trigonal dodecahedron (D_{2d})



Cube (O_h)

Square antiprism (D_{4d})

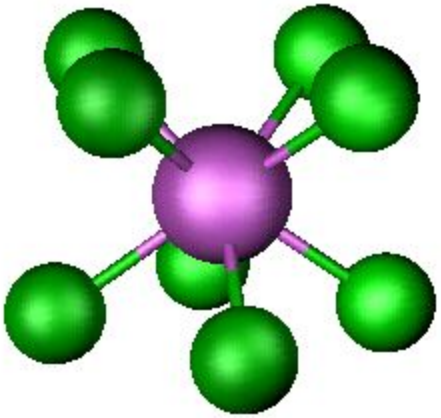
C.N. 8, trigonal dodecahedron

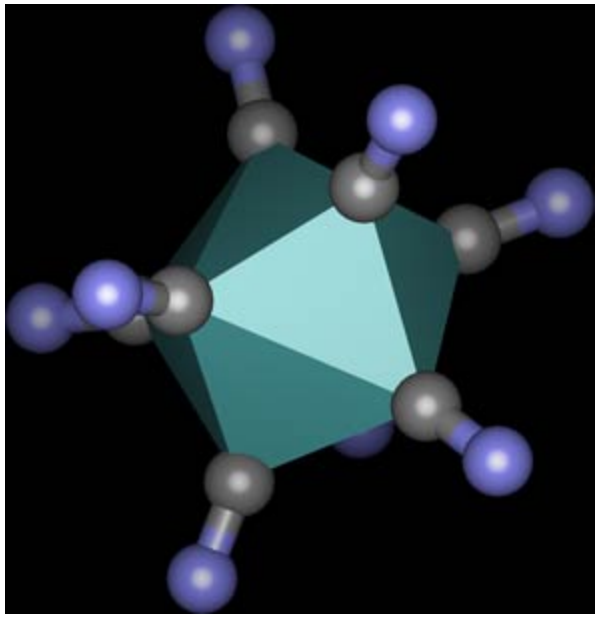


$[Zr(acac)_2(NO_3)_2]$

Also $Cr(O_2)_4^{3-}$ and B_6Cl_8

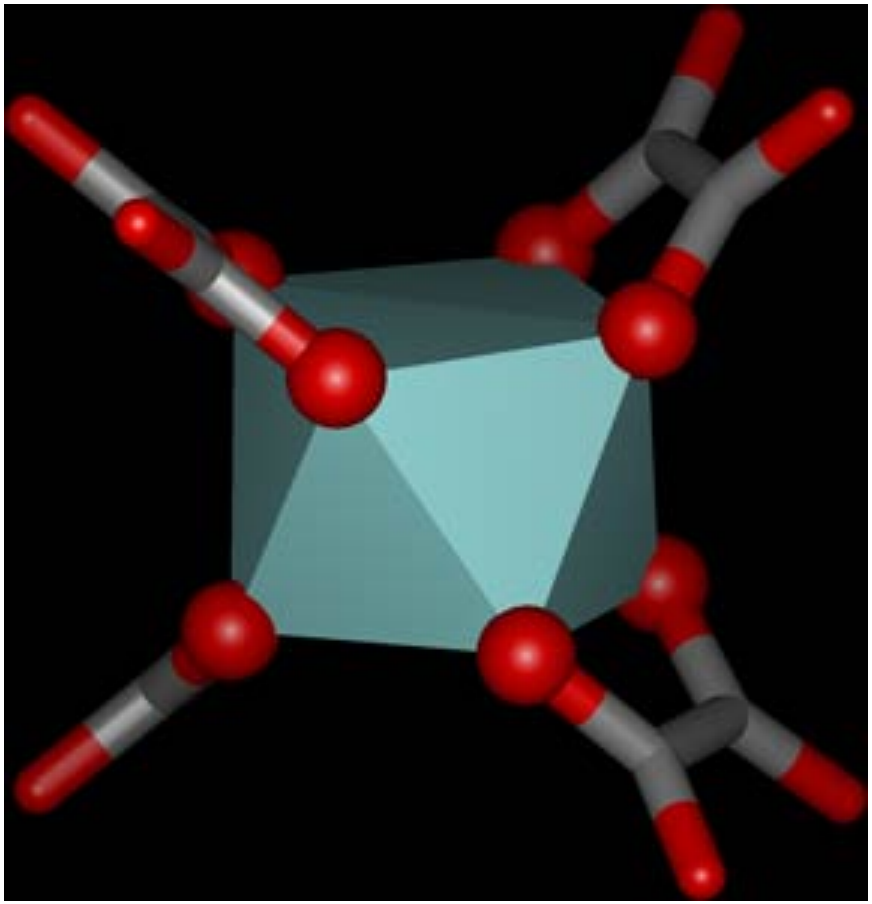
C.N. 8, square antiprism and trigonal dodecahedron





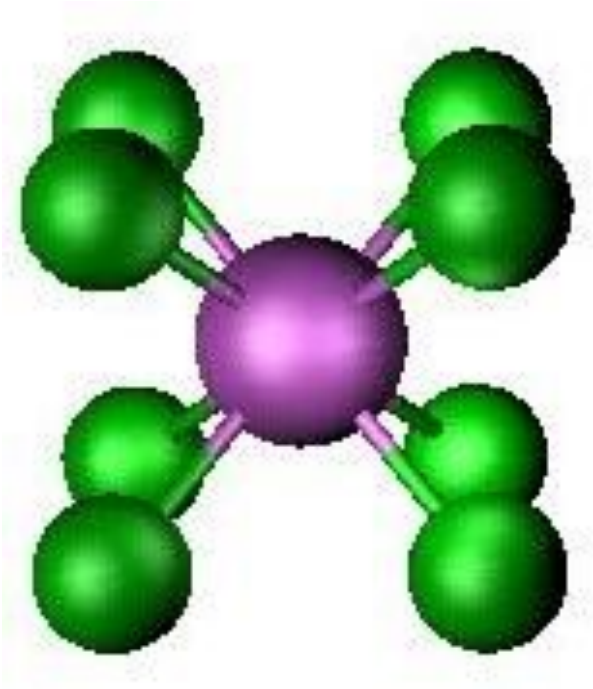
$[W(CN)_8]$ is trigonal dodecahedron in $K_4W(CN)_8.2H_2O$ and square antiprism in $H_4W(CN)_8.6H_2O$

Another example of square antiprism

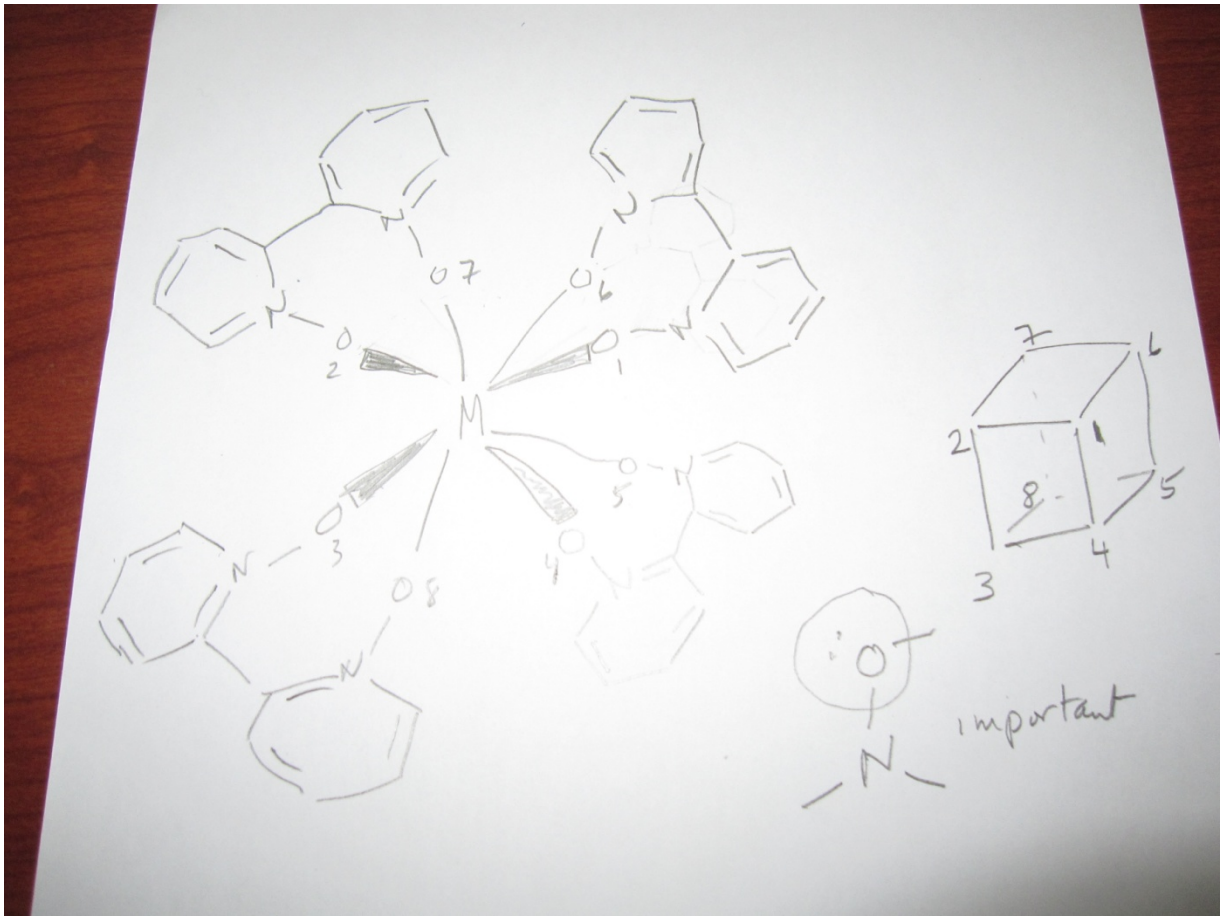


$Zr(ox)_4$

C.N. 8, cube

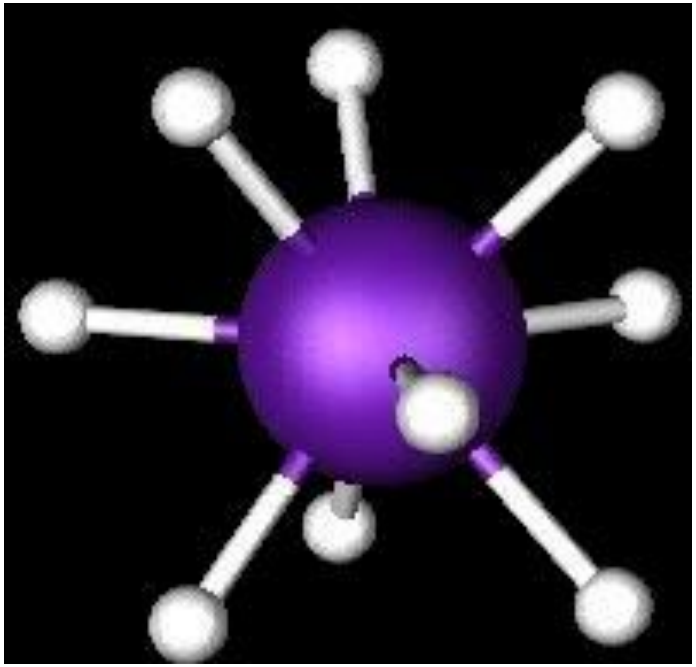


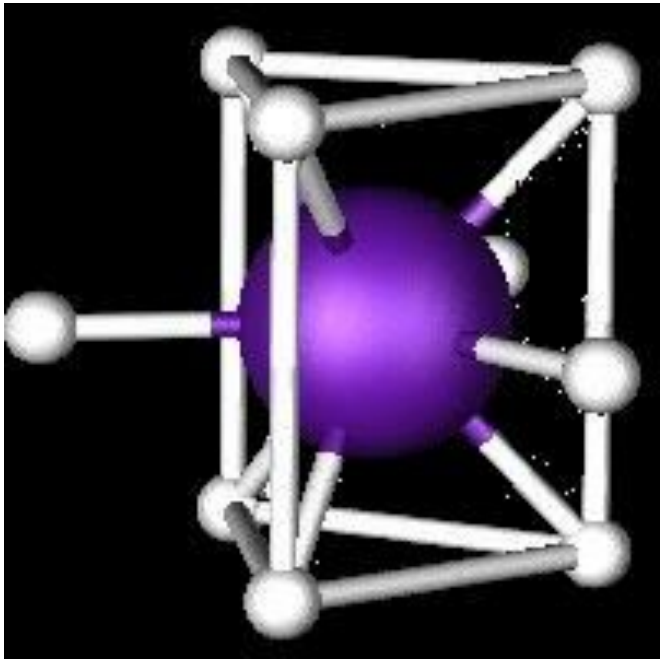
CsCl



$La(bpyO_2)_4^+$

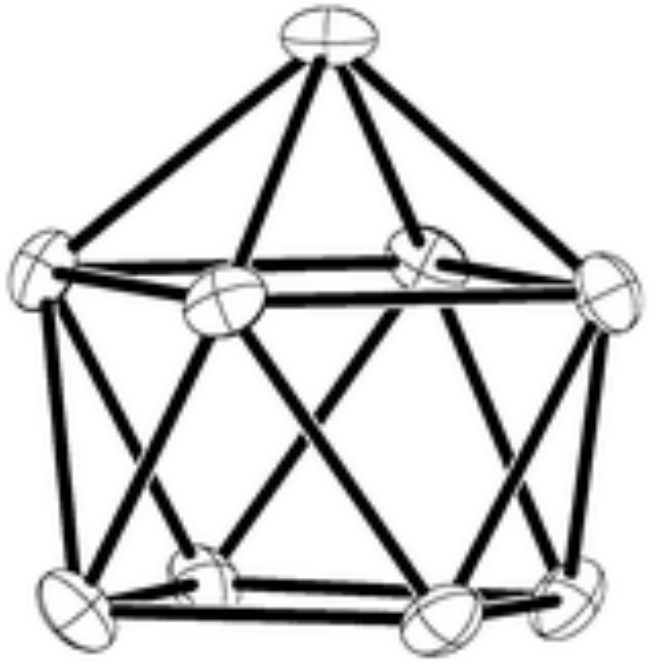
Coordination number 9: tricapped trigonal prism





$[ReH_9]^{2-}$ Also B_9Cl_9

C.N. 9, monocapped square antiprism



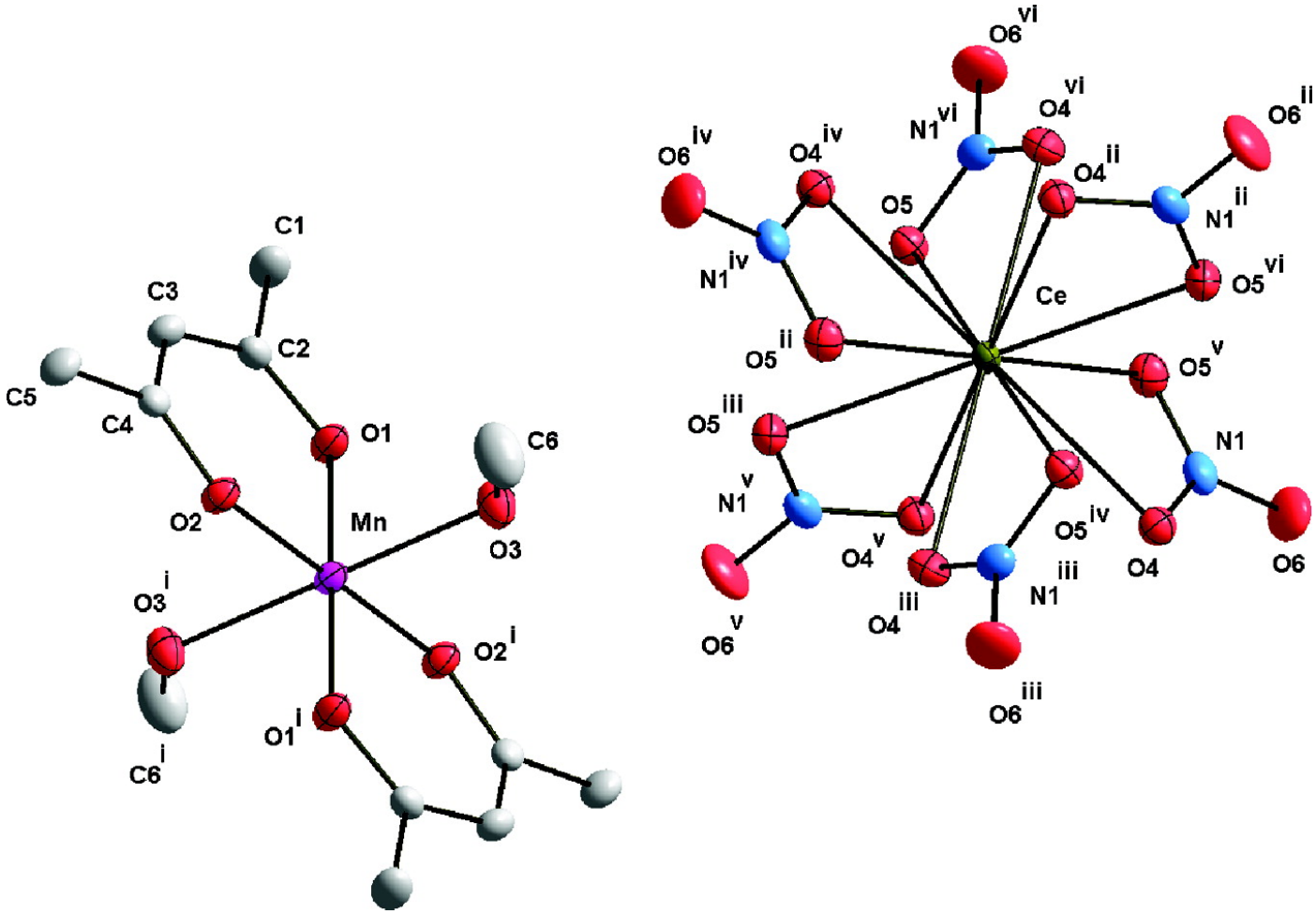
Pb_9^{4-}

Coordination number 10 and 11, bicapped square antiprism, and all face capped trigonal prism

$Th(C_2O_4)_4^{2-}$, bicapped square antiprism

Th in $[Th^{IV}(NO_3)_4(H_2O)_3]$ (NO_3^- is bidentate), all face capped trigonal prism

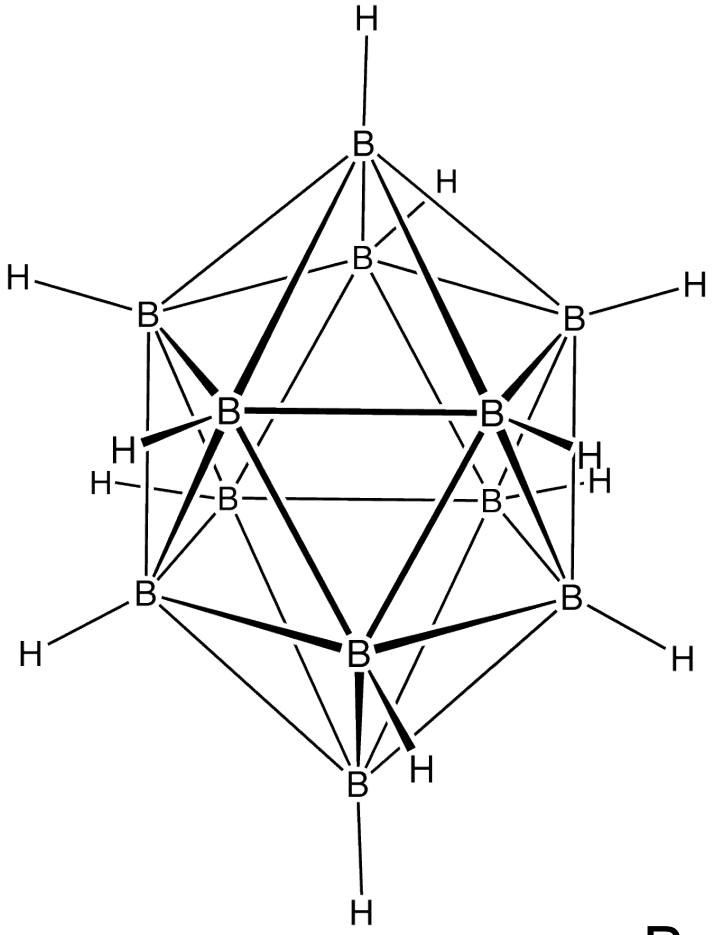
Coordination number 12, icosahedron

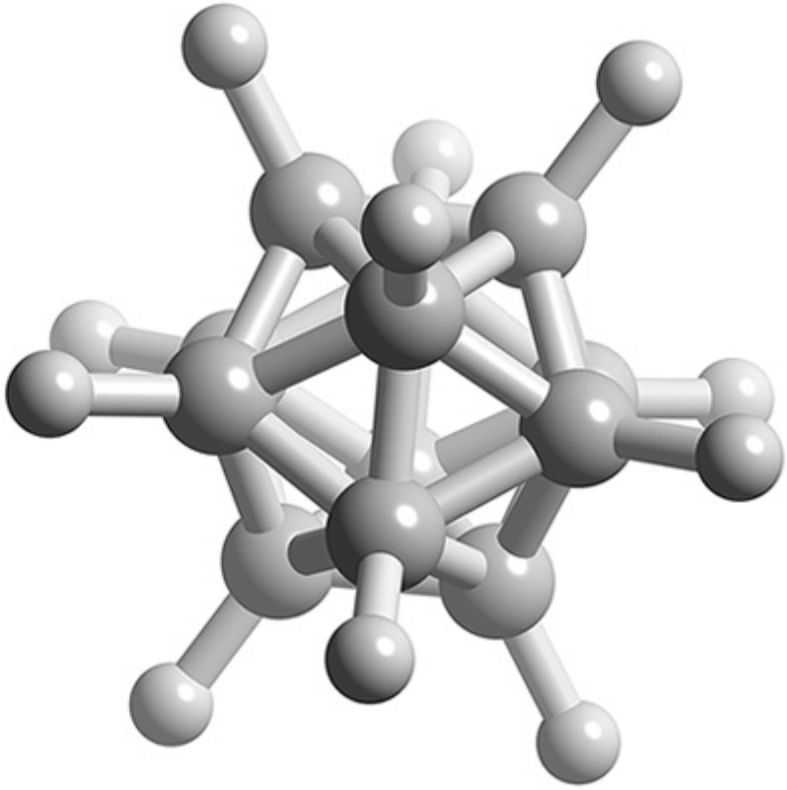


$[Mn(acac)_2(HOCH_3)_2]_3[Ce(NO_3)_6]$ (**1**). The icosahedrally coordinated $Ce(NO_3)_6^{3-}$ ion

C.N. 12, icosahedron

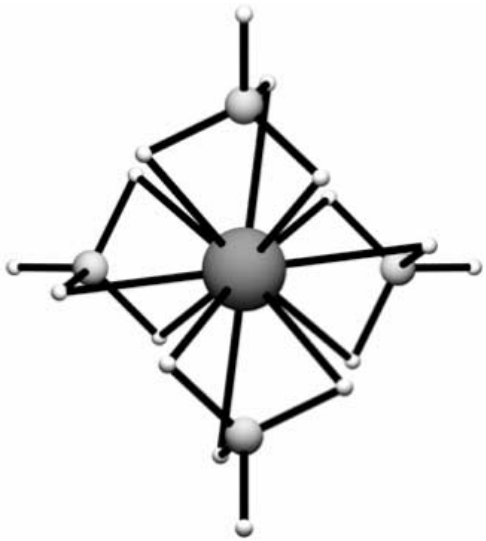
2 Cs^+

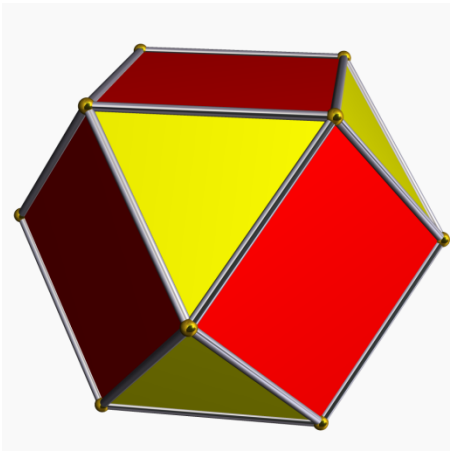




$B_{12}H_{12}^{2-}$

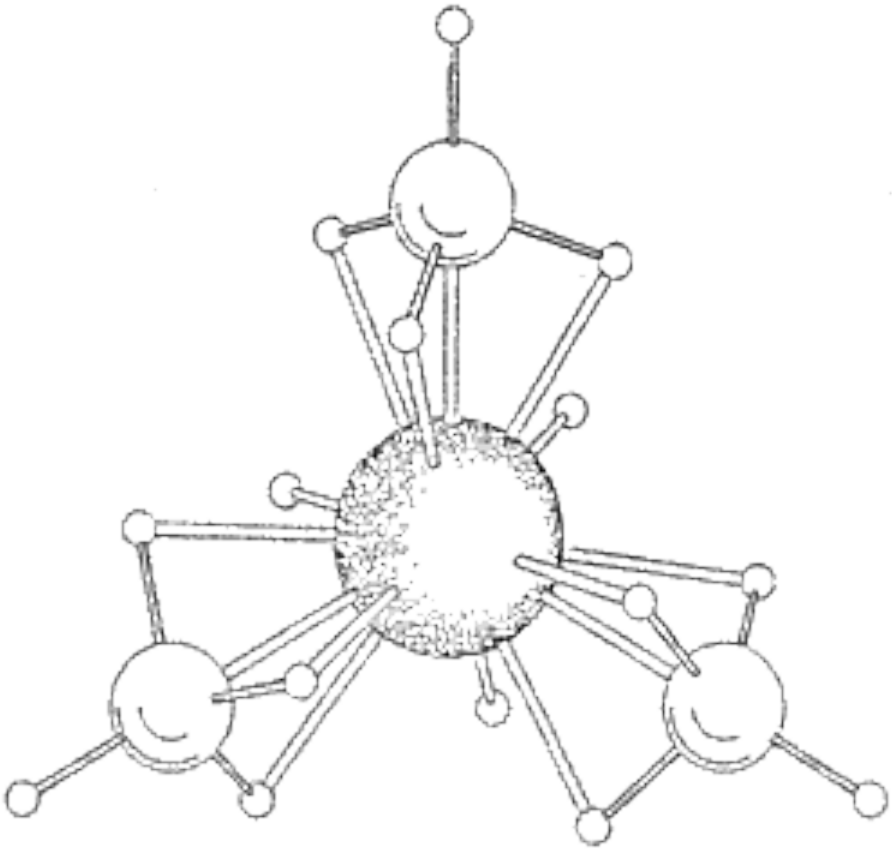
C.N. 12, cuboctahedron

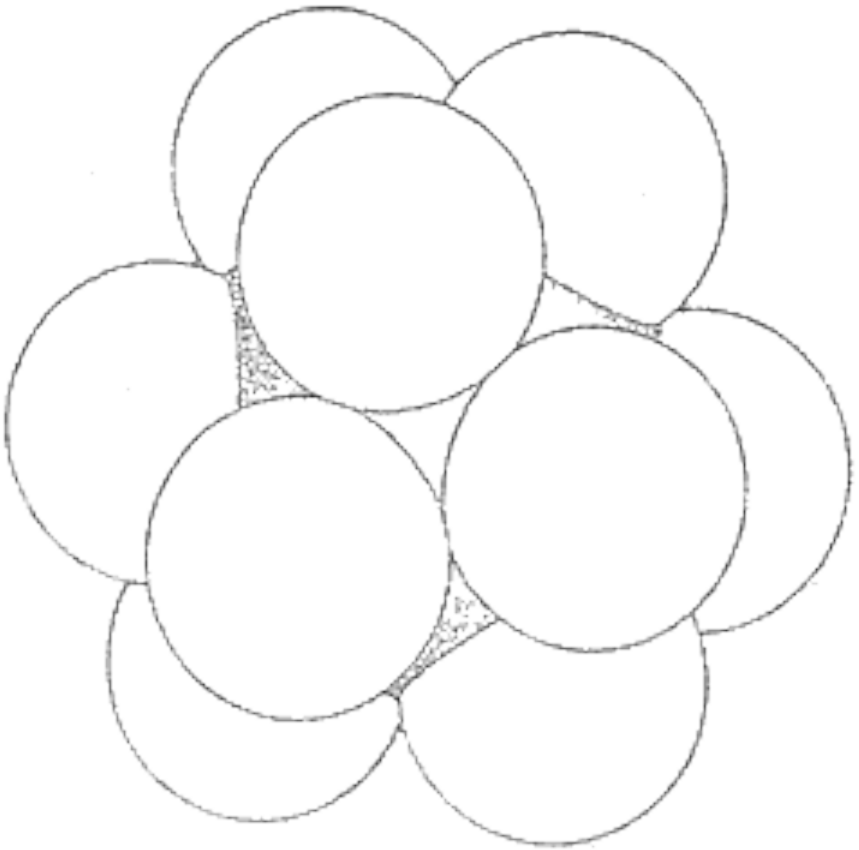




$Zr^{IV}(\eta^3-(BH_4)_4$

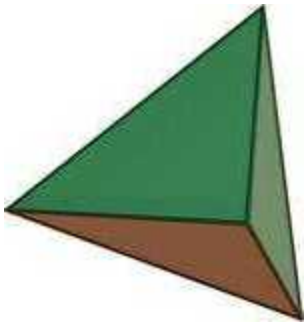
Coordination number 14: bicapped hexagonal antiprismatic



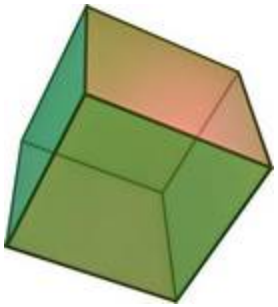


$U(BH_4)_4$ also $Zr(BH_4)_4$

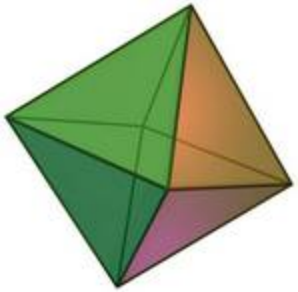
The Platonic solids



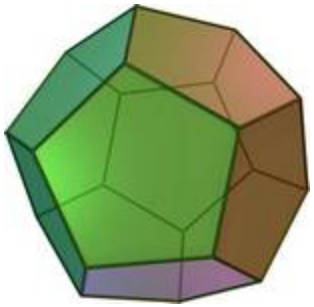
Tetrahedron



cube



octahedron



pentagonal dodechedron

icosahedron

4 faces	6	8	12	20
4 vertices	8	6	20	12
6 edges	12	12	30	30

Images courtesy of Wikipedia

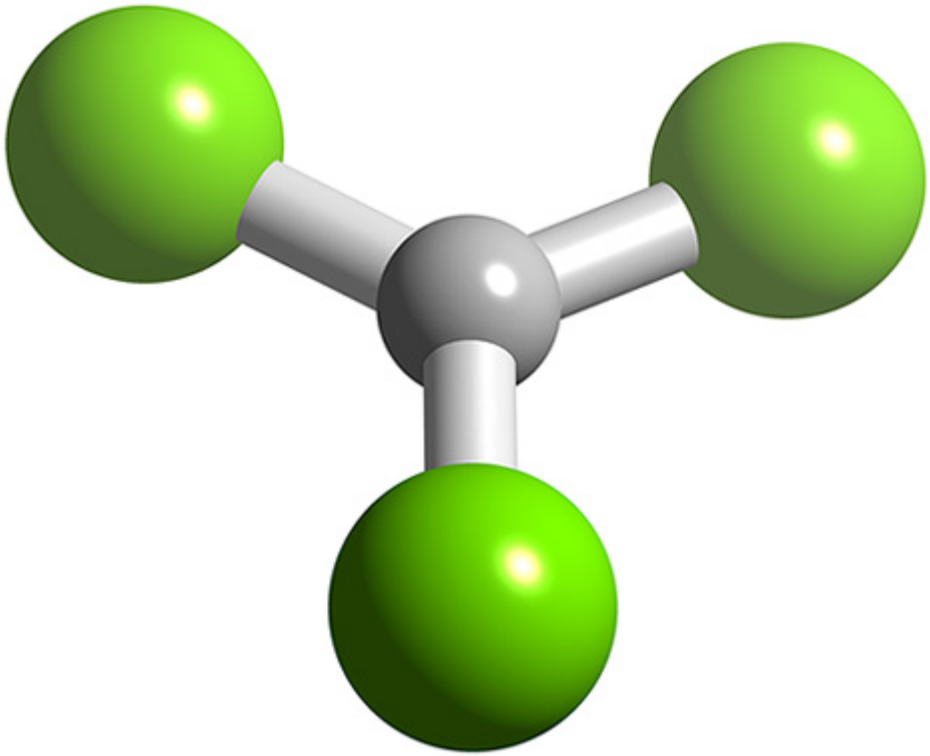
Exercises for molecules and ions

Derive a plausible structure from each of the following chemical formulae:

Exercises for molecules and ions

BCl_3

Exercises for molecules and ions

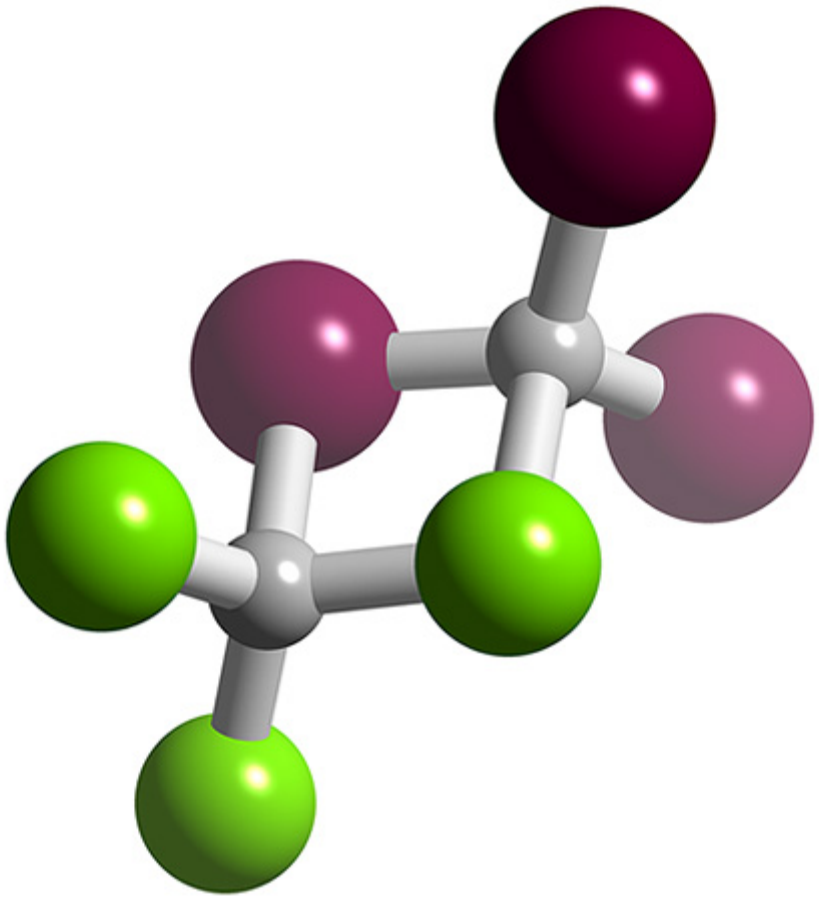


BCl_3

Exercises for molecules and ions

BCl_3BBr_3

Exercises for molecules and ions

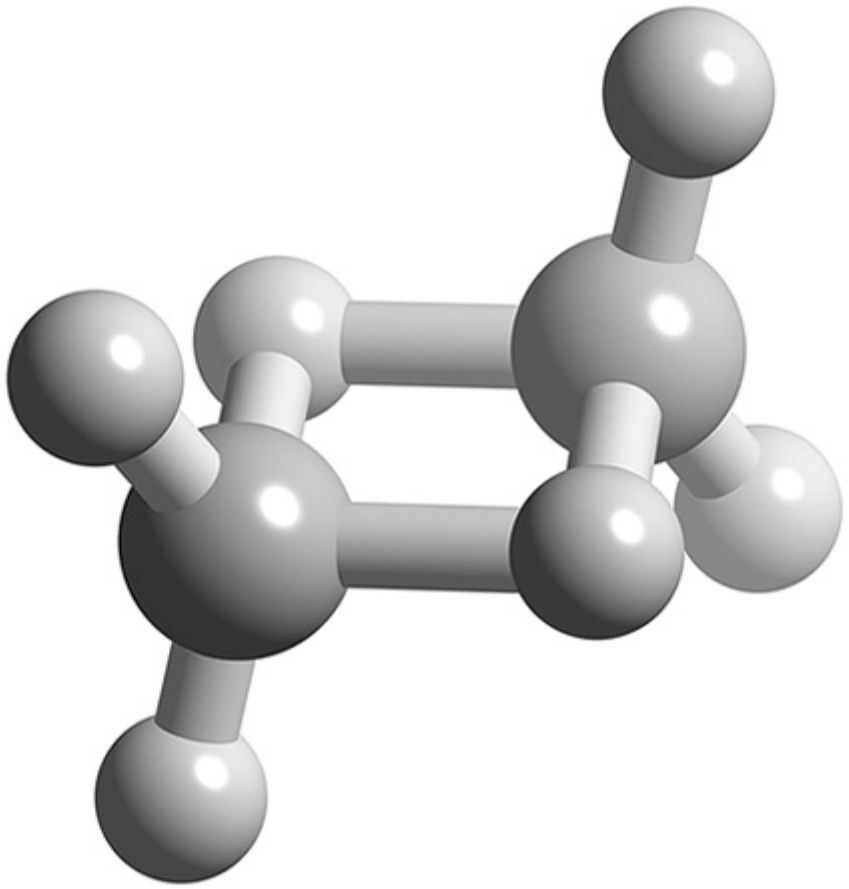


BCl_3BBr_3

Exercises for molecules and ions

B_2H_6

Exercises for molecules and ions

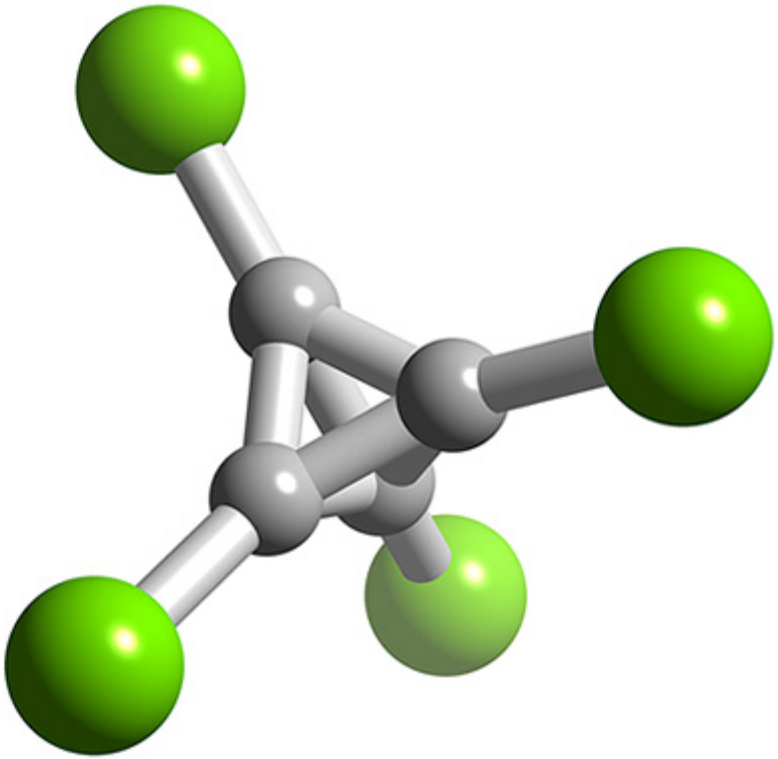


B_2H_6

Exercises for molecules and ions

$[B_4Cl_4]$

Exercises for molecules and ions

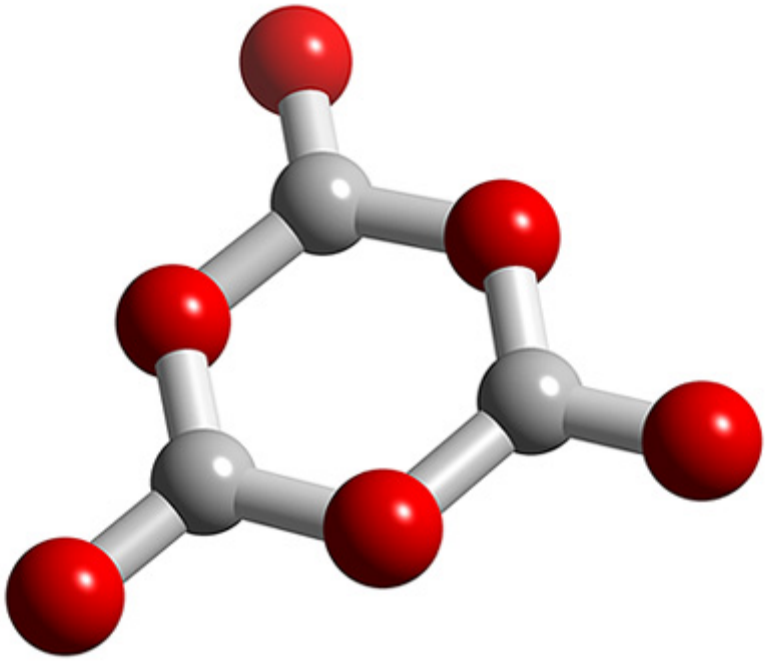


$[B_4Cl_4]$

Exercises for molecules and ions

$[B_3O_6]^{3-}$

Exercises for molecules and ions

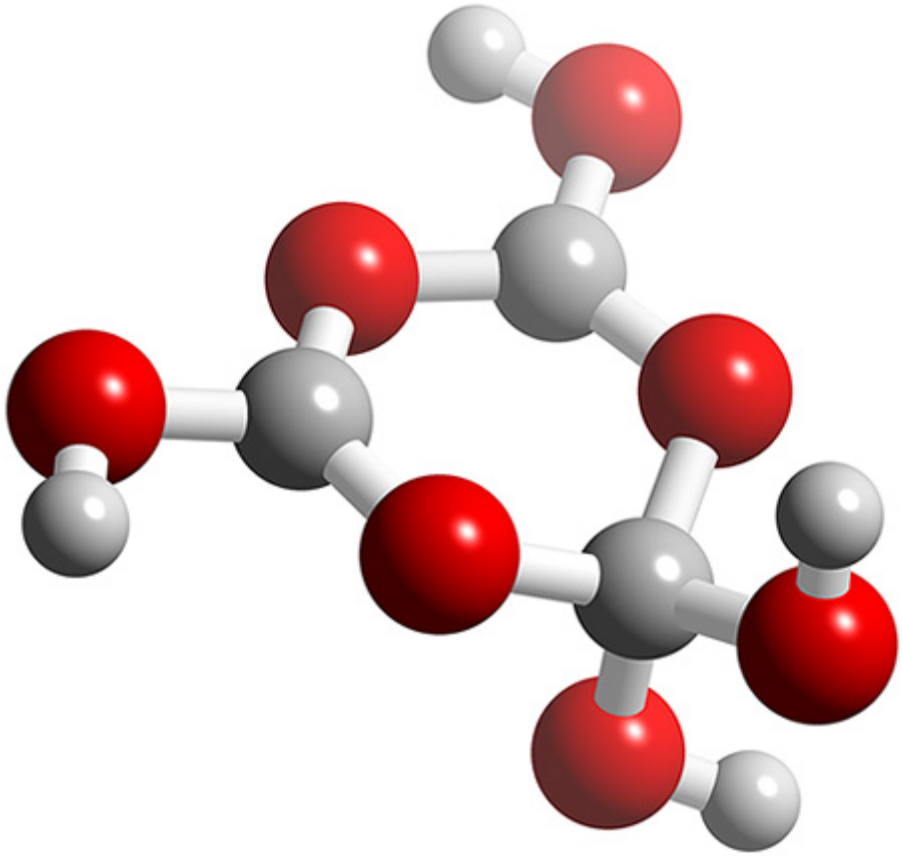


$[B_3O_6]^{3-}$

Exercises for molecules and ions

$[B_3O_3(OH)_4]^-$

Exercises for molecules and ions

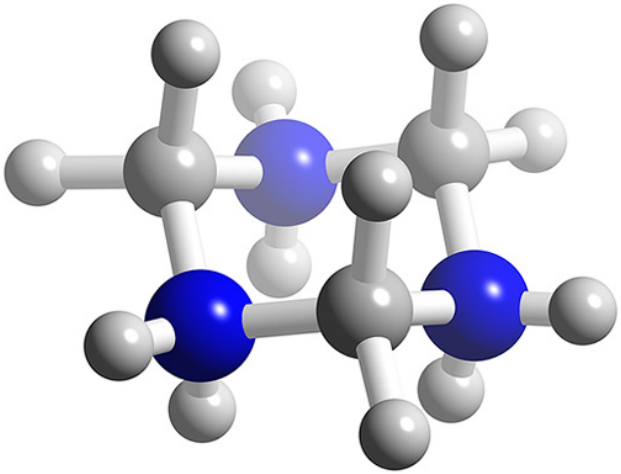


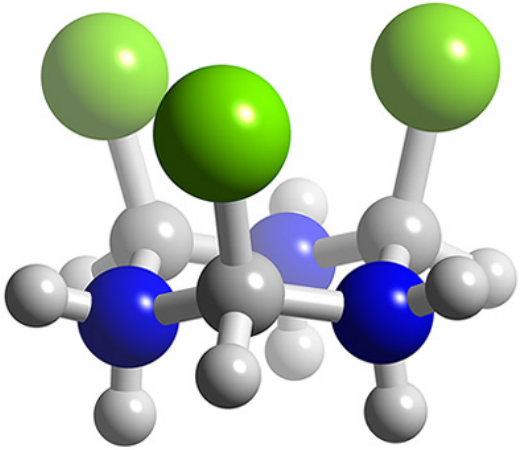
$[B_3O_3(OH)_4]^-$

Exercises for molecules and ions

$B_3N_3H_{12}$ also
$B_3N_3H_9Cl_3$

Exercises for molecules and ions



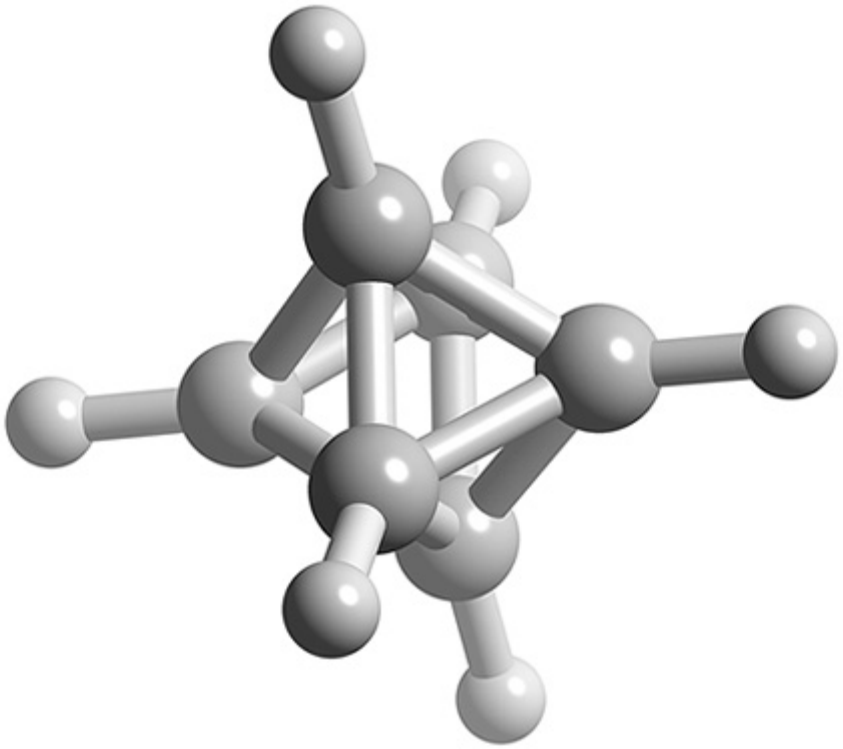


$B_3N_3H_{12}$ also
$B_3N_3H_9Cl_3$

Exercises for molecules and ions

B_6H_6

Exercises for molecules and ions

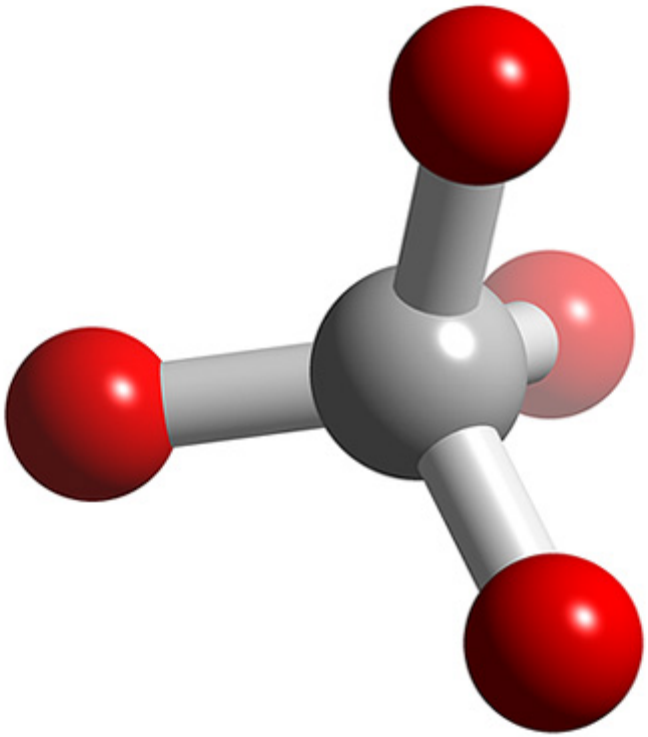


B_6H_6

Exercises for molecules and ions

$[AlO_4]^{5-}$

Exercises for molecules and ions

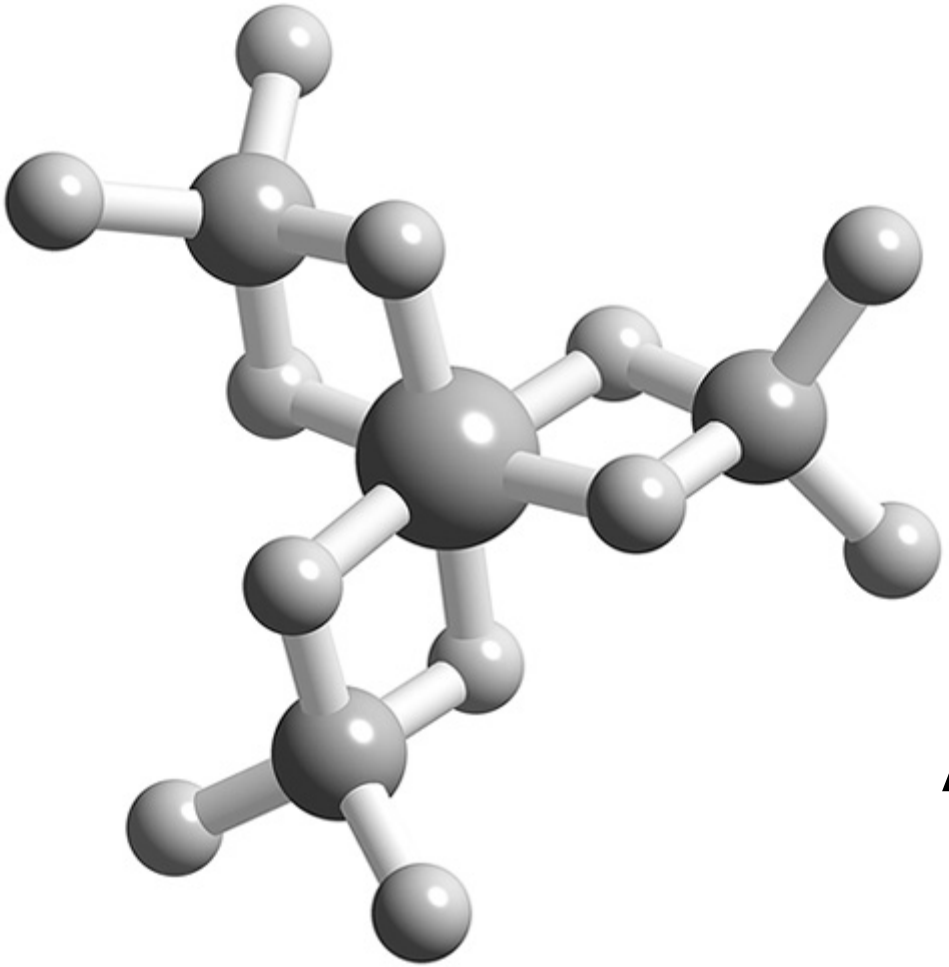


$[AlO_4]^{5-}$

Exercises for molecules and ions

$Al(BH_4)_3$

Exercises for molecules and ions

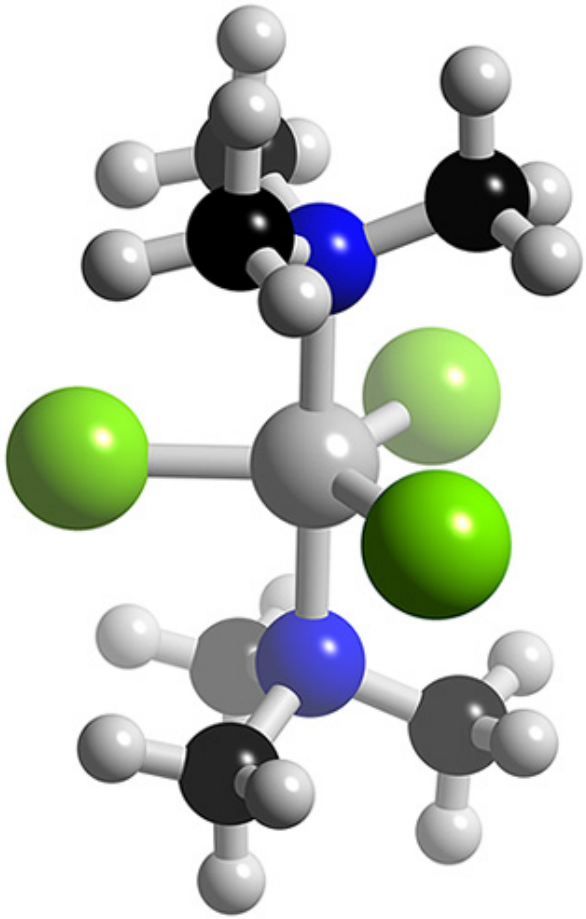


$Al(BH_4)_3$

Exercises for molecules and ions

$AlCl_3(NMe_3)_2$

Exercises for molecules and ions

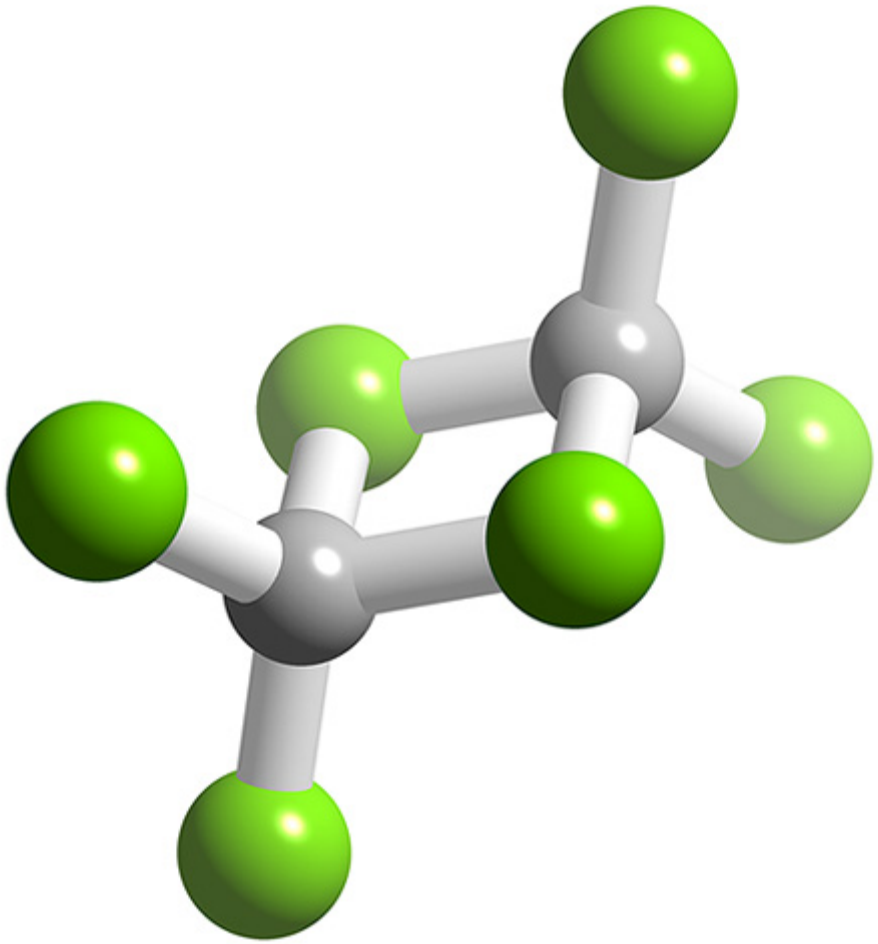


$AlCl_3(NMe_3)_2$

Exercises for molecules and ions

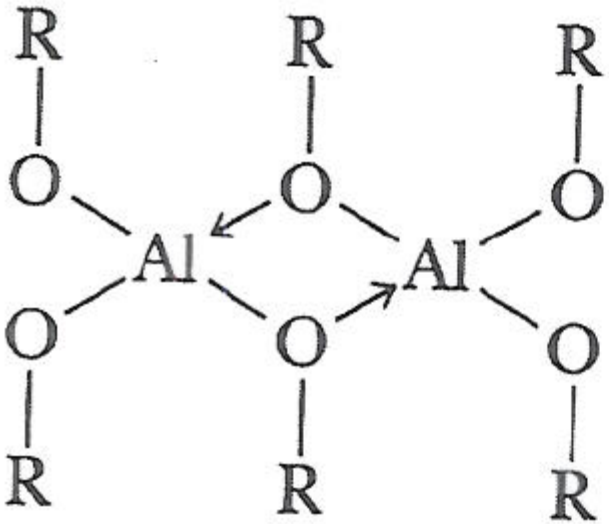
Al_2Cl_6

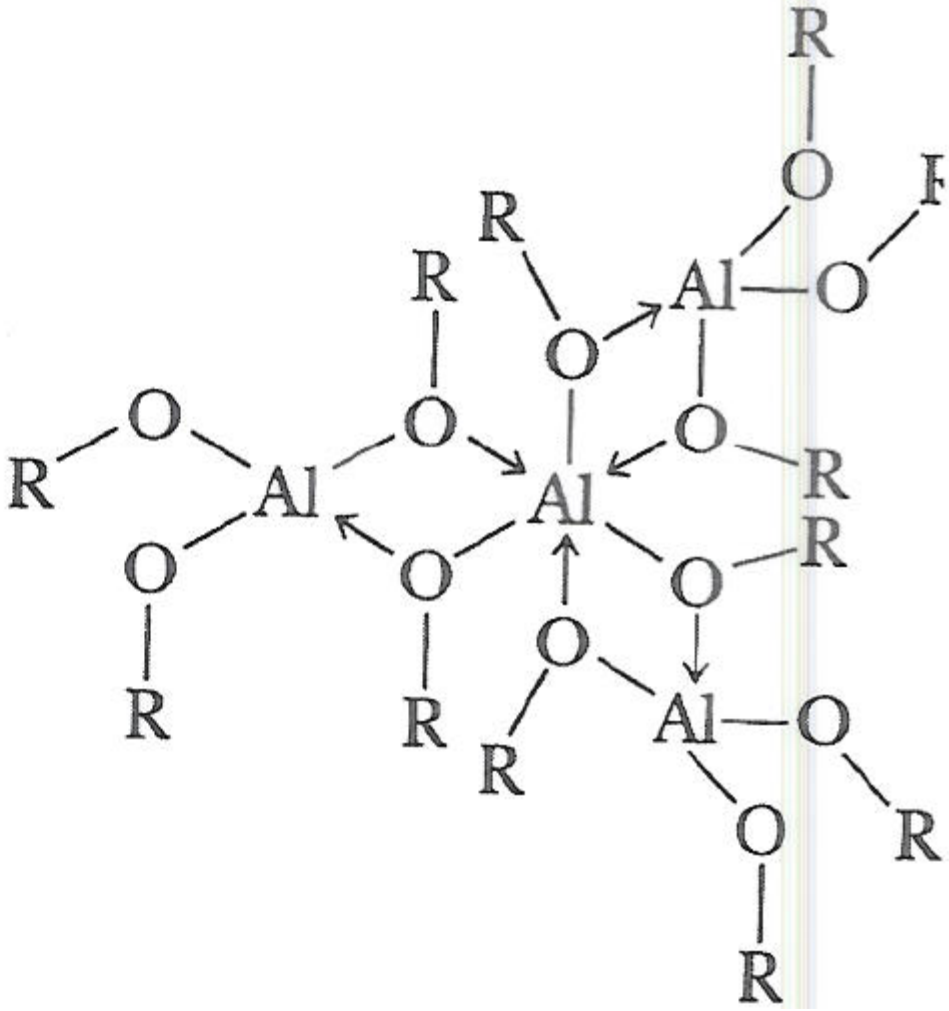
Exercises for molecules and ions



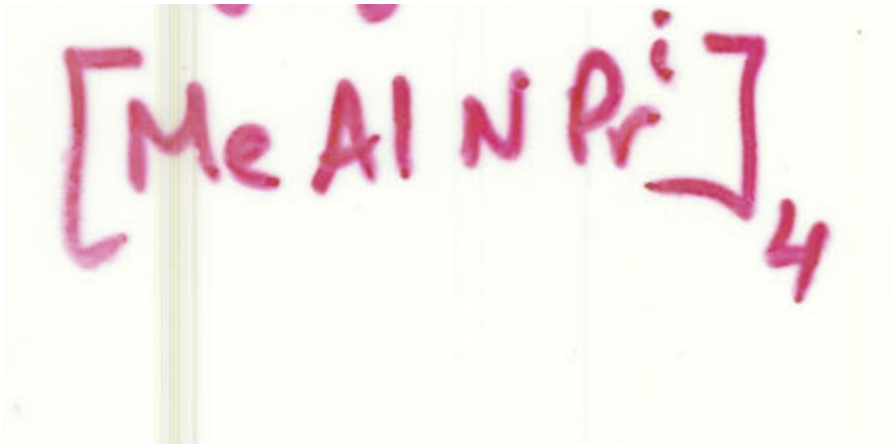
Al_2Cl_6

Exercises for molecules and ions





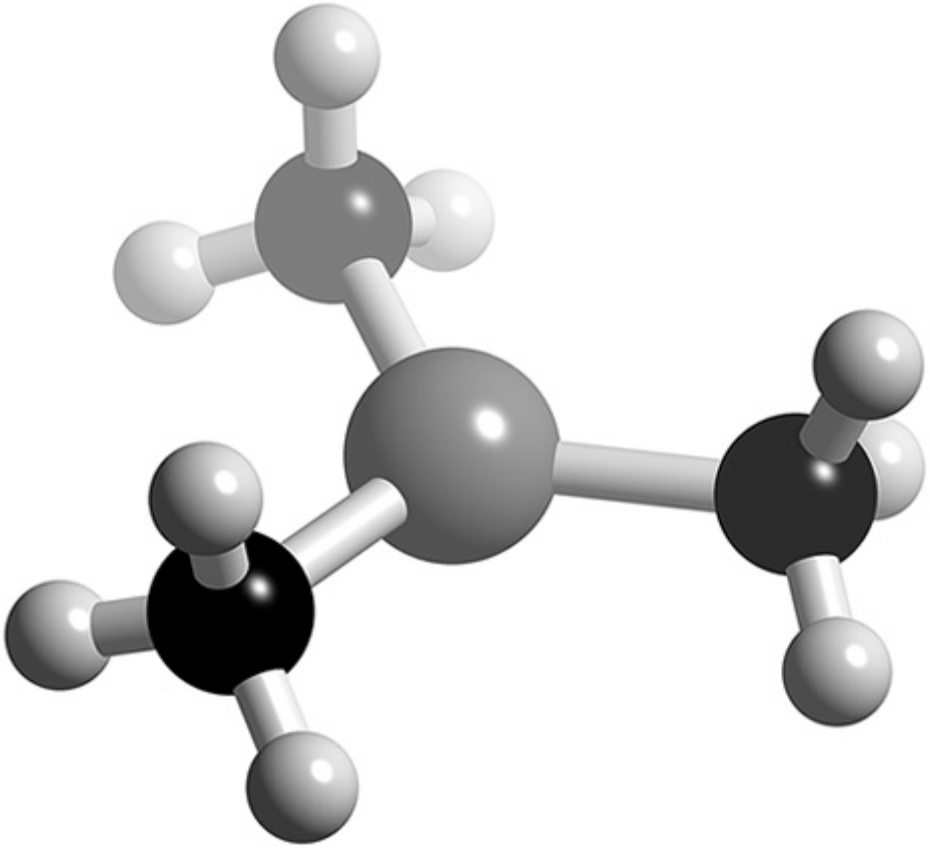
Exercises for molecules and ions



Exercises for molecules and ions

$GaMe_3$

Exercises for molecules and ions

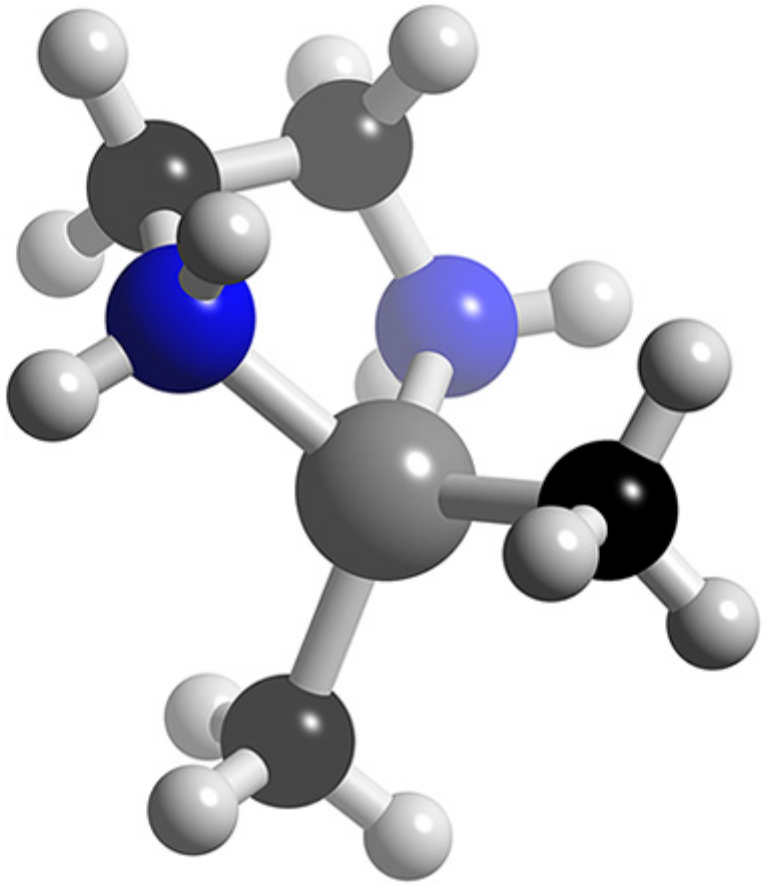


$GaMe_3$

Exercises for molecules and ions

$[GaMe_2(en)]^+$

Exercises for molecules and ions



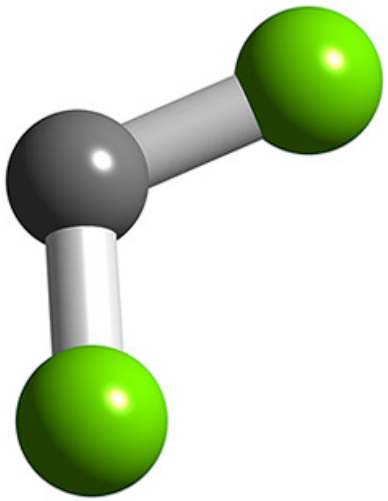
$[GaMe_2(en)]^+$

Exercises for molecules and ions

$GaCl_2$ (gas)

Ga_2Cl_4 (solid)

Exercises for molecules and ions



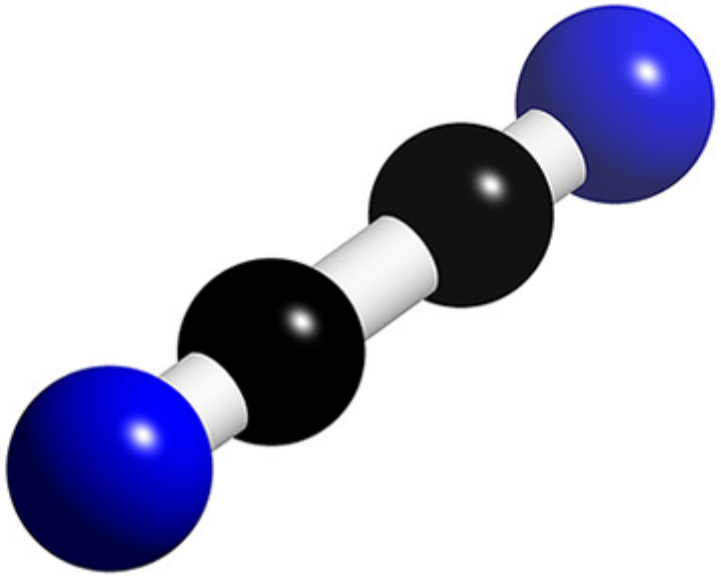
$GaCl_2$ (gas)

$Ga^+(GaCl_4)^-$

Exercises for molecules and ions

$(CN)_2$

Exercises for molecules and ions

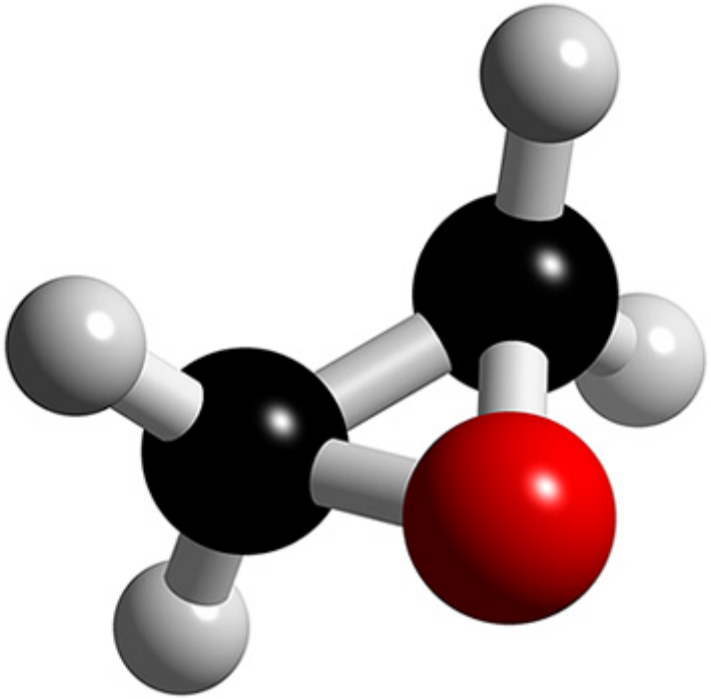


$(CN)_2$

Exercises for molecules and ions

CH_2CH_2O

Exercises for molecules and ions

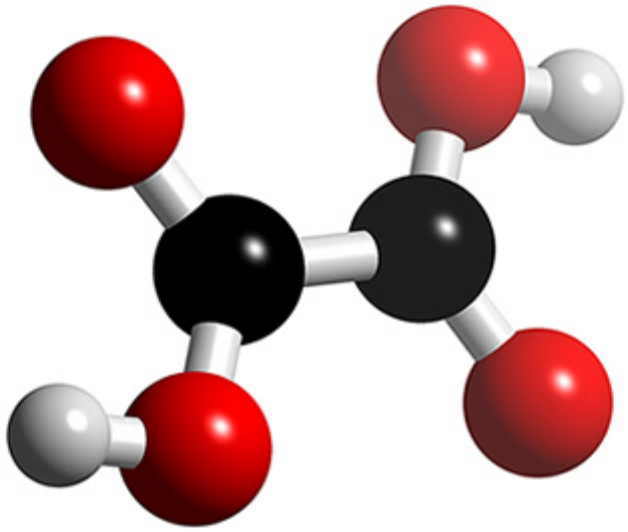


CH_2CH_2O

Exercises for molecules and ions

$[C_2O_4]^{2-}$

Exercises for molecules and ions

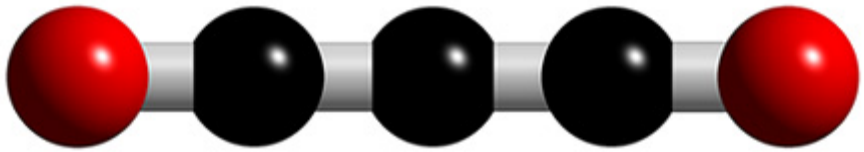


$[C_2O_4]^{2-}$

Exercises for molecules and ions

C_3O_2

Exercises for molecules and ions

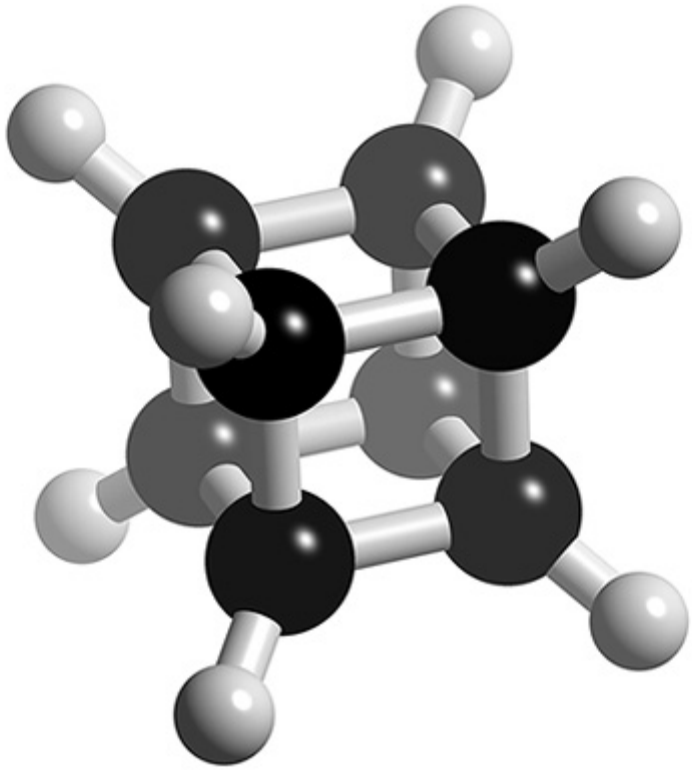


C_3O_2

Exercises for molecules and ions

C_8H_8

Exercises for molecules and ions

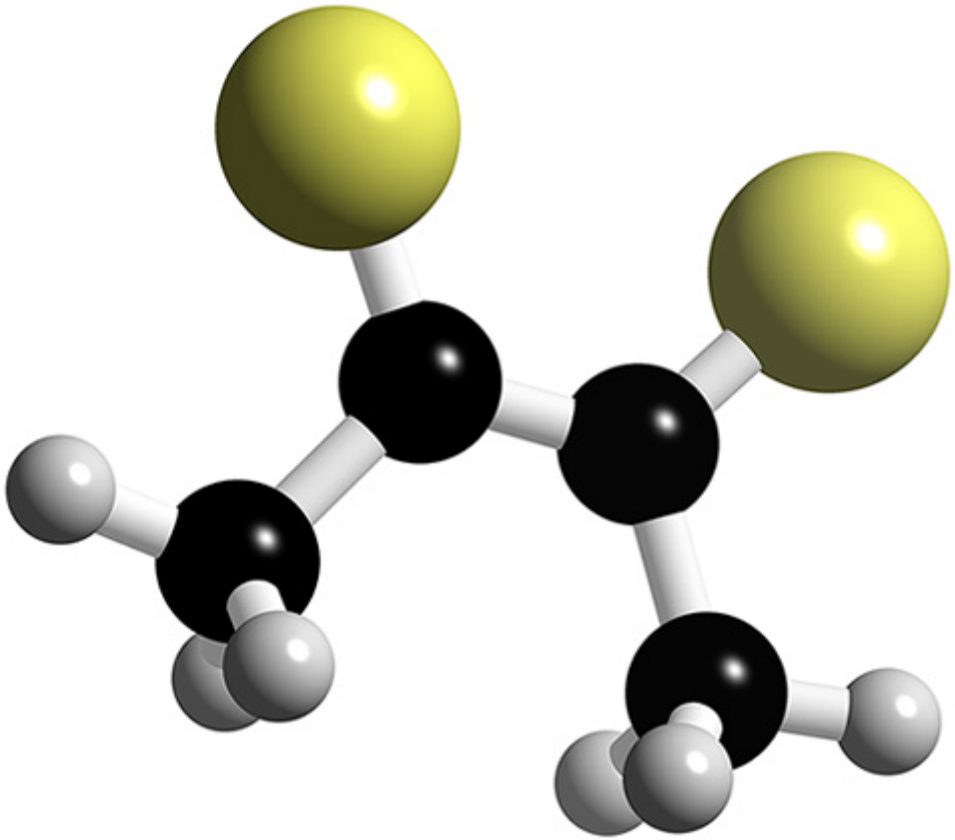


C_8H_8

Exercises for molecules and ions

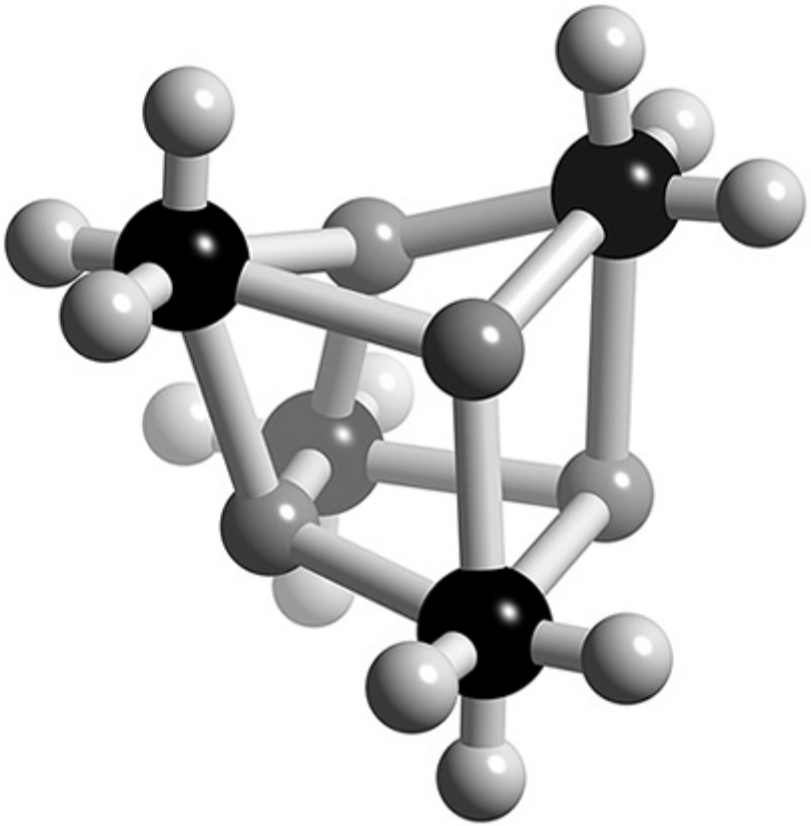
$S_2C_2Me_2$

Exercises for molecules and ions



$S_2C_2Me_2$

Exercises for molecules and ions

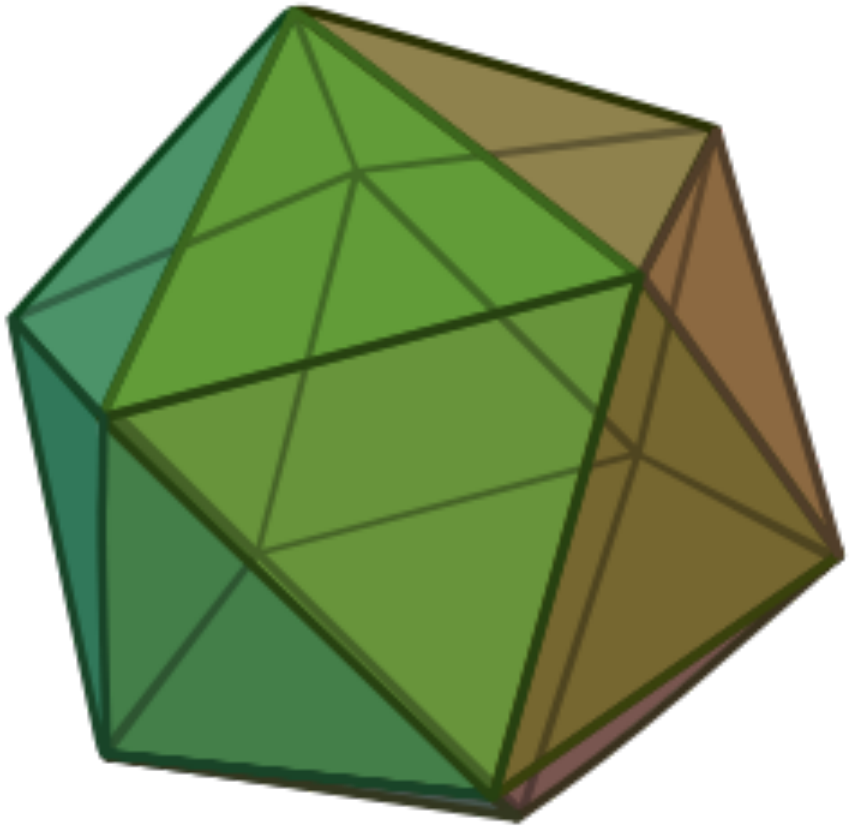


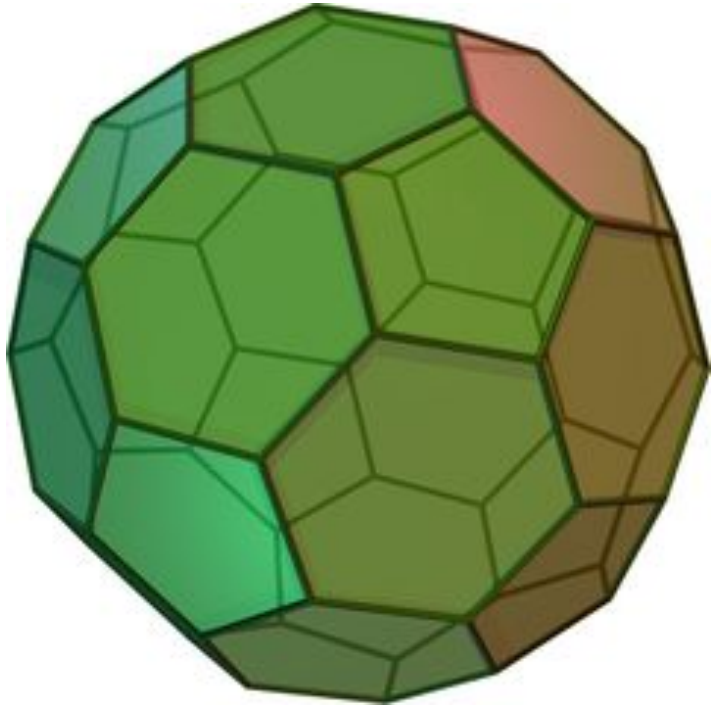
Li_4Me_4

Exercises for molecules and ions

C_{60}

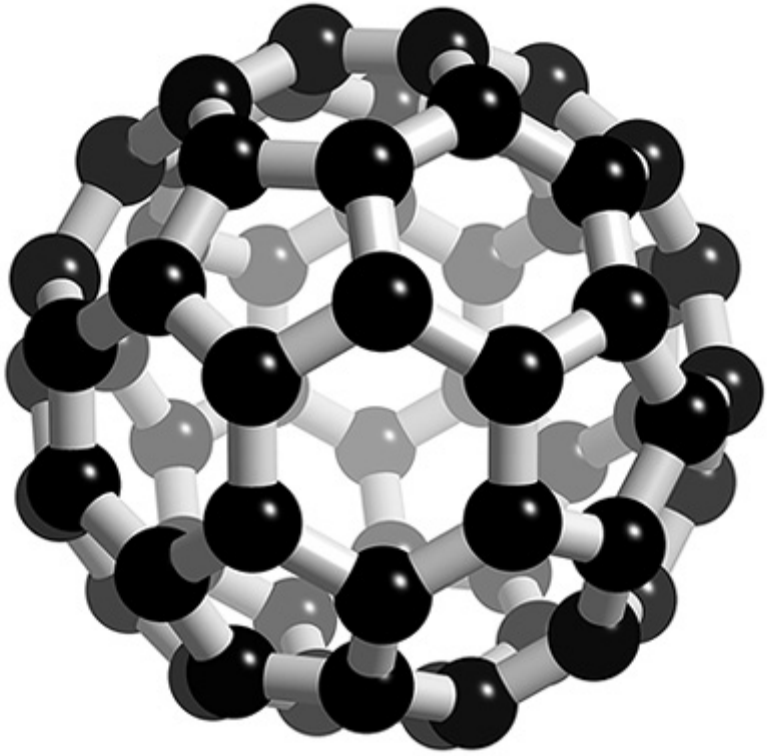
Icosahedron and truncated icosahedron





C_{60}

Exercises for molecules and ions

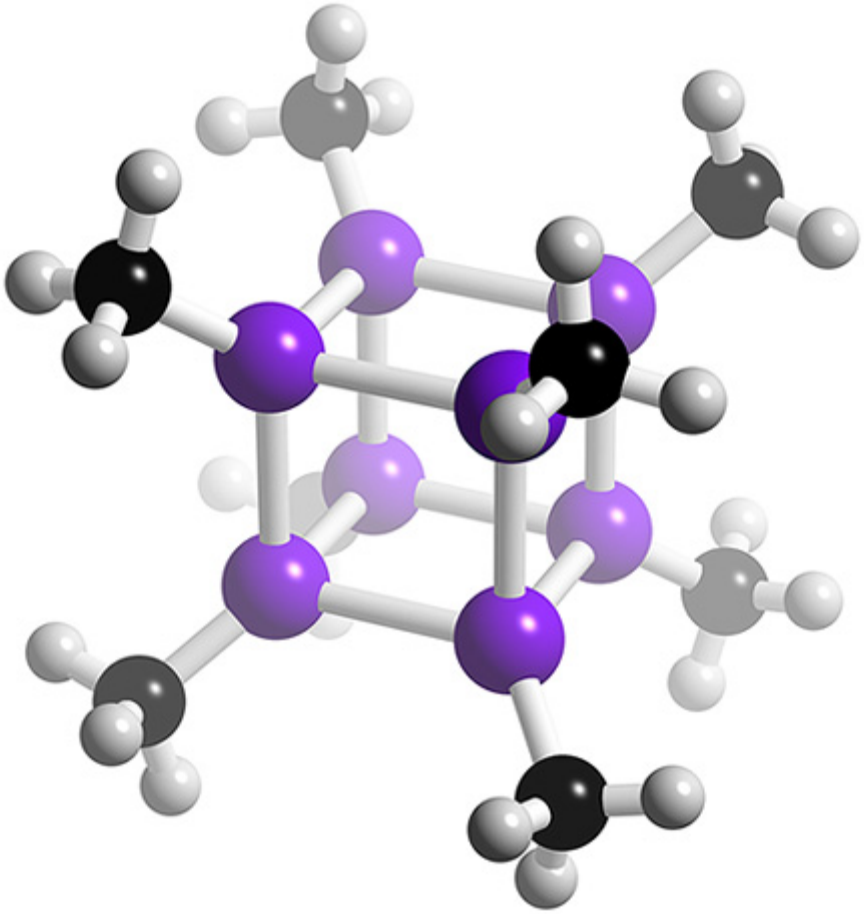


C_{60}

Exercises for molecules and ions

Si_8R_8

Exercises for molecules and ions

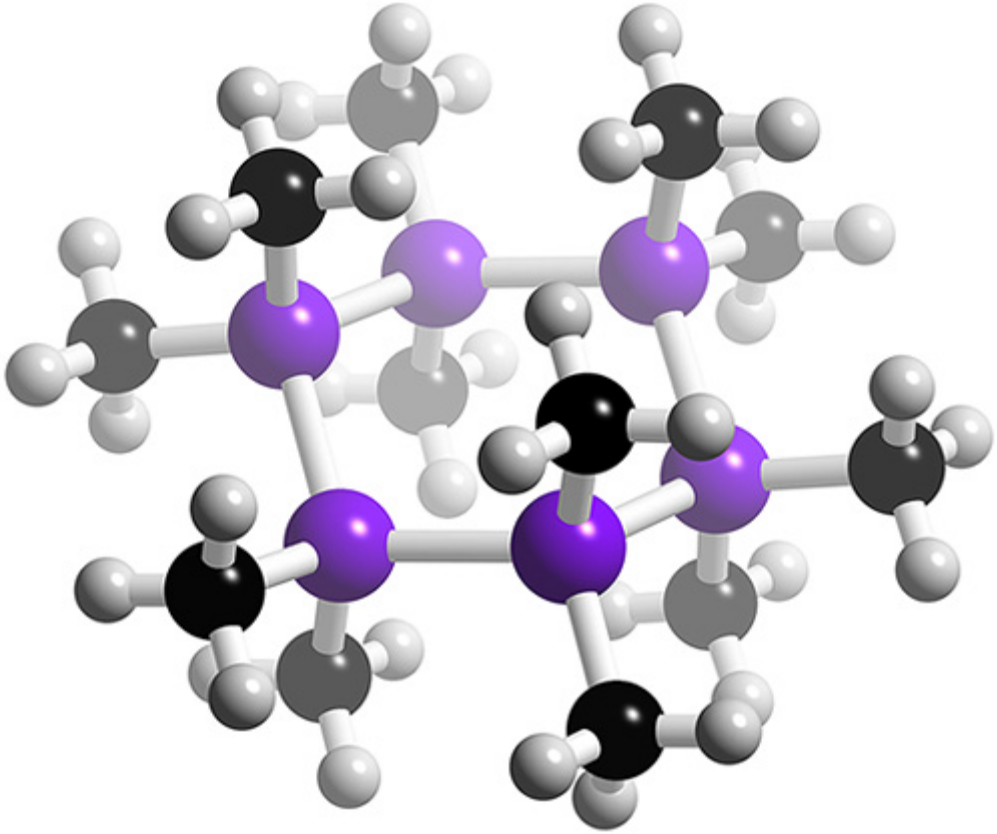


Si_8R_8

Exercises for molecules and ions

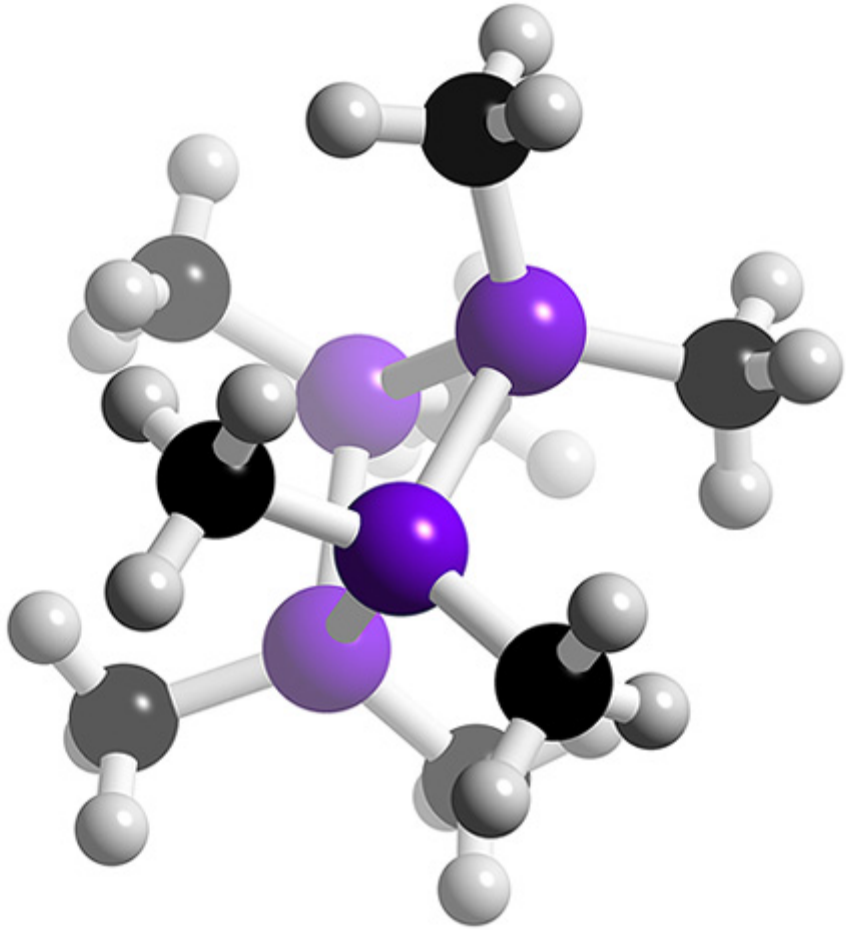
$(SiMe_2)_6$

Exercises for molecules and ions



$(SiMe_2)_6$

Exercises for molecules and ions

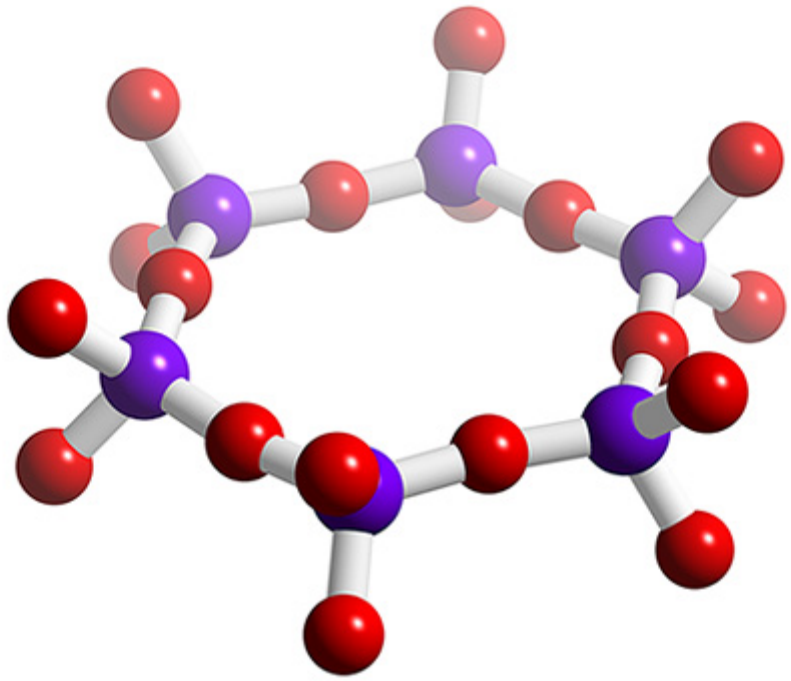


$(SiMe_2)_4$

Exercises for molecules and ions

$[Si_6O_{18}]^{12-}$

Exercises for molecules and ions

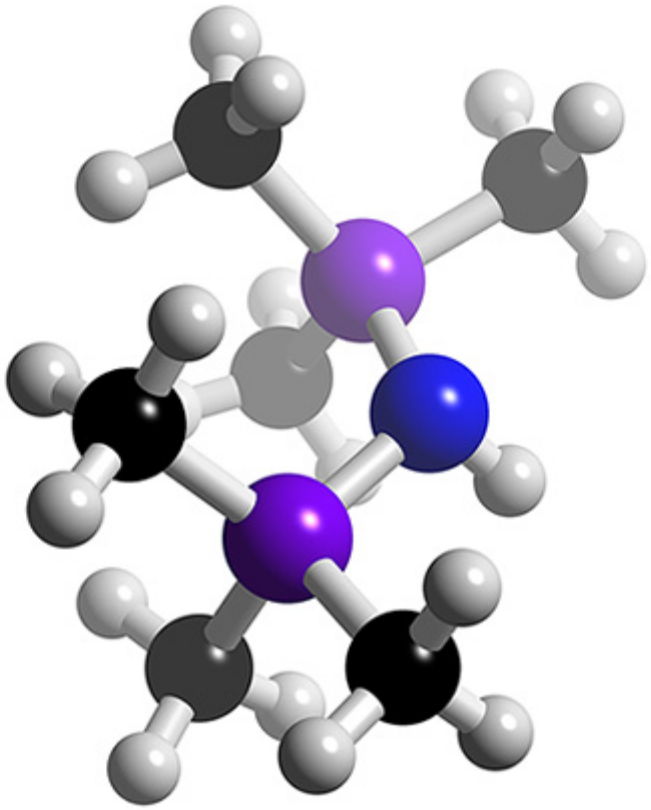


$[Si_6O_{18}]^{12-}$

Exercises for molecules and ions

$NH(SiMe_3)_2$

Exercises for molecules and ions

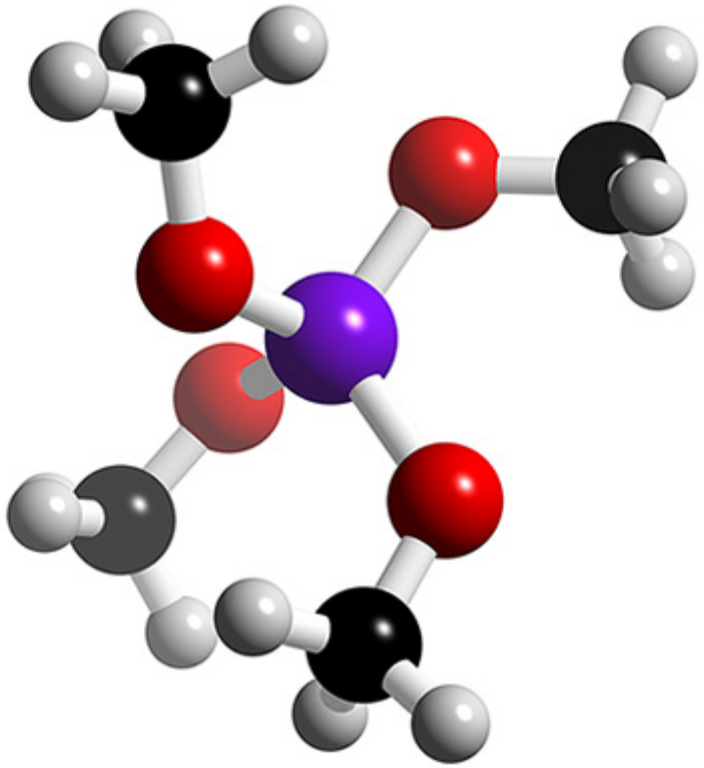


$NH(SiMe_3)_2$

Exercises for molecules and ions

$Si(OMe)_4$

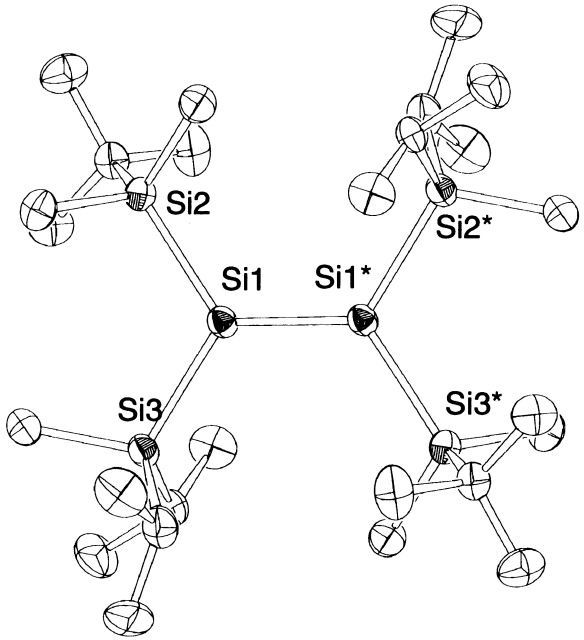
Exercises for molecules and ions



$Si(OMe)_4$

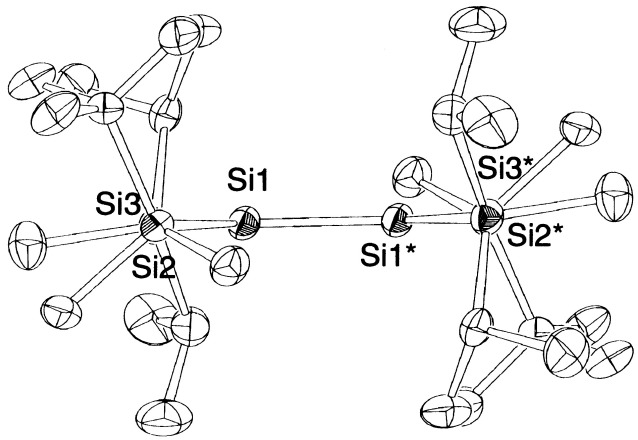
Exercises for molecules and ions

(a)

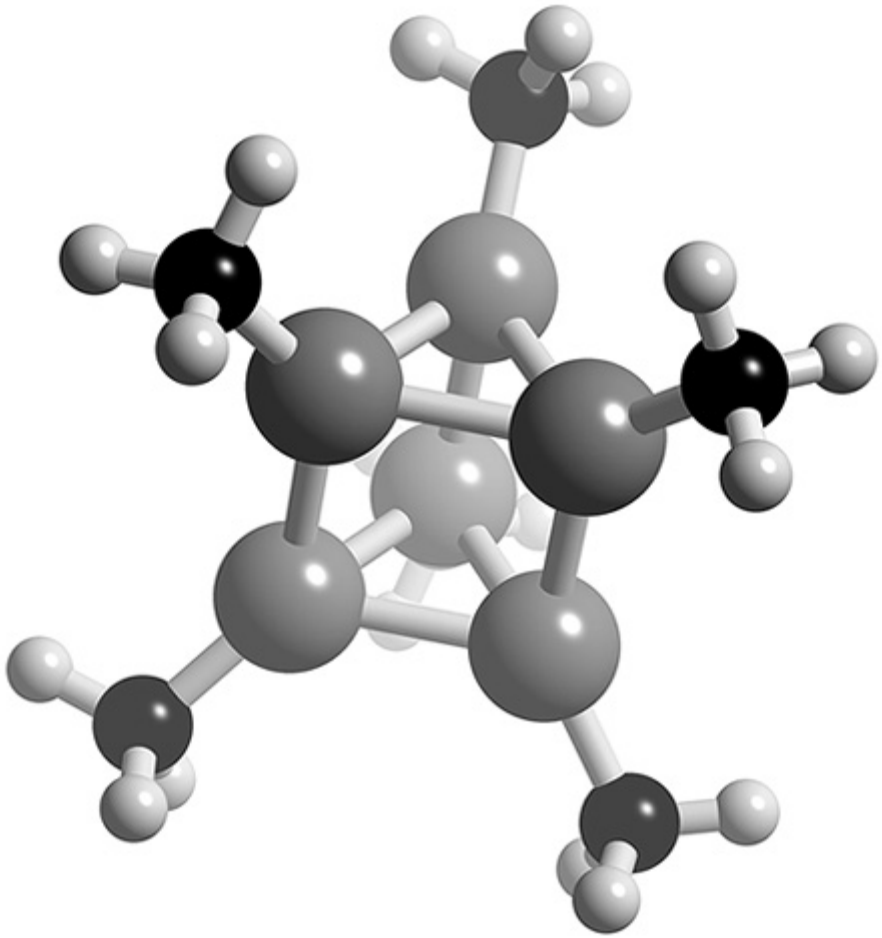


Doubly bonded Si-Si are disfavored

(b)



Exercises for molecules and ions

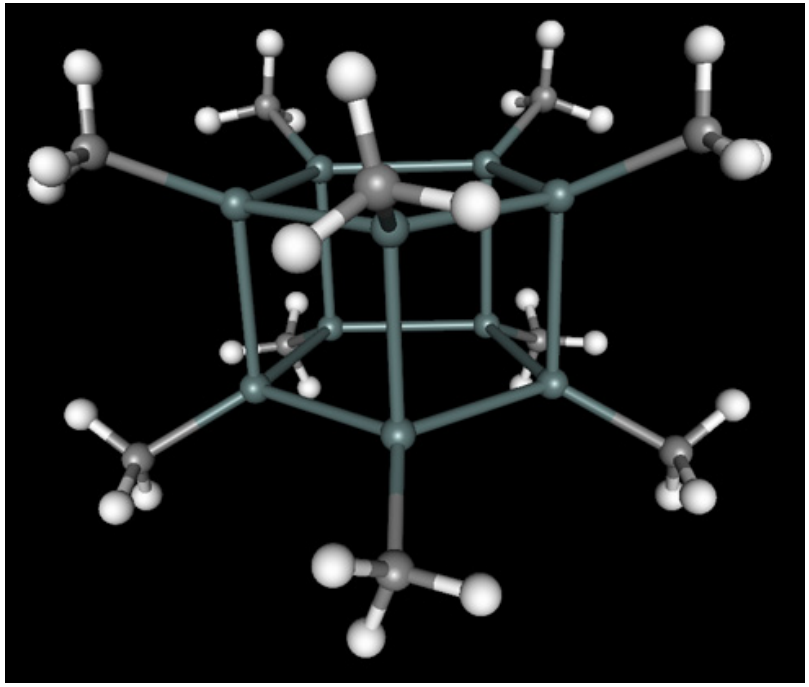


Ge_6R_6

Exercises for molecules and ions

$Sn_{10}R_{10}$

Exercises for molecules and ions

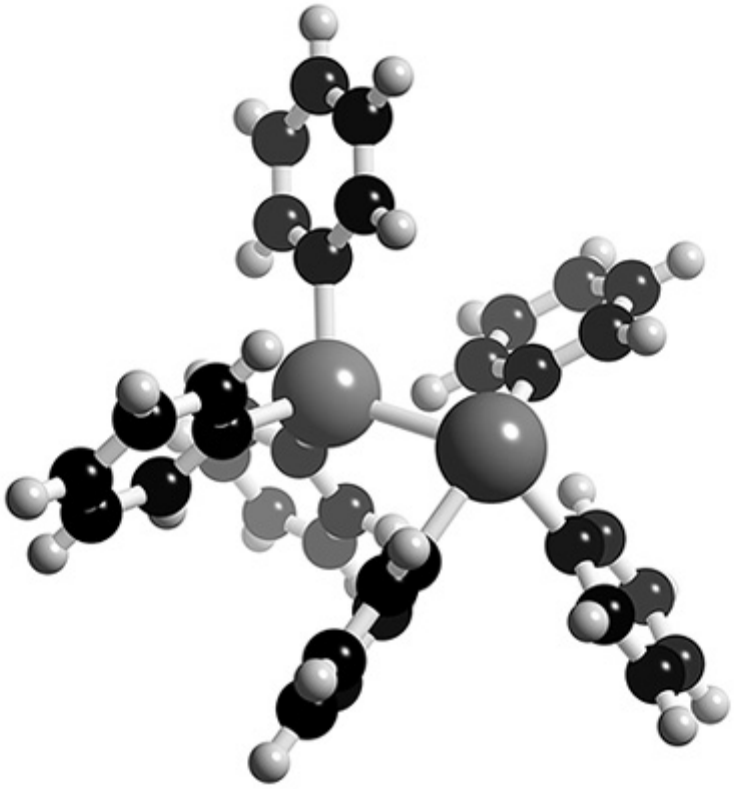


$Sn_{10}R_{10}$

Exercises for molecules and ions

Pb_2R_6

Exercises for molecules and ions

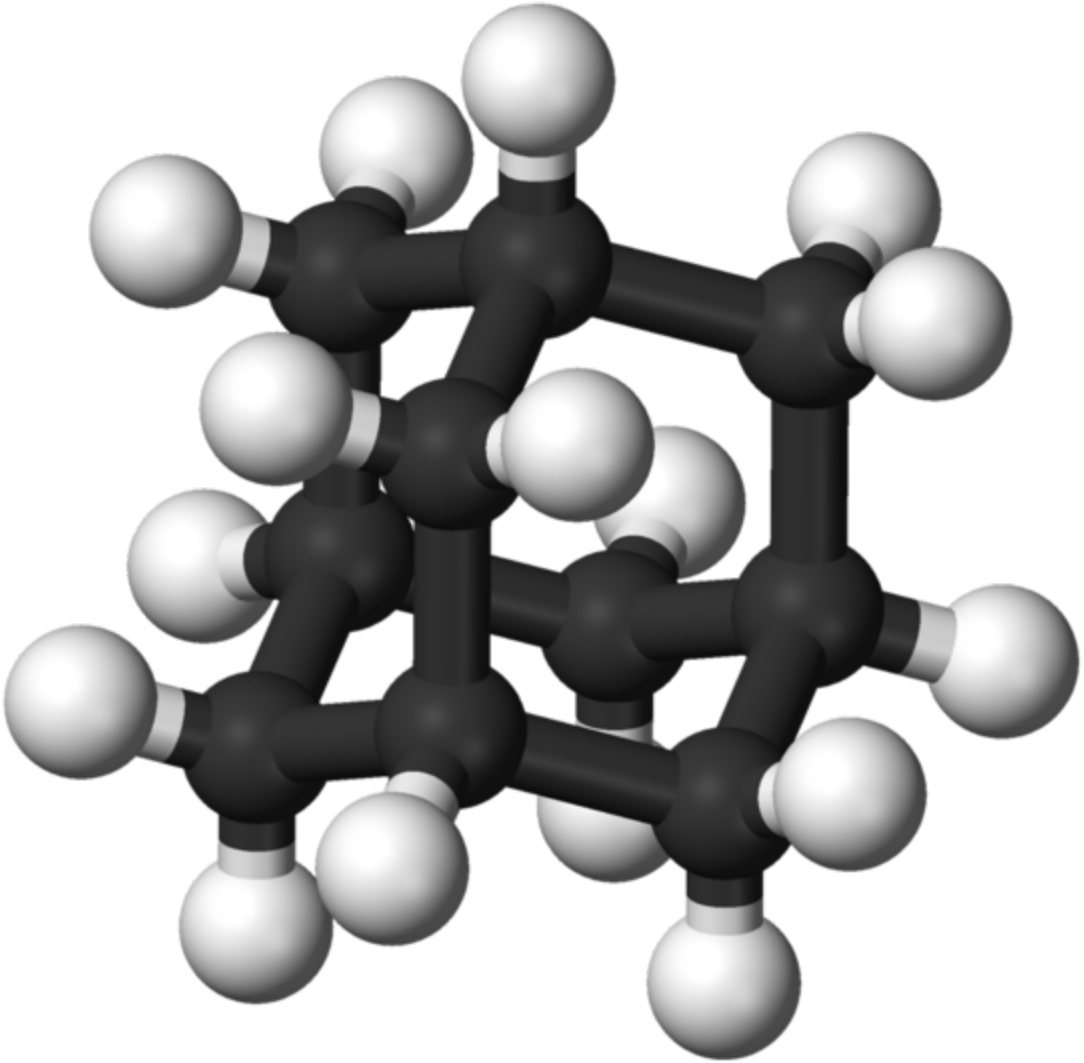


Pb_2R_6

Exercises for molecules and ions

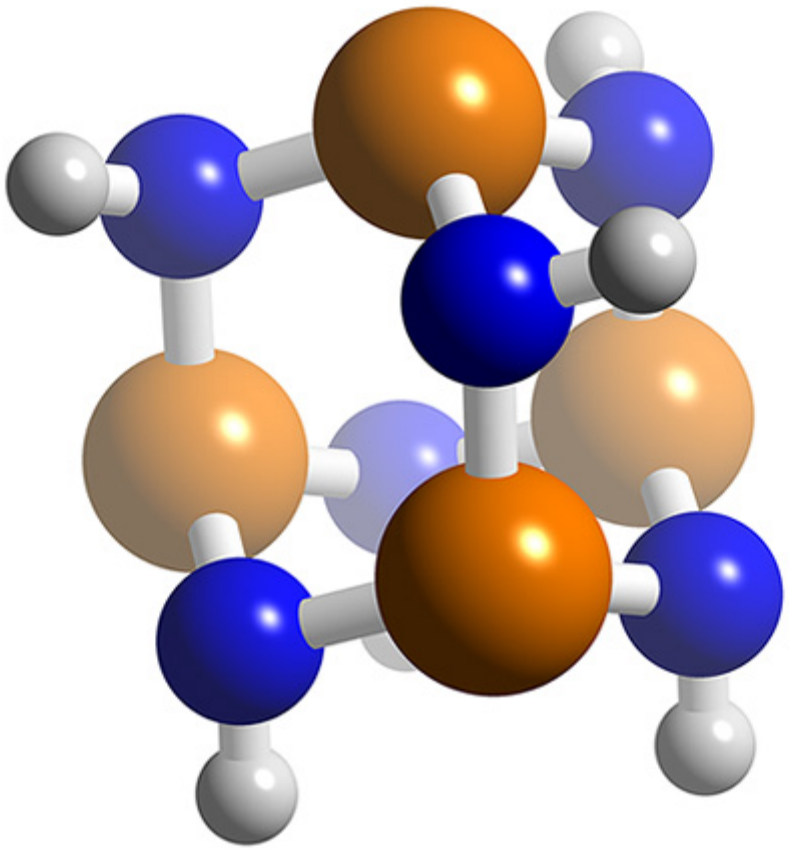
$P_4(NR)_6$

Exercises for molecules and ions



$C_{10}H_{16}$

Exercises for molecules and ions

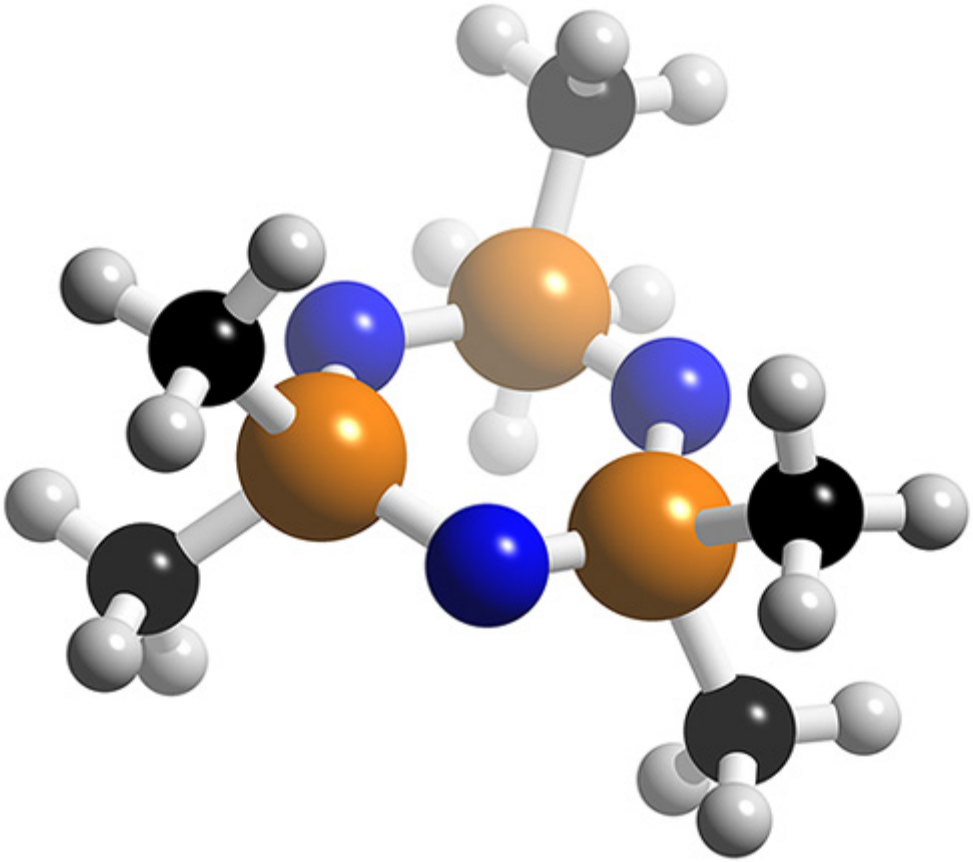


$P_4(NR)_6$

Exercises for molecules and ions

$(PN)_3(Me)_6$

Exercises for molecules and ions

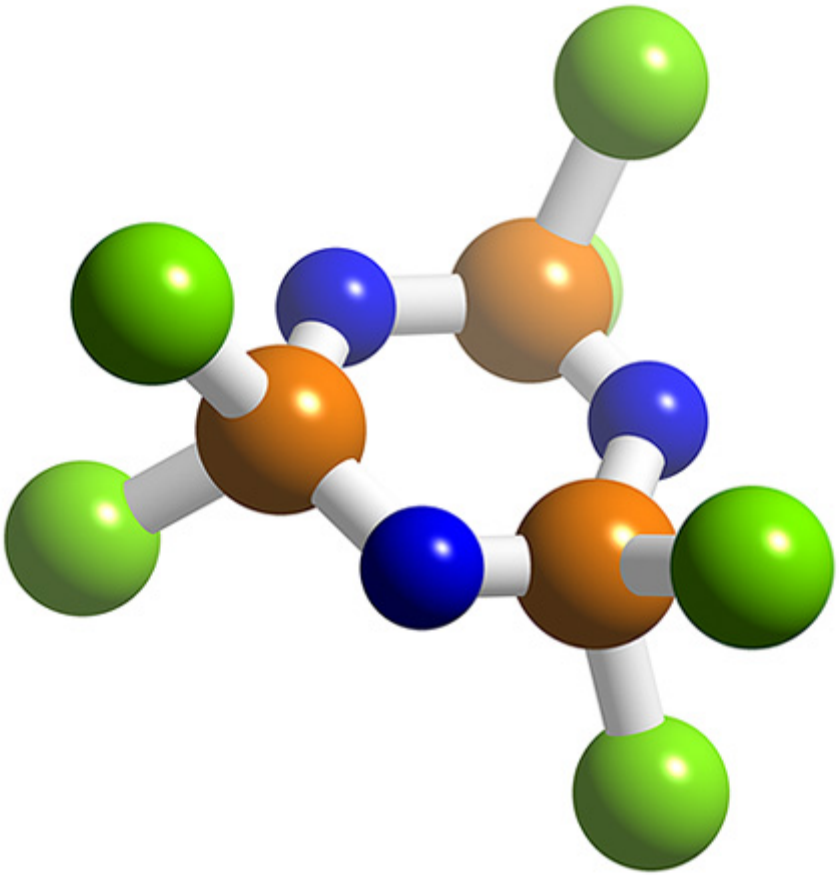


$(PN)_3(Me)_6$

Exercises for molecules and ions

$(PNCl_2)_3$

Exercises for molecules and ions



$(PNCl_2)_3$

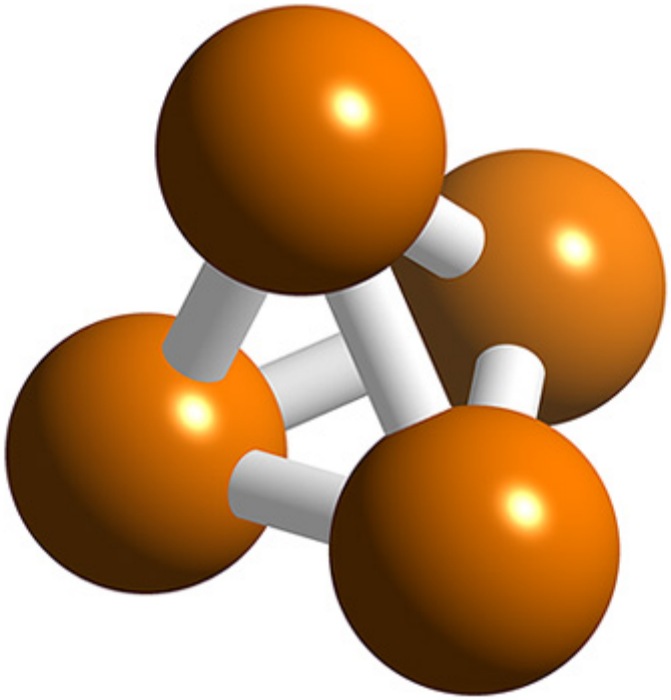
Exercises for molecules and ions

P_4

Exercises for molecules and ions

P_4

Exercises for molecules and ions

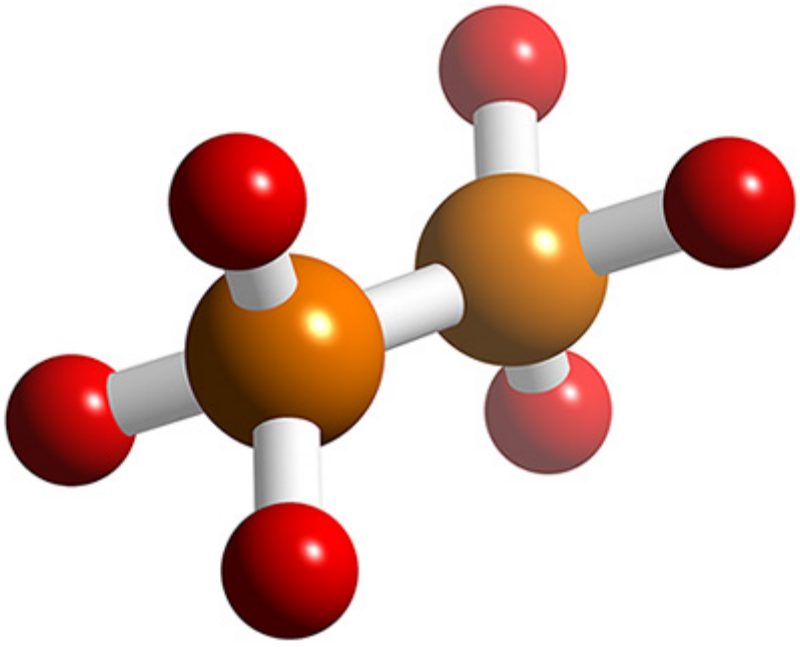


P_4

Exercises for molecules and ions

$[P_2O_6]^{4-}$

Exercises for molecules and ions

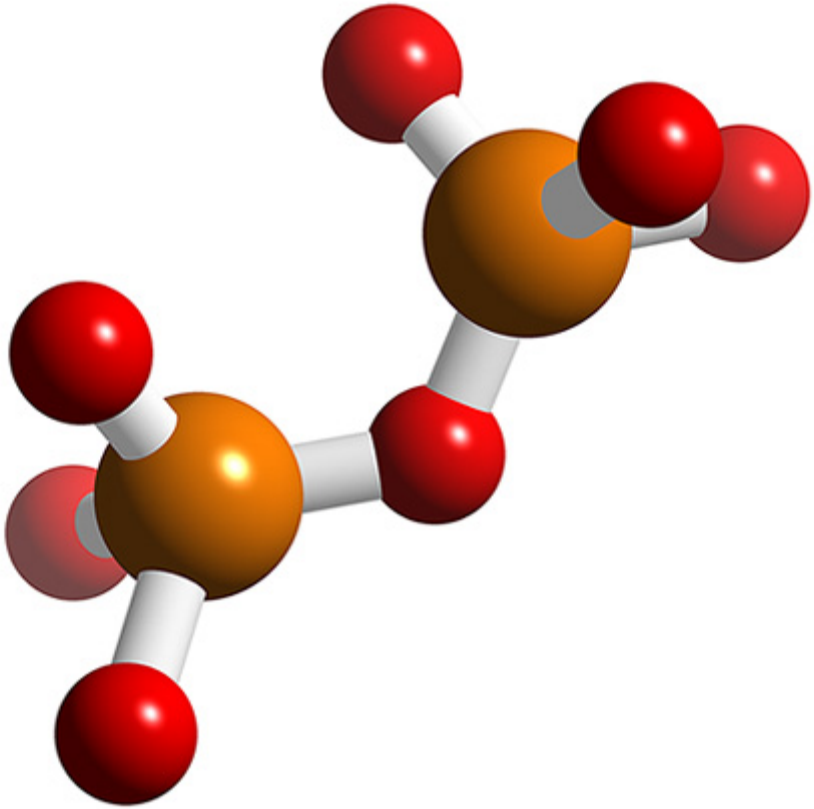


$[P_2O_6]^{4-}$

Exercises for molecules and ions

$[P_2O_7]^{4-}$

Exercises for molecules and ions

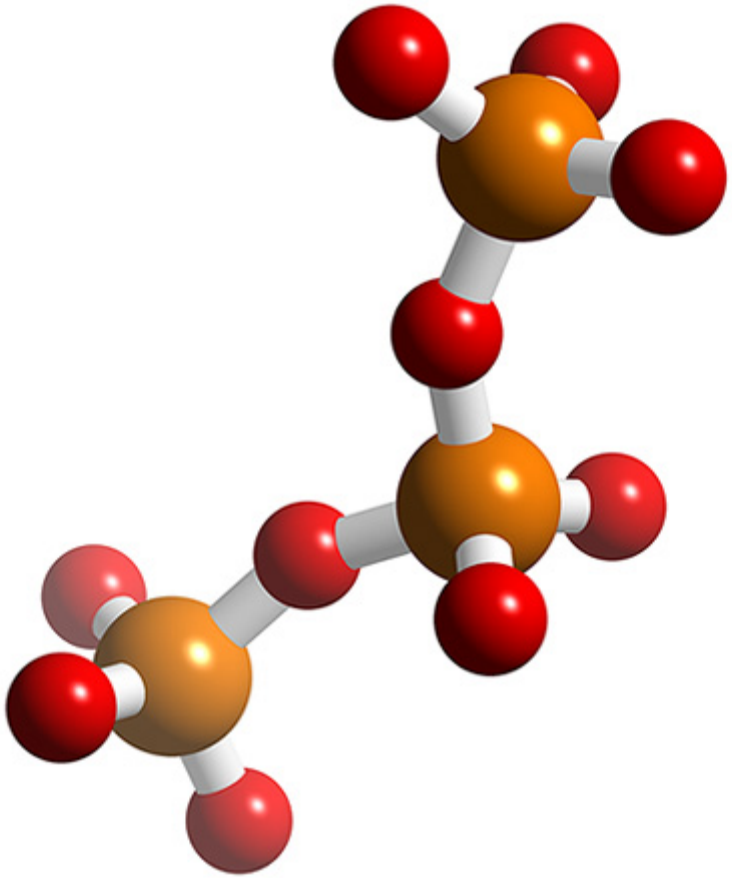


$[P_2O_7]^{4-}$

Exercises for molecules and ions

$[P_3O_{10}]^{5-}$

Exercises for molecules and ions

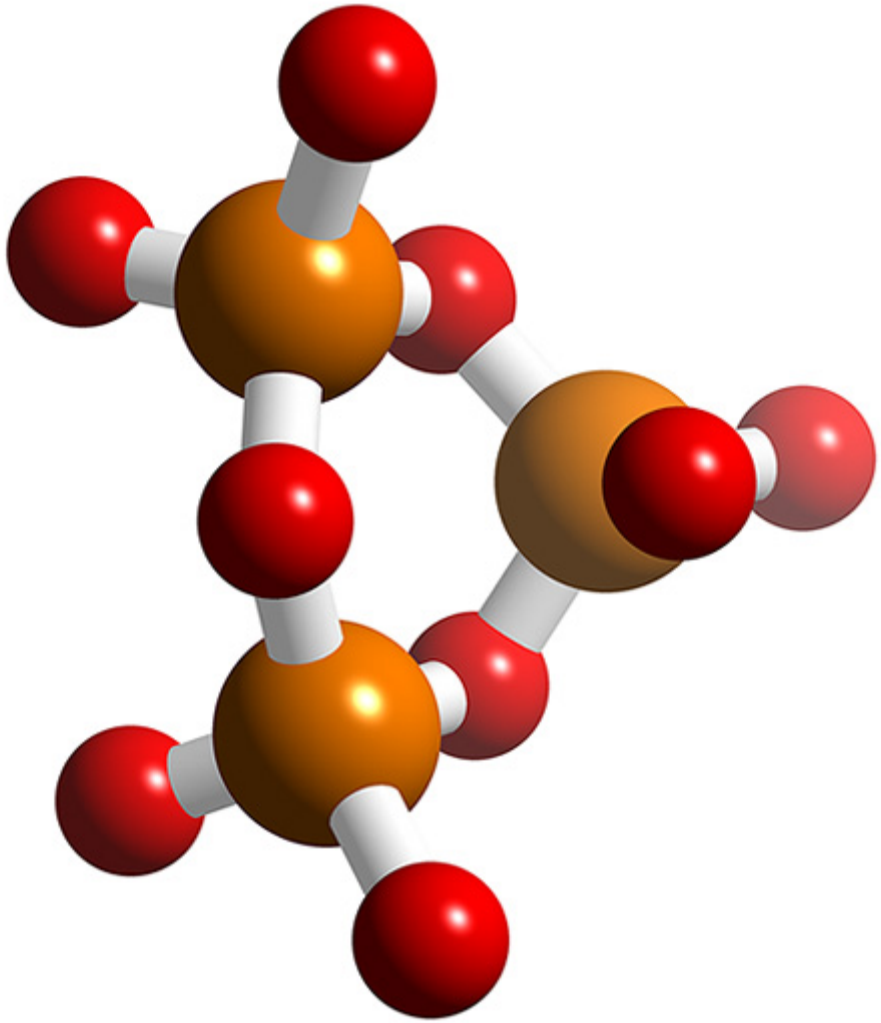


$[P_3O_{10}]^{5-}$

Exercises for molecules and ions

$[P_3O_9]^{3-}$

Exercises for molecules and ions

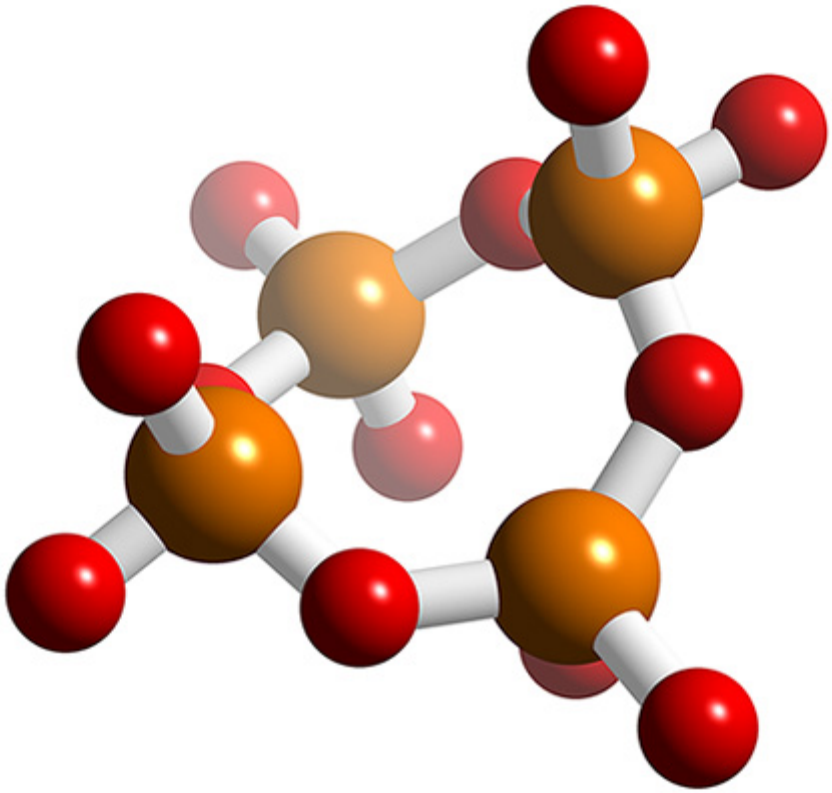


$[P_3O_9]^{3-}$

Exercises for molecules and ions

$[P_4O_{12}]^{4-}$

Exercises for molecules and ions

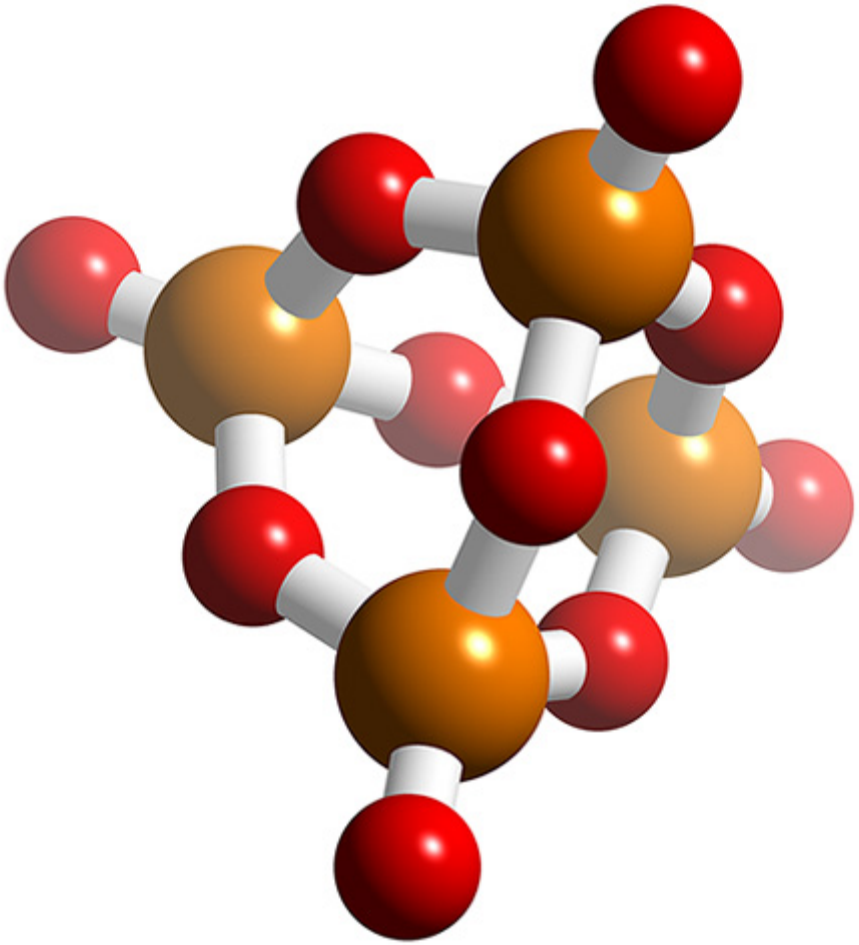


$[P_4O_{12}]^{4-}$

Exercises for molecules and ions

P_4O_{10}

Exercises for molecules and ions

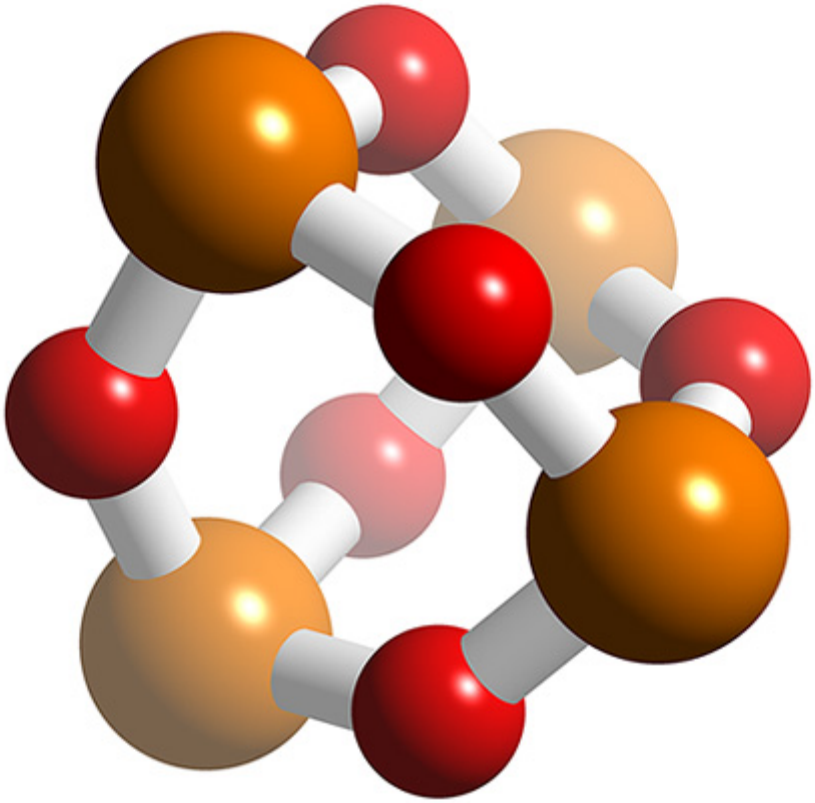


P_4O_{10}

Exercises for molecules and ions

P_4O_6

Exercises for molecules and ions

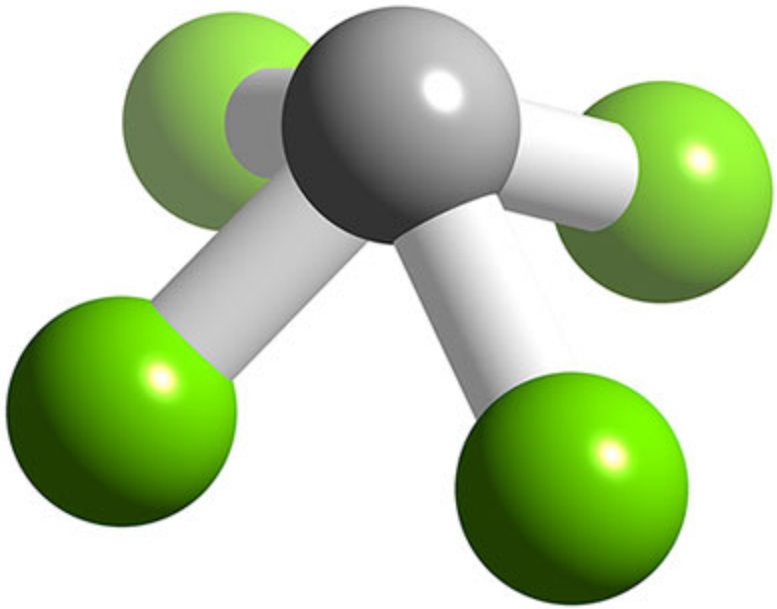


P_4O_6

Exercises for molecules and ions

$[AsCl_4]^-$

Exercises for molecules and ions



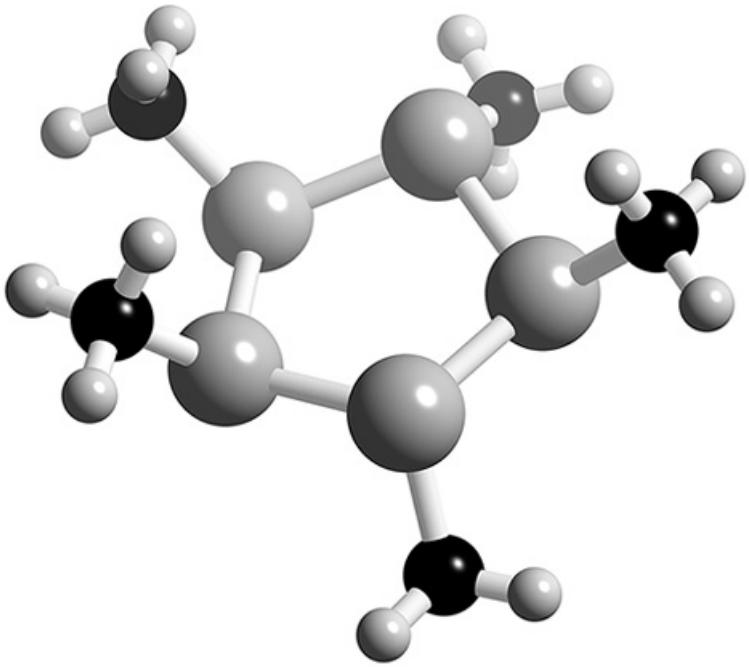
$[AsCl_4]^-$

Exercises for molecules and ions

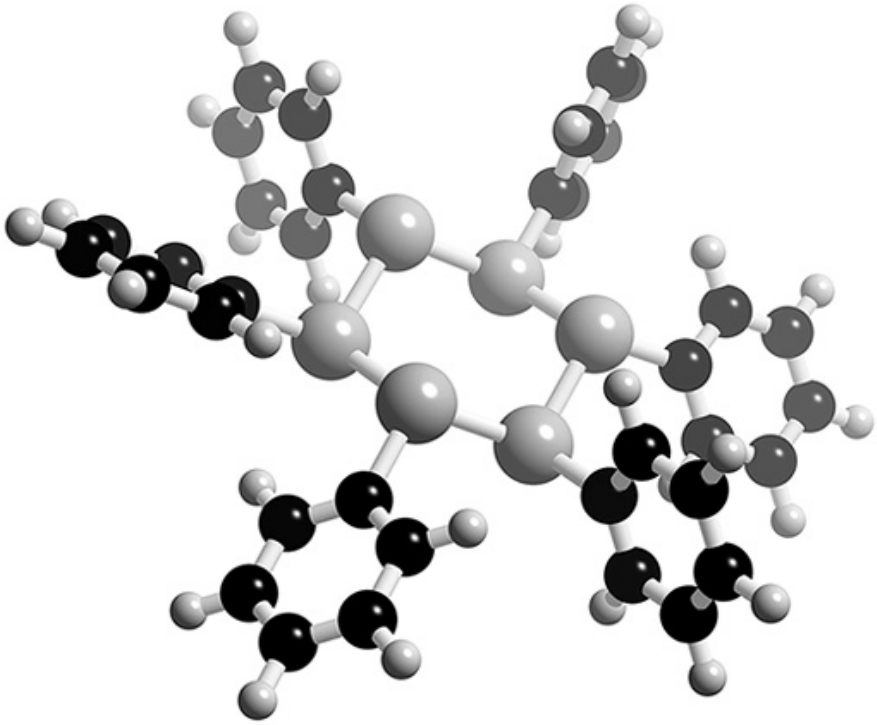
As_5Me_5

As_6Me_6

Exercises for molecules and ions



As_5Me_5

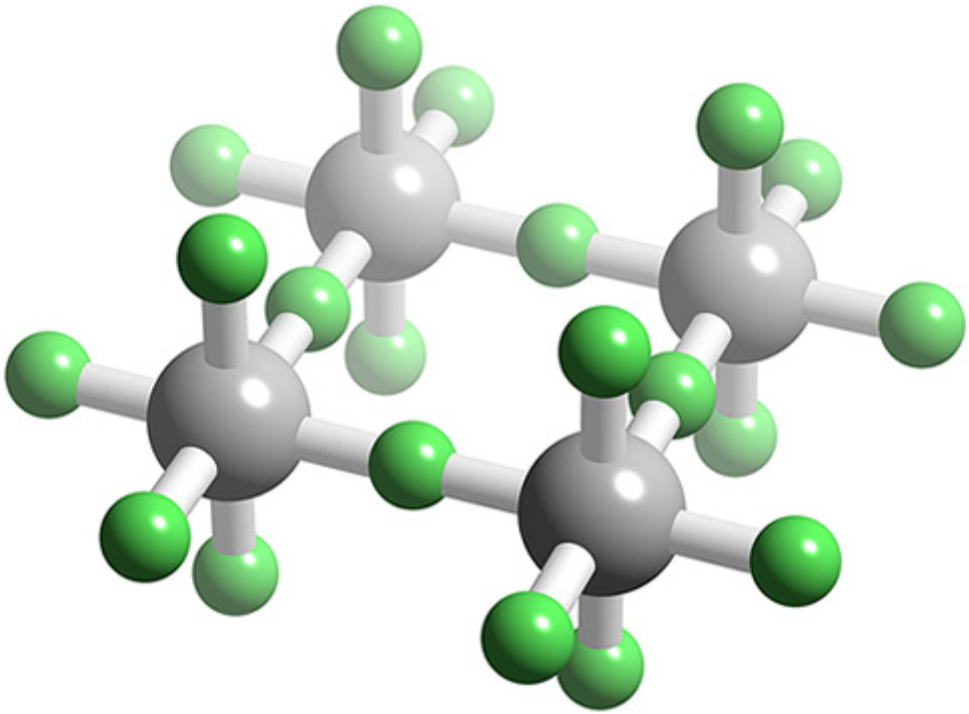


As_6Me_6

Exercises for molecules and ions

$(SbF_5)_4$

Exercises for molecules and ions

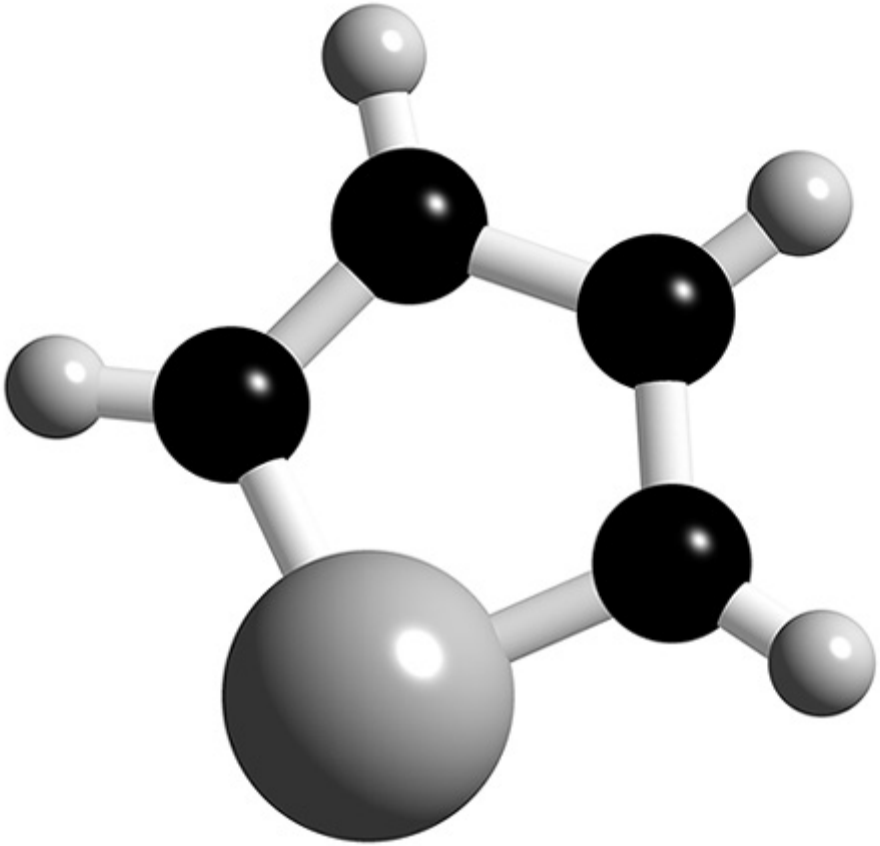


$(SbF_5)_4$

Exercises for molecules and ions

SbC_4H_4

Exercises for molecules and ions

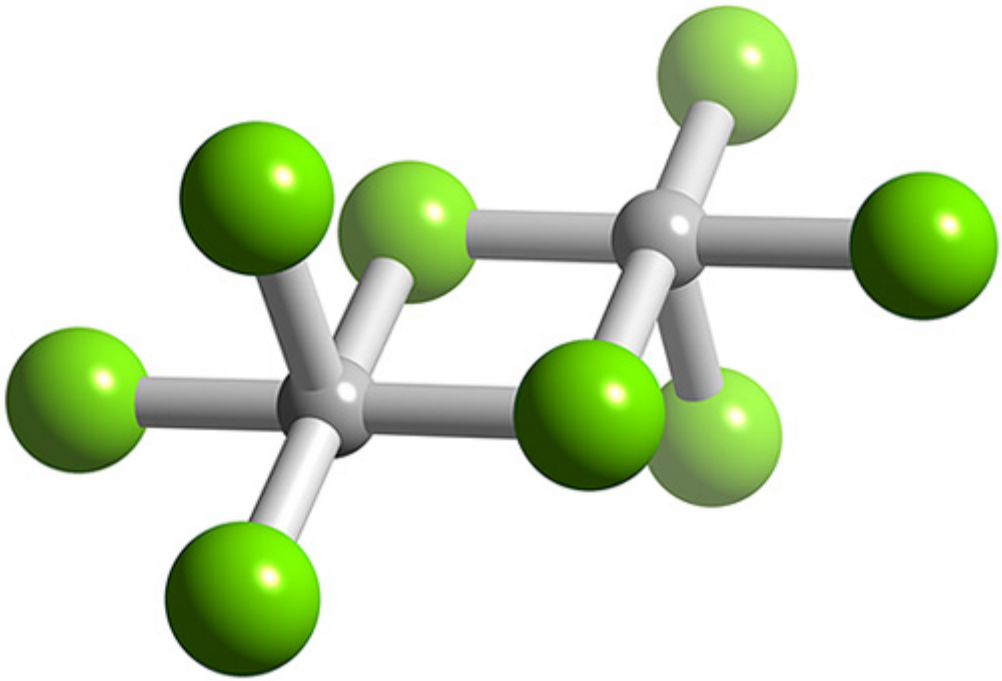


SbC_4H_4

Exercises for molecules and ions

$[Bi_2Cl_8]^{2-}$

Exercises for molecules and ions

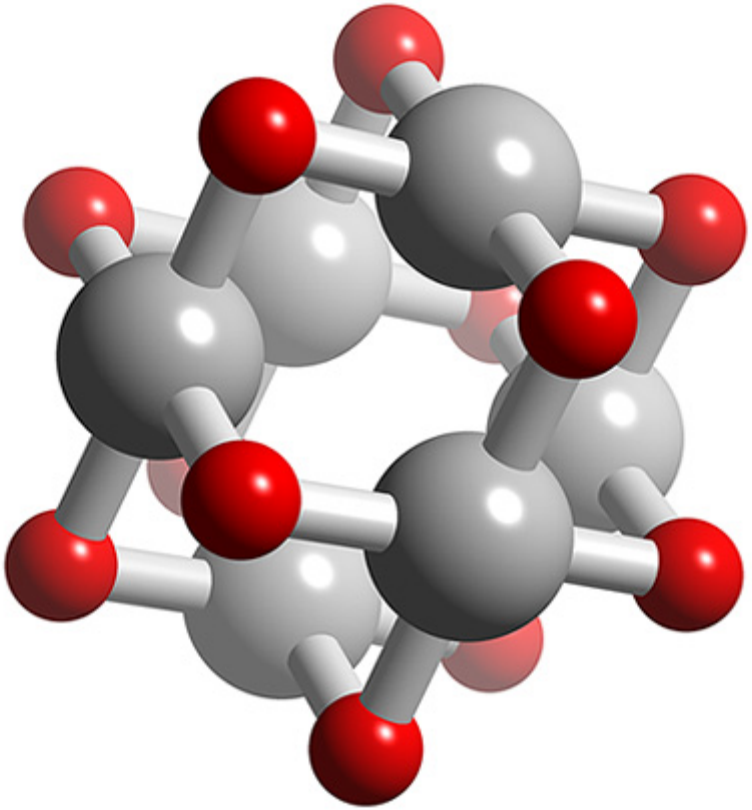


$[Bi_2Cl_8]^{2-}$

Exercises for molecules and ions

$Bi_6(OH)_{12}^{6+}$

Exercises for molecules and ions

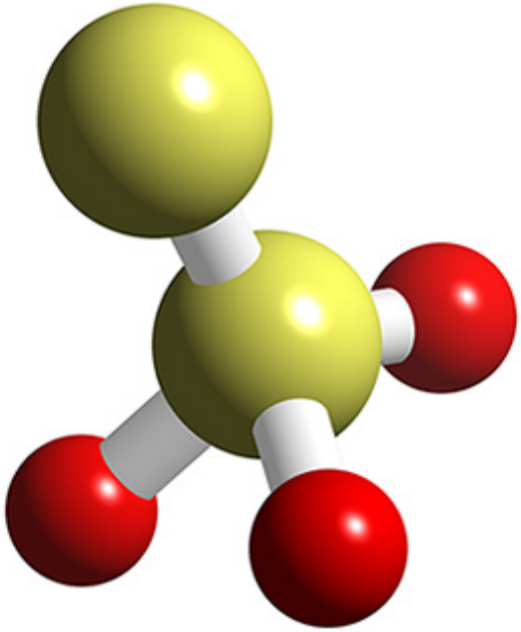


$Bi_6(OH)_{12}^{6+}$

Exercises for molecules and ions

$[S_2O_3]^{2-}$

Exercises for molecules and ions

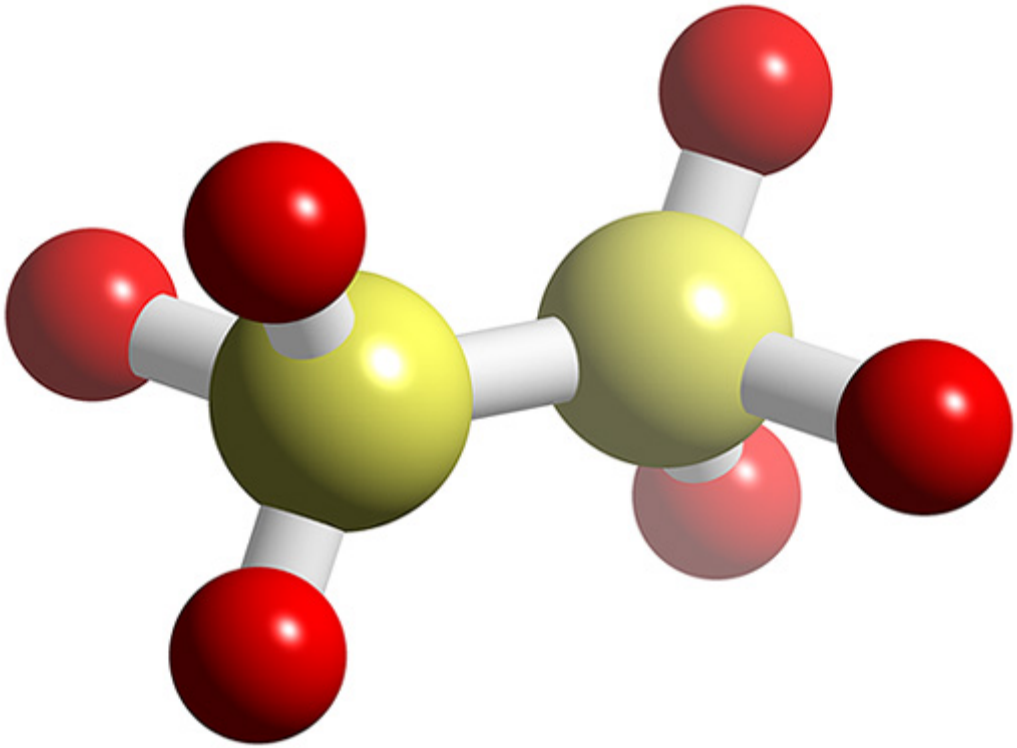


$[S_2O_3]^{2-}$

Exercises for molecules and ions

$[S_2O_6]^{2-}$

Exercises for molecules and ions

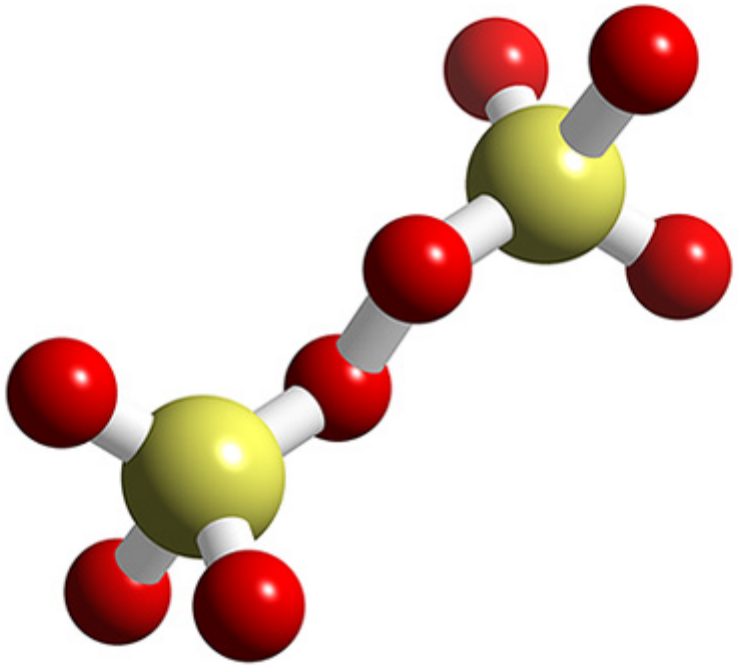


$[S_2O_6]^{2-}$

Exercises for molecules and ions

$[S_2O_8]^{2-}$

Exercises for molecules and ions

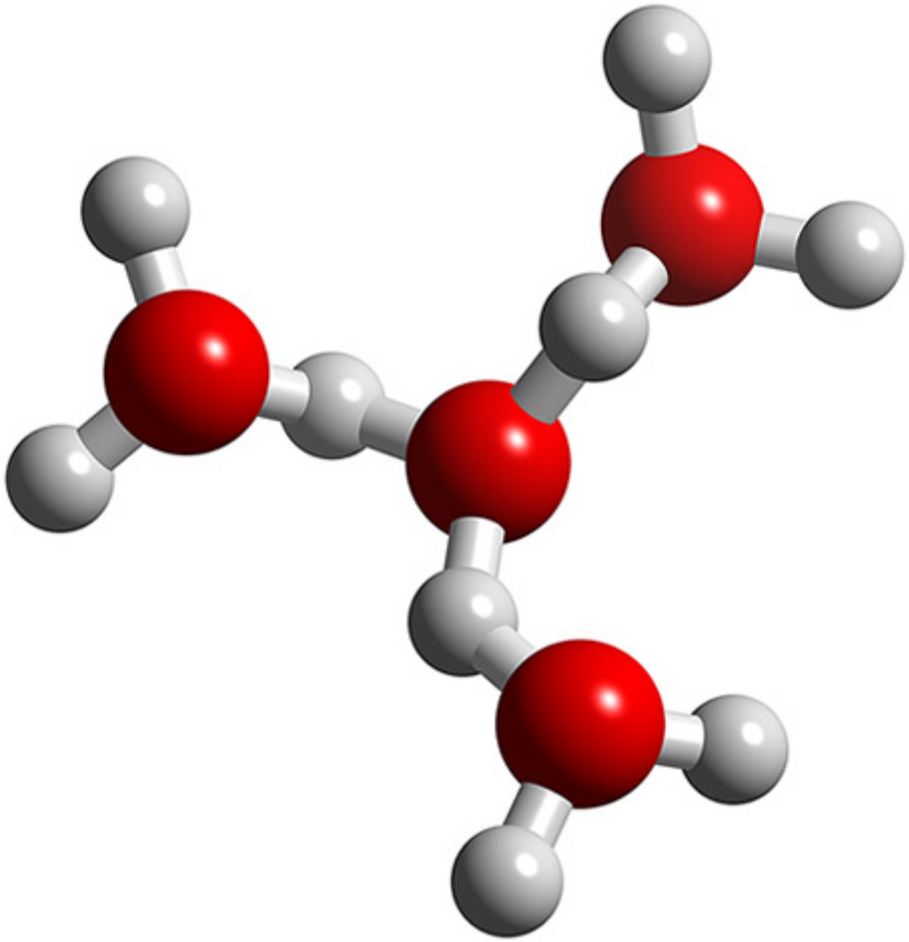


$[S_2O_8]^{2-}$

Exercises for molecules and ions

$[H_9O_4]^+$

Exercises for molecules and ions

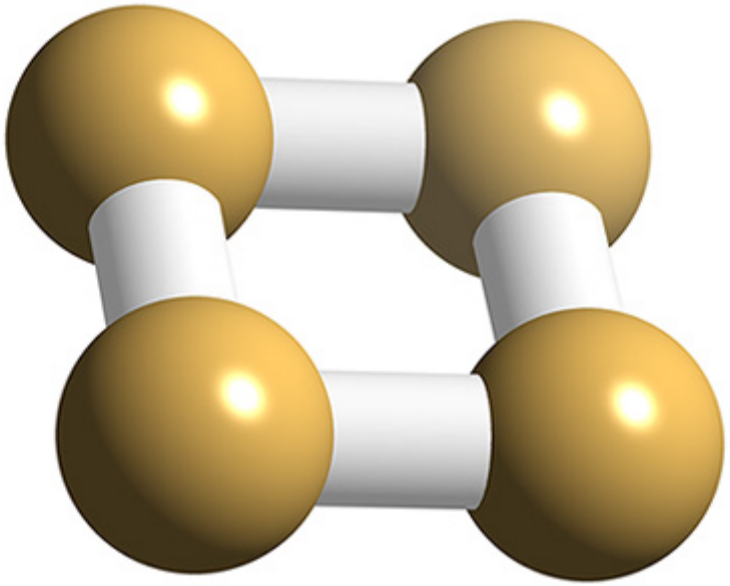


$[H_9O_4]^+$

Exercises for molecules and ions

$[Se_4]^{2+}$

Exercises for molecules and ions

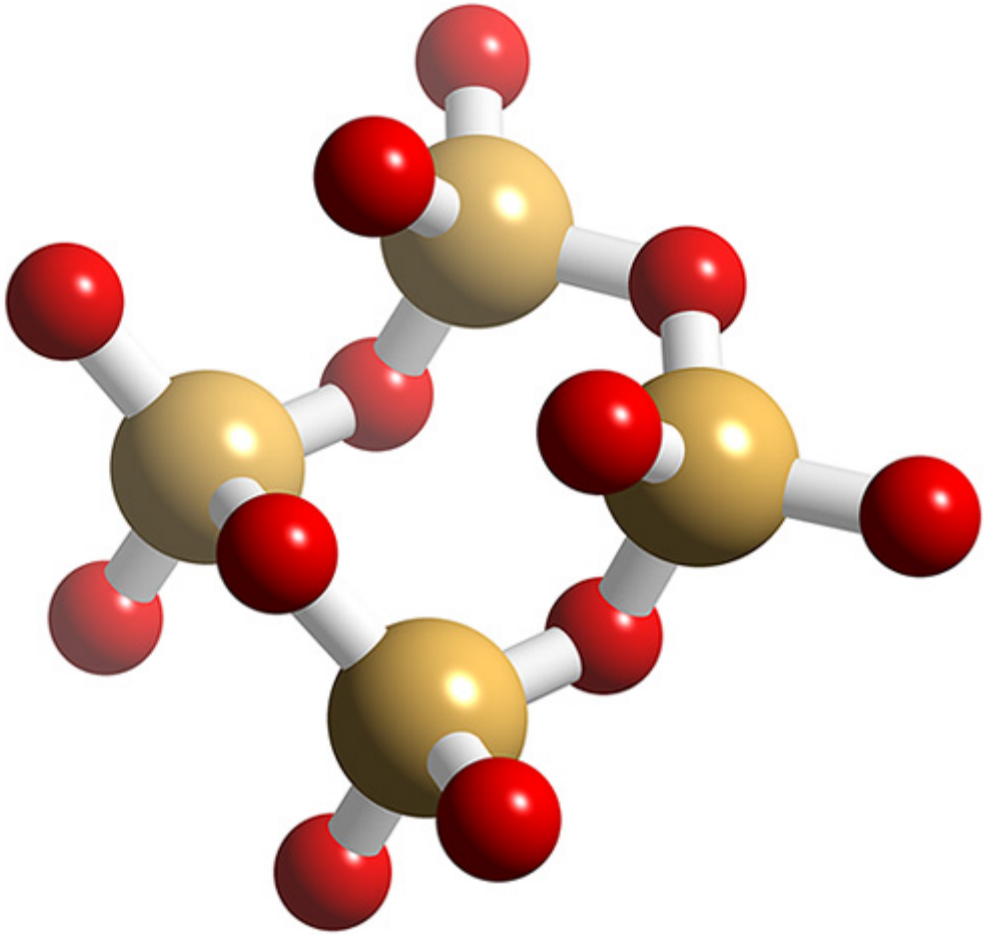


$[Se_4]^{2+}$

Exercises for molecules and ions

$(SeO_3)_4$

Exercises for molecules and ions

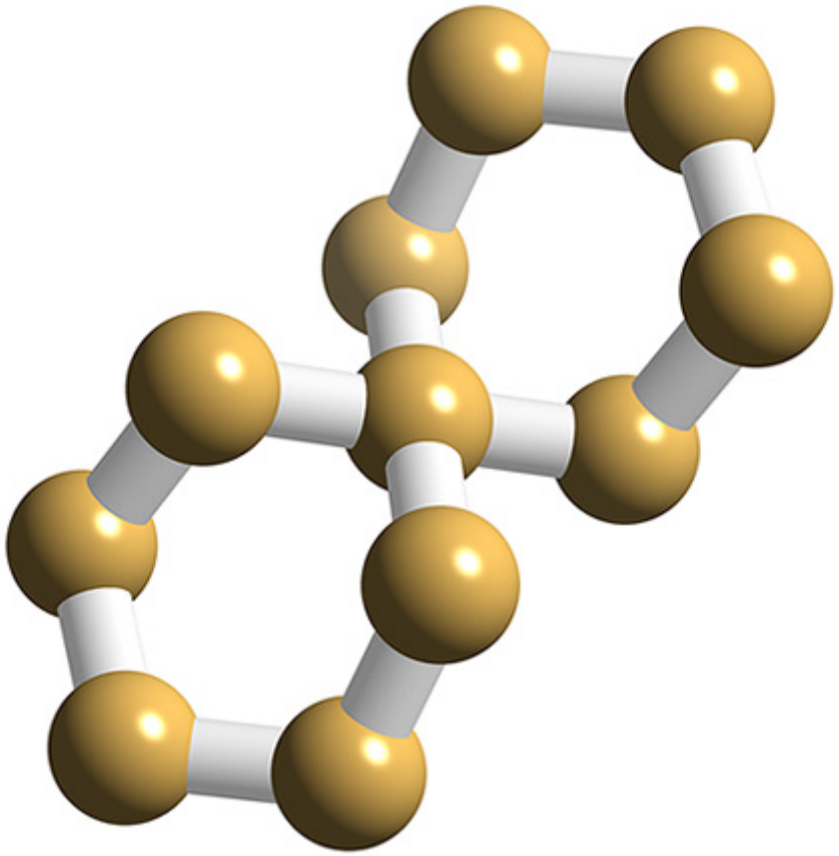


$(SeO_3)_4$

Exercises for molecules and ions

$[Se_{11}]^{2-}$

Exercises for molecules and ions

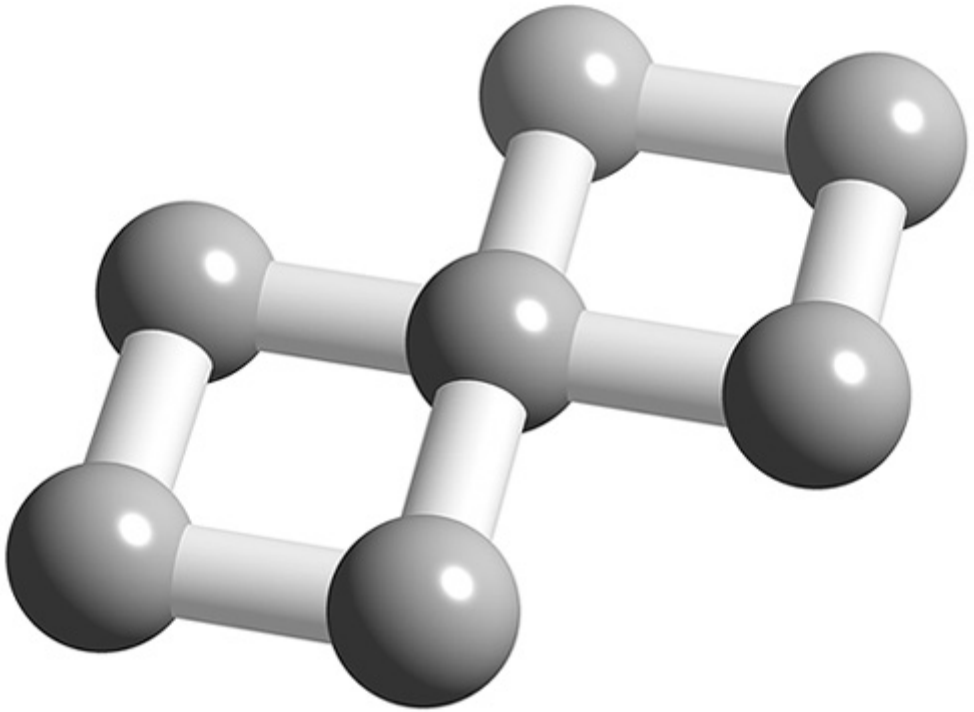


$[Se_{11}]^{2-}$

Exercises for molecules and ions

$[Te_7]^{2-}$

Exercises for molecules and ions



$[Te_7]^{2-}$

Further exercises

P_4, As_4

B_4Cl_4

$Li_4(C_2H_5)_4$, $Tl_4(OAlk)_4$, $Pb_4(OH)_4^{4+}$

$Cu_4I_4(AsEt_3)_4$, $Fe_4S_4(S\phi)_4^{2-}$

$Al_4N_4\phi_8$

$Pt_4I_4(CH_3)_{12}$

P_4O_6, As_4O_6, Sb_4O_6, $N_4(CH_2)_6$, $(CH)_4S_6$, $(CH)_4(CH_2)_6$, $(SiR)_4S_6$

P_4O_{10}, $P_4O_6[Ni(CO)_3]_4$

$OBe_4(ac)_6$, $OZn_4(ac)_6$, $OZn_4(S_2PR_2)_6$, $OZn_4(OSPR_2)_6$, $OCo_4[C(CH_3)_3COO]_6$

$OMg_4Br_6(C_4H_{10}O)_4$, $OCu_4Cl_6(pyr)_4$, $(OCu_4Cl_{10})^{4-}$

$B_6H_6^{2-}$

$Sn_6O_4(OCH_3)_4$

$Mo_6Cl_{14}^{2-}$, $Mo_6Br_{12}(H_2O)_2$

Pd_6Cl_{12}, Pt_6Cl_{12}, $Bi_6(OH)_{12}^{6+}$

$W_6Cl_{12}Cl_6$, $Nb_6Cl_{18}^{4-}$, $Ta_6Cl_{12}Cl_2(H_2O)_4$

C_8H_8

$Cu_8[S_2C_2(CN)_2]_6$

$Si_8O_{12}\phi_8$

TABLE 3.8

Polyhedral molecules and ions

	Fig. 3.18		
Tetrahedral	(a)	A_4	P_4, As_4
		A_4Y_4	B_4Cl_4
	(b)	A_4X_4 [a]	$Li_4(C_2H_5)_4$, $Tl_4(OAlk)_4$, $Pb_4(OH)_4^{4+}$
		$A_4X_4Y_4$	$Cu_4I_4(AsEt_3)_4$, $Fe_4S_4(S\phi)_4^{2-}$
		$A_4X_4Y_8$	$Al_4N_4\phi_8$
		$A_4X_4Y_{12}$	$Pt_4I_4(CH_3)_{12}$
	(c)	A_4X_6	P_4O_6, As_4O_6, Sb_4O_6, $N_4(CH_2)_6$, $(CH)_4S_6$, $(CH)_4(CH_2)_6$, $(SiR)_4S_6$
		$A_4X_6Y_4$	P_4O_{10}, $P_4O_6[Ni(CO)_3]_4$
	(d)	OA_4X_6	$OBe_4(ac)_6$, $OZn_4(ac)_6$, $OZn_4(S_2PR_2)_6$, $OZn_4(OSPR_2)_6$, $OCo_4[C(CH_3)_3COO]_6$
		$OA_4X_6Y_4$ [b]	$OMg_4Br_6(C_4H_{10}O)_4$, $OCu_4Cl_6(pyr)_4$, $(OCu_4Cl_{10})^{4-}$
Octahedral		A_6Y_6	$B_6H_6^{2-}$
	(e)	A_6X_8	$Sn_6O_4(OCH_3)_4$
		$A_6X_8Y_6$	$Mo_6Cl_{14}^{2-}$, $Mo_6Br_{12}(H_2O)_2$
	(f)	A_6X_{12}	Pd_6Cl_{12}, Pt_6Cl_{12}, $Bi_6(OH)_{12}^{6+}$
		$A_6X_{12}Y_6$	$W_6Cl_{12}Cl_6$, $Nb_6Cl_{18}^{4-}$, $Ta_6Cl_{12}Cl_2(H_2O)_4$
Cubic		A_8X_8	C_8H_8
	(g)	A_8X_{12}	$Cu_8[S_2C_2(CN)_2]_6$
		$A_8X_{12}Y_8$	$Si_8O_{12}\phi_8$

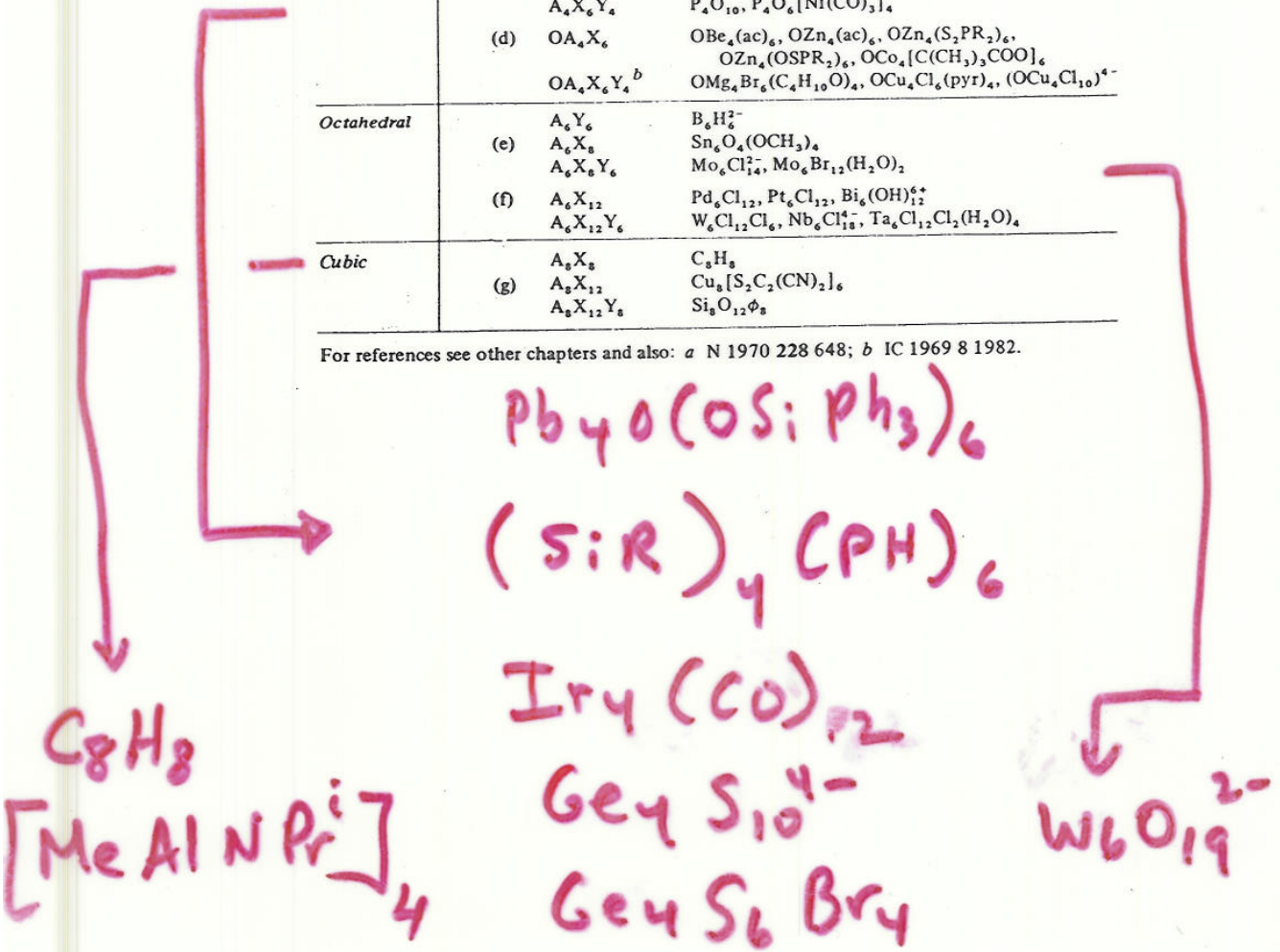
For references see other chapters and also: *a* N 1970 228 648; *b* IC 1969 8 1982.

TABLE 3.8

Polyhedral molecules and ions

	Fig. 3.18		
Tetrahedral	(a)	A_4	P_4, As_4
		A_4Y_4	B_4Cl_4
	(b)	A_4X_4 [a]	$Li_4(C_2H_5)_4$, $Tl_4(OAlk)_4$, $Pb_4(OH)_4^{4+}$
		$A_4X_4Y_4$	$Cu_4I_4(AsEt_3)_4$, $Fe_4S_4(S\phi)_4^{2-}$
		$A_4X_4Y_8$	$Al_4N_4\phi_8$
		$A_4X_4Y_{12}$	$Pt_4I_4(CH_3)_{12}$
	(c)	A_4X_6	P_4O_6, As_4O_6, Sb_4O_6, $N_4(CH_2)_6$, $(CH)_4S_6$, $(CH)_4(CH_2)_6$, $(SiR)_4S_6$
		$A_4X_6Y_4$	P_4O_{10}, $P_4O_6[Ni(CO)_3]_4$
	(d)	OA_4X_6	$OBe_4(ac)_6$, $OZn_4(ac)_6$, $OZn_4(S_2PR_2)_6$, $OZn_4(OSPR_2)_6$, $OCo_4[C(CH_3)_3COO]_6$
		$OA_4X_6Y_4$ [b]	$OMg_4Br_6(C_4H_{10}O)_4$, $OCu_4Cl_6(pyr)_4$, $(OCu_4Cl_{10})^{4-}$
Octahedral		A_6Y_6	$B_6H_6^{2-}$
	(e)	A_6X_8	$Sn_6O_4(OCH_3)_4$
		$A_6X_8Y_6$	$Mo_6Cl_{14}^{2-}$, $Mo_6Br_{12}(H_2O)_2$
	(f)	A_6X_{12}	Pd_6Cl_{12}, Pt_6Cl_{12}, $Bi_6(OH)_{12}^{6+}$
		$A_6X_{12}Y_6$	$W_6Cl_{12}Cl_6$, $Nb_6Cl_{18}^{4-}$, $Ta_6Cl_{12}Cl_2(H_2O)_4$
Cubic		A_8X_8	C_8H_8
	(g)	A_8X_{12}	$Cu_8[S_2C_2(CN)_2]_6$
		$A_8X_{12}Y_8$	$Si_8O_{12}\phi_8$

For references see other chapters and also: *a* N 1970 228 648; *b* IC 1969 8 1982.



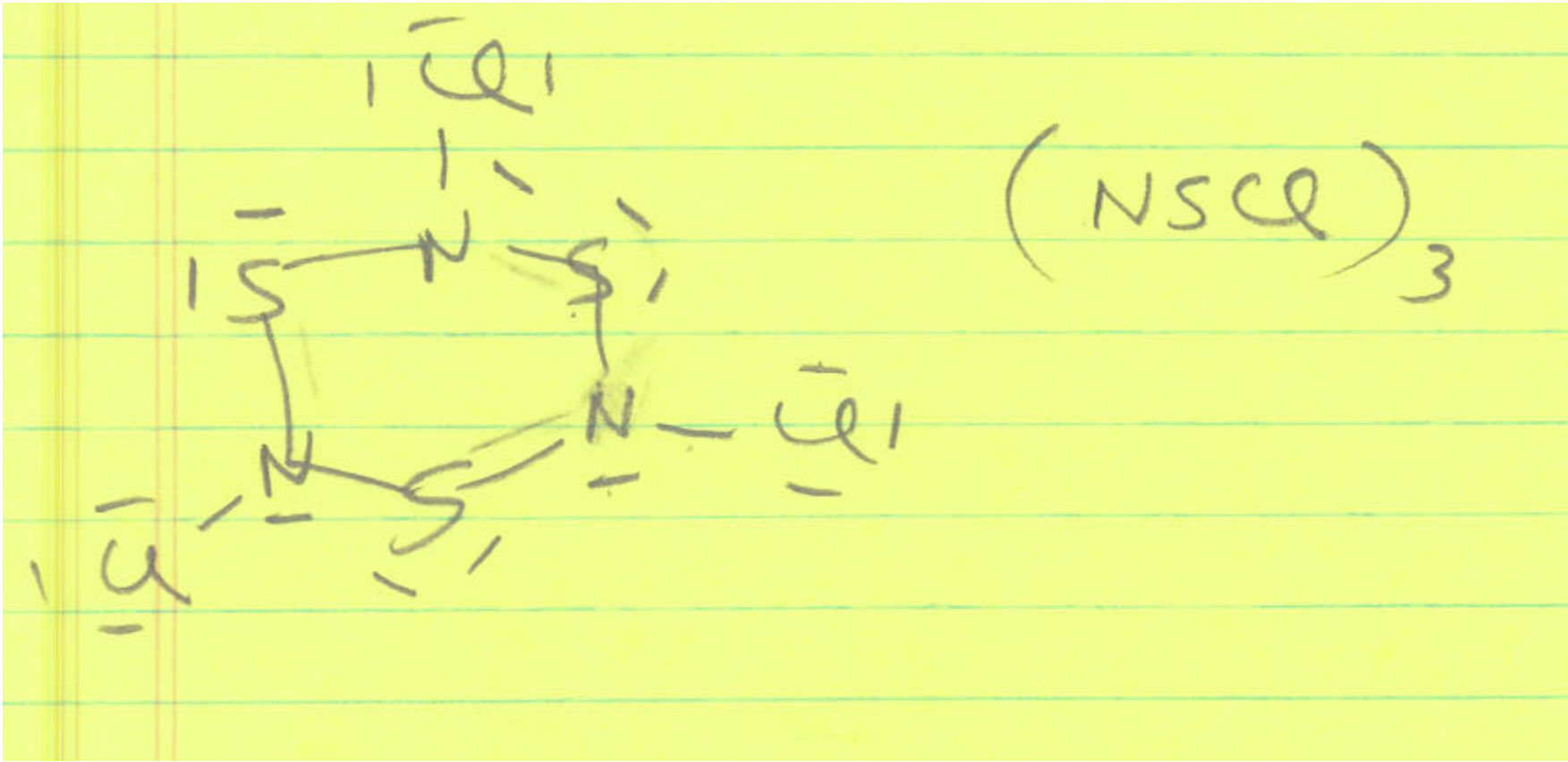
Some additional cluster compounds

ANGEW CHEM. INT. ED., **1990**, *29*, 840

CHEM. SOC. REV., **2009**, *38*, 1257

- More challenging ones:

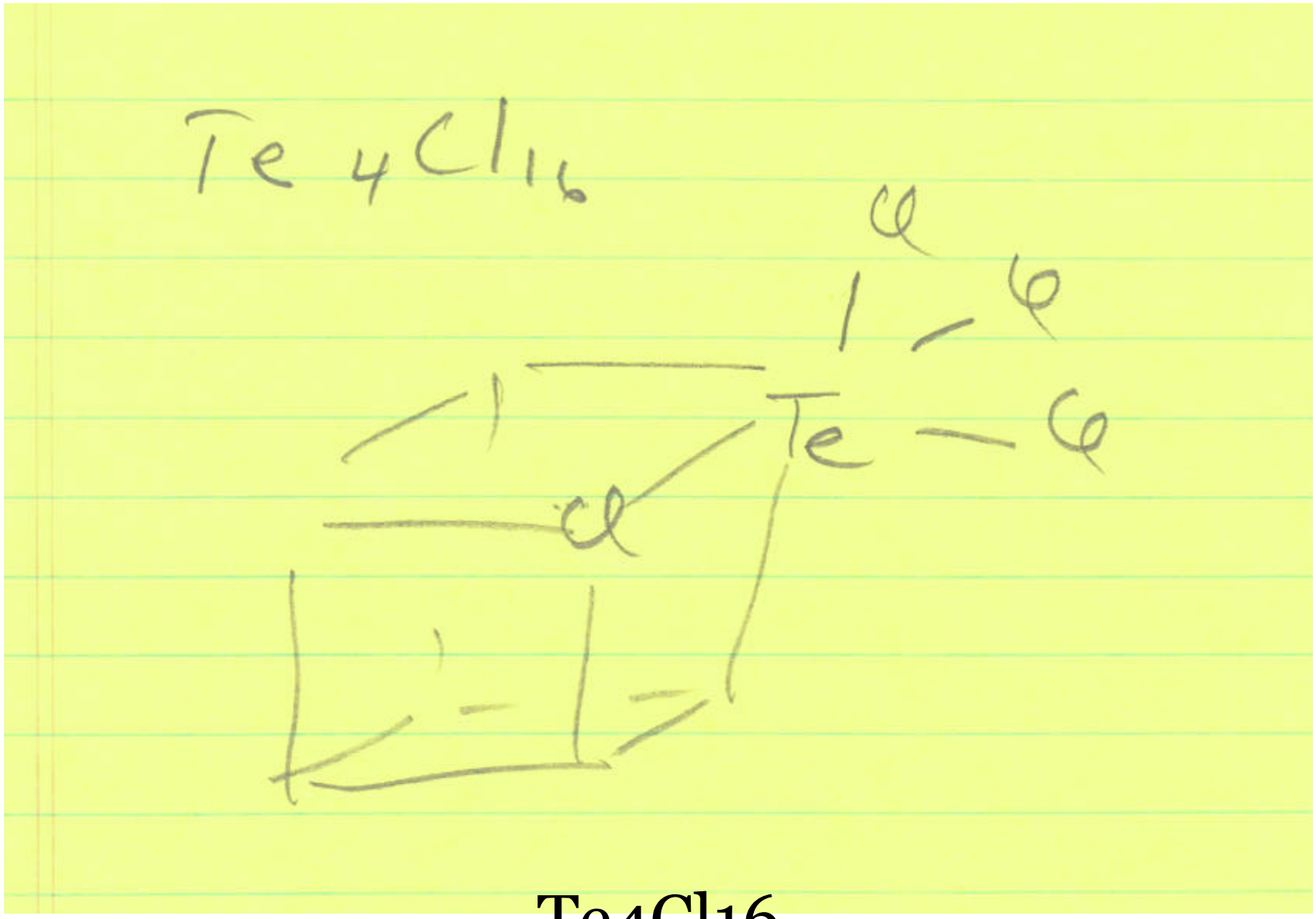
$[NSCl]_3$



$[NSCl]_3$

- More challenging ones:

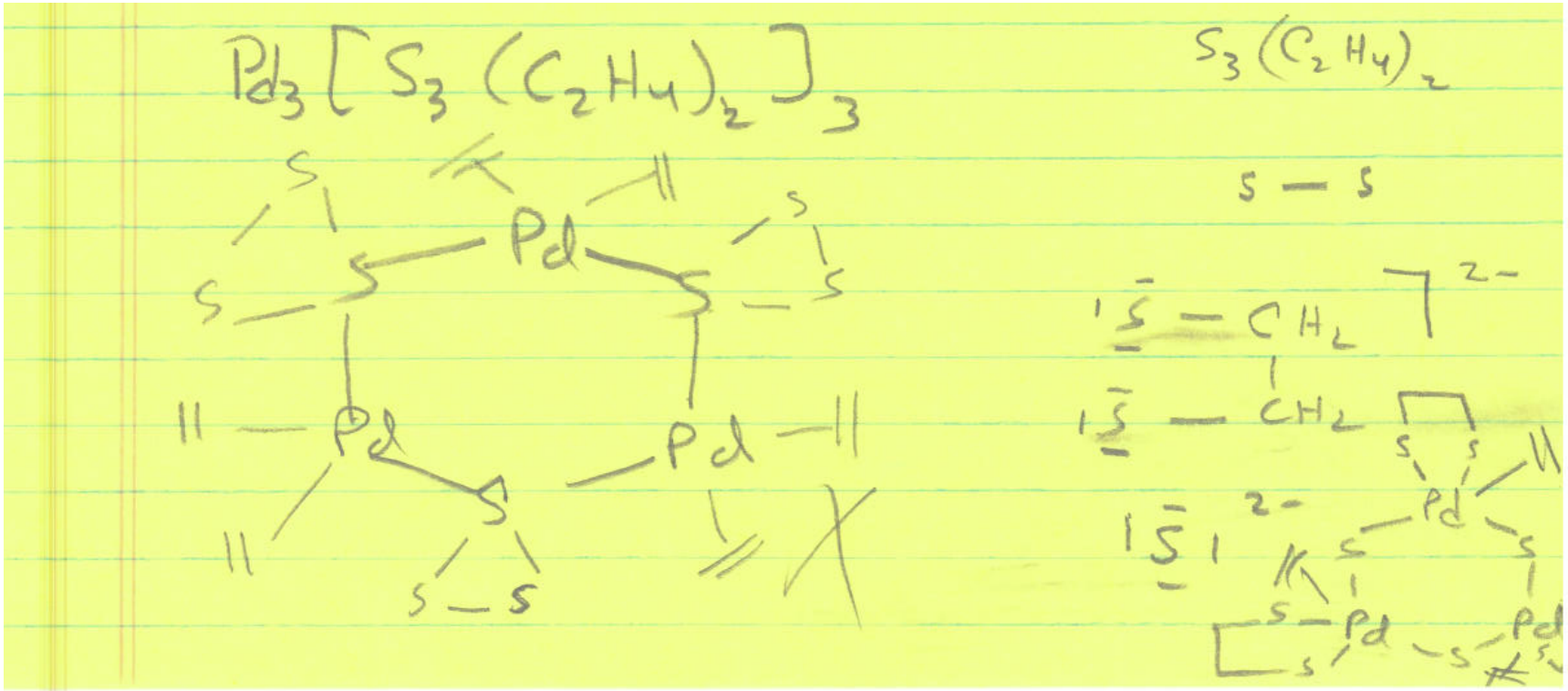
Te_4Cl_{16}



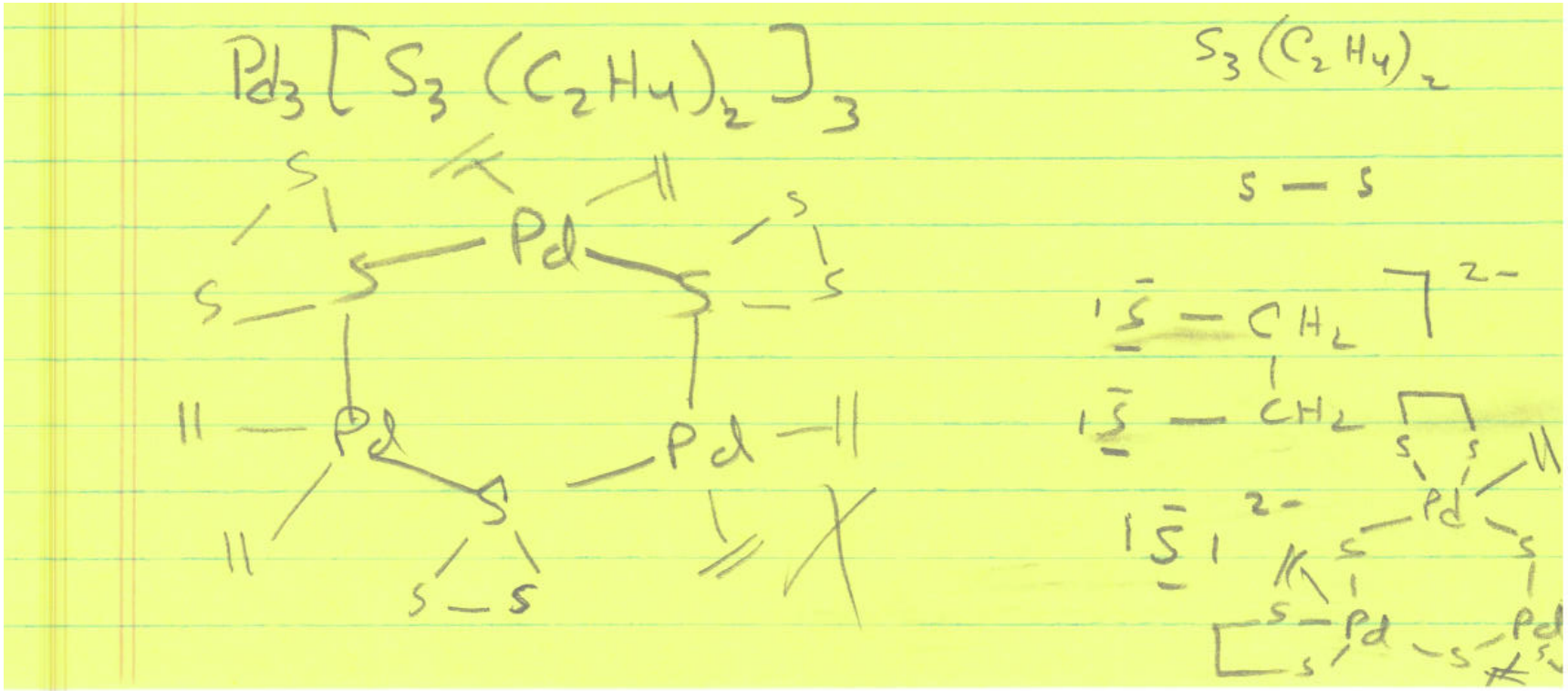
Te4Cl16

- More challenging ones:

$Pd_3[S_3(C_2H_4)_2]_3$



Pd3[S3(C2H4)2]3



Pd3[S3(C2H4)2]3

Summary

- For molecules involving second and third row main group elements. Follow the Lewis dot structure rules (note: B can have less than 8 electrons and third row elements can have more than octet.
- For larger molecules (clusters) especially those having B and fourth row and higher main group elements, and those of transition metals, you should rely on the common Platonic and related solids for geometric arrangements, and recognize that these follow different schemes of counting electrons. Note that lines in these structures do not always represent 2 electrons. Most likely less than two electrons (i.e. 2c3e, 3c2e bonds,…)

18-Electron Rule

In main group chemistry, electron counts in molecules are often (but not always) described by the octet rule, in which the electronic structures can be rationalized on the basis of a valence shell requirement of eight electrons (two valence *s* electrons plus six valence *p* electrons). Similarly, in organometallic chemistry the electronic structures of many compounds are based on a total valence electron count of 18 on the central metal atom (ten valence *d* electrons in addition to the *s* and *p* electrons of the "octet"). As in the case of the octet rule, there are many exceptions to the **18-electron rule**,[1] but the rule nevertheless provides some useful guidelines to the chemistry of many organometallic complexes. In this chaper we will first examine how electrons are counted according to this rule. Then we will consider the basis for its usefulness (and some of the reasons why it is not always valid).

3-1 Counting Electrons

Several schemes exist for counting electrons in organometallic compounds. We will describe two of these using several examples. The first two examples will be of classic 18-electron species.

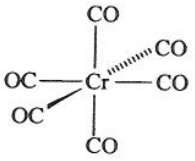
[1]Often called the effective atomic number (EAN) rule.

3-1-1 Method A: Donor Pair Method

This method considers ligands to donate electron pairs to the metal. To determine the total electron count, one must take into account the charge on each ligand and determine the formal oxidation state of the metal. We demonstrate this method using two examples of classic 18–electron species: $Cr(CO)_6$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$.

$Cr(CO)_6$

A chromium atom has six electrons outside its noble gas core. Each CO is considered to act as a donor of two electrons (from an electron dot standpoint, :C≡O:, these correspond to the lone pair on carbon). Thus the total electron count is



Cr — 6 electrons
6(CO) — 6 × 2 electrons = 12 electrons
Total = 18 electrons

$Cr(CO)_6$ is therefore considered to be an 18–electron complex. It is thermally stable; for example, it can be sublimed without decomposition. $Cr(CO)_5$, a 16–electron species, and $Cr(CO)_7$, a 20–electron species, are, on the other hand, much less stable and known only as transient species. Likewise, the 17–electron $[Cr(CO)_6]^+$ and 19–electron $[Cr(CO)_6]^-$ are much less stable than the neutral, 18–electron $Cr(CO)_6$. The bonding in $Cr(CO)_6$, which provides a rationale for the special stability of many 18–electron systems, is discussed in Section **3-2**.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$

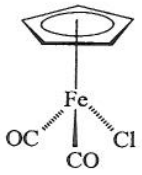
As usual, CO is counted as a two–electron donor. Chloride is considered Cl^-, also a donor of two electrons. Pentahapto–C_5H_5 (see diagram on p. 43) is considered by this method to be $C_5H_5^-$, a donor of three electron pairs; it is a six–electron donor. Therefore, since this complex[2] is considered to contain the two negative ligands, Cl^- and $C_5H_5^-$, the oxidation state of iron in $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ is 2+. Iron(II) has six electrons beyond its noble gas core:

iron(0) has the electron configuration [Ar] $4s^2 3d^6$
iron(II) has the electron configuration [Ar] $3d^6$

[2]The η^5 notation (read "pentahapto" and signifying that the ligand has a *hapticity* of 5) designates that all five carbon atoms in the C_5H_5 ring are bonded to the iron (in general the superscript in this notation indicates the number of atoms in a ligand bonded to a metal; this type of notation will be discussed further in Chapter 5).

The electron count in the molecule $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ therefore is

Fe(II)	6 electrons
$\eta^5\text{-}C_5H_5^-$	6 electrons
2 (CO)	4 electrons
Cl^-	2 electrons
Total =	18 electrons



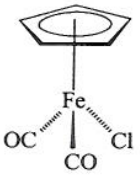
3-1-2 Method B: Neutral Ligand Method

This method uses the number of electrons that would be donated by ligands *if they were neutral*. For simple, inorganic ligands this usually means that ligands are considered to donate the number of electrons equal to their negative charge as free ions (Cl is a one-electron donor if singly bonded to a metal, O is a two-electron donor if doubly bonded, N is a three-electron donor if triply bonded, etc.). To determine the total electron count by this method, one does not need to determine the oxidation state of the metal.

$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$

In this method, $\eta^5\text{-}C_5H_5$ is now considered as if it were a neutral ligand (or radical), in which case it would contribute five electrons. CO is a two-electron donor and Cl (counted as if it were a neutral species) is a one-electron donor. An iron atom has eight electrons beyond its noble gas core. The electron count is as follows:

Fe atom	8 electrons
$\eta^5\text{-}C_5H_5$	5 electrons
2 (CO)	4 electrons
Cl	1 electron
Total =	18 electrons



Method B gives the same result as Method A; $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ is an 18-electron species.

3-1-3 Other Considerations

Many organometallic complexes are charged, and this charge must be included when determining the total electron count. We can verify, by either method of

electron counting, that $[Mn(CO)_6]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ are both 18-electron ions.

In addition, metal-metal bonds must be counted. For example, in the dimeric complex $(CO)_5Mn\text{-}Mn(CO)_5$ the electron count per manganese atom is (by both methods):

Mn	7 electrons
5 (CO)	10 electrons
Mn-Mn bond	1 electron[3]
	Total = 18 electrons

For future reference, the electron counts for common ligands according to both schemes are given in Table **3-1**.

Table 3-1 Electron Counting Schemes for Common Ligands

Ligand	Method A	Method B
H	2 (:H$^-$)	1
F, Cl, Br, I	2 (:$\ddot{X}$:$^-$)	1
OH	2 (:$\ddot{O}$:H$^-$)	1
CN	2 (:C≡N:$^-$)	1
CH_3	2 (:CH_3^-)	1
NO (bent M - N - O)	2 (:$\ddot{N}$ = $\ddot{O}$:$^-$)	1
CO, PR_3	2	2
NH_3, H_2O	2	2
= CRR′ (carbene)	2	2
$H_2C = CH_2$	2	2
= O, = S	4 (:$\ddot{O}$:$^{2-}$, :$\ddot{S}$:$^{2-}$)	2
NO (linear M - N - O)	2 (:N ≡ O:$^+$)	3
$\eta^3\text{-}C_3H_5$	2 ($C_3H_5^+$)	3
≡ CR (carbyne)	3	3
≡ N	6 (N^{3-})	3
butadiene	4	4
$\eta^5\text{-}C_5H_5$	6 ($C_5H_5^-$)	5
$\eta^6\text{-}C_6H_6$	6	6
$\eta^7\text{-}C_7H_7$	6 ($C_7H_7^+$)	7

[3]For a Mn=Mn bond, each metal atom contributes two electrons; for a Mn≡Mn bond, each metal contributes three electrons.

Example 3-1

Both methods of electron counting are illustrated for the following three complexes:

Complex	Method A		Method B	
$ClMn(CO)_5$	Mn(I)	6 e^-	Mn	7 e^-
	Cl^-	2 e^-	Cl	1 e^-
	5 CO	10 e^-	5 CO	10 e^-
		18 e^-		18 e^-
$(\eta^5\text{-}C_5H_5)_2Fe$ (Ferrocene)	Fe(II)	6 e^-	Fe	8 e^-
	2 $\eta^5\text{-}C_5H_5^-$	12 e^-	2 $\eta^5\text{-}C_5H_5$	10 e^-
		18 e^-		18 e^-
$[Re(CO)_5(PF_3)]^+$	Re(I)	6 e^-	Re	7 e^-
	5 CO	10 e^-	5 CO	10 e^-
	PF_3	2 e^-	PF_3	2 e^-
	+ charge	a	+ charge	- 1 e^-
		18 e^-		18 e^-

[a]Charge on ion is accounted for in assignment of oxidation state to Re.

The electron counting method used is a matter of individual preference. Method A has the advantage of including the formal oxidation state of the metal but may tend to overemphasize the ionic nature of some metal-ligand bonds. Counting electrons for some otherwise simple ligands (such as O^{2-} and N^{3-}) may seem cumbersome and unrealistic. Method B is often quicker, especially for ligands having extended π systems; for example, η^5 ligands have an electron count of five, η^3 ligands an electron count of three, and so on (see footnote 2). Also, Method B has the advantage of not requiring that the oxidation state of the metal be assigned. Other electron counting schemes have also been developed. It is generally best to select one method and to use it consistently.

Electron counting (by any method) does *not* imply anything about the degree of covalent or ionic bonding; it is strictly a bookkeeping procedure, as are the oxidation numbers that may be used in the counting. Physical measurements are necessary to provide evidence about the actual electron distribution in molecules. Linear and cyclic organic π systems interact with metals in more complicated ways and will be discussed in Chapter 5.

Exercise 3-1

Determine the valence electron counts for the metals in the following complexes:

a. $[Fe(CO)_4]^{2-}$

b. $[(\eta^5\text{-}C_5H_5)_2Co]^{+}$

c. $(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Fe(CO)$

Exercise 3-2

Identify the first-row transition metal for the following 18-electron species:

a. $[M(CO)_3(PPh_3)]^{-}$

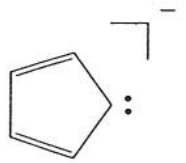
b. $HM(CO)_5$

c. $(\eta^4\text{-}C_8H_8)M(CO)_3$

d. $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (assume single M-M bond)

L-X Notation

It is useful to introduce some symbolism that will appear often in later chapters in this book. Most ligands may be classified as "L-type" or "X-type."[4] L-Type ligands are neutral, two-electron donors such as CO or PR_3. Ligands such as Cl or CH_3 are designated as X-type. X-Type ligands typically carry a negative charge and would be two-electron donors according to the Donor Pair Method (Method A) and one-electron donors according to the Neutral Ligand Method (Method B). Some ligands, such as $\eta^5\text{-}C_5H_5$, contain both types of classifications. If we consider the structure of $\eta^5\text{-}C_5H_5$ to have the following structural representation, it would be symbolized in L-X notation as L_2X.



[4]For a more complete discussion of this notation, see R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2nd. ed. John Wiley & Sons, New York, 1994, 24-38.

In general, any organometallic complex containing L- and X-type ligands may be represented by the general formula:

$[MX_aL_b]^c$

where a = the number of X-type ligands,
b = the number of L-type ligands,
and c = the charge.

Several useful relationships result from the following notation:

1. Electron count (EAN):
   EAN = N + a + 2b – c
   where N = the group number of the metal in the Periodic Table

Example:
$HFe(CO)_4^- \equiv [MXL_4]^-$
EAN = 8 + 1 + 8 + 1 = 18 electrons

2. Coordination number (CN):
   CN = a + b

Example:
$[ReH(PPh_3)_3(CO)_3]^+ \equiv [MXL_6]^+$
CN = 1 + 6 = 7

3. Oxidation state of the metal (OS):
   OS = a + c

Example:
$Rh(H)(H)(PPh_3)_2(CO)Cl \equiv [MX_3L_3]^0$
OS = 3 + 0 = 3

4. Number of *d* electrons (d^n):
   d^n = N - OS = N - (a + c)

Example:
$(\eta^5\text{-}C_5H_5)_2Zr(H)(Cl) \equiv [MX_4L_4]^0$
$d^n = 4 - (4 + 0) = 0$

Exercise 3-3

Represent the complex $[Ir(CO)(PPh_3)_2(Cl)(NO)]^+$ in L-X notation. Calculate the electron count, coordination number, oxidation state of the metal, and the number of *d* electrons for the metal.

Types of Crystalline Solids

Form of Unit Particles	Forces Between Particles	Properties	Examples
Atoms or molecules	London dispersion, dipole-dipole forces, hydrogen bonds	Fairly soft, low to moderately high melting point, poor thermal and electrical conduction	Argon, Ar; methane, CH_4; sucrose, $C_{12}H_{22}O_{11}$; Dry Ice™, CO_2
Atoms connected in a network of covalent bonds	Covalent bonds	Very hard, very high melting point, often poor thermal and electrical conduction	Diamond, C; quartz, SiO_2
Positive and negative ions	Electrostatic attractions	Hard and brittle, high melting point, poor thermal and electrical conduction	Typical salts—for example, NaCl, $Ca(NO_3)_2$
Atoms	Metallic bonds	Soft to very hard, low to very high melting point, excellent thermal and electrical conduction, malleable and ductile	All metallic elements—for example, Cu, Fe, Al, Pt