CHEM 208 – Coordination Chemistry

Physical and Chemical Properties of Coordination Compounds

Midterm Exam #2

November 9th, 2016

Family/Last Name: _____	*First Name:* _____
CHEM 208 Team: _____	*SUID:* _____
Signature: _____	

INSTRUCTIONS

1. You have 50 minutes for this exam.
2. Check that this exam booklet consists of **5 PAGES PRINTED ON BOTH SIDES**. There is one blank page in case you need extra space to work on problems and a datasheet including a periodic table and some character tables.
3. The datasheet and periodic table (last page of this booklet) may be removed.
4. Write all answers on the answer sheet provided. Answer written in this question booklet will not be marked.
5. The only calculator allowed is the Sharp EL-510R. All other calculators/electronic devices will be confiscated.
6. Molecular model kits may be used and may be pre-assembled.

RULES GOVERNING FORMAL EXAMINATIONS

1. Each examination candidate must be prepared to produce, upon the request of the invigilator or examiner, their UBCcard for identification.
2. Examination candidates are not permitted to ask questions of the examiners or invigilators, except in cases of supposed errors or ambiguities in examination questions, illegible or missing material, or the like.
3. No examination candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination. Should the examination run forty-five (45) minutes or less, no examination candidate shall be permitted to enter the examination room once the examination has begun.
4. Examination candidates must conduct themselves honestly and in accordance with established rules for a given examination, which will be articulated by the examiner or invigilator prior to the examination commencing. Should dishonest behaviour be observed by the examiner(s) or invigilator(s), pleas of accident or forgetfulness shall not be received.
5. Examination candidates suspected of any of the following, or any other similar practices, may be immediately dismissed from the examination by the examiner/invigilator, and may be subject to disciplinary action:
   - speaking or communicating with other examination candidates, unless otherwise authorized;
   - purposely exposing written papers to the view of other examination candidates or imaging devices;
   - purposely viewing the written papers of other examination candidates;
   - using or having visible at the place of writing any books, papers or other memory aid devices other than those authorized by the examiner(s); and,
   - using or operating electronic devices including but not limited to telephones, calculators, computers, or similar devices other than those authorized by the examiner(s)—(electronic devices other than those authorized by the examiner(s) must be completely powered down if present at the place of writing).
6. Examination candidates must not destroy or damage any examination material, must hand in all examination papers, and must not take any examination material from the examination room without permission of the examiner or invigilator.
7. Examination candidates must follow any additional examination rules or directions communicated by the examiner(s) or invigilator(s).

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Part 1. ***(16 marks total, 2 mark each)***

For each question below, enter the best answer on the separate answer sheet provided. **Answers recorded here will NOT be graded.**

1. What is the correct label that describes the symmetry of a $3d_{xy}$ orbital in a ***D_{6h}*** **complex**?

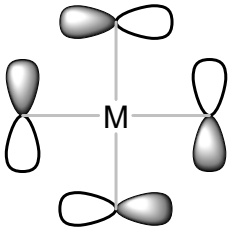
   a) e_{1u}
   b) e_{1g}
   c) e_{2g}
   d) a_{1g}
   e) t_{2g}
   f) none of the above

2. Which other orbitals have the same symmetry as that of a $5d_{x^2-y^2}$ orbital in a D_{2h} complex?

   a) $5d_{z^2}$
   b) $6s$
   c) $3d_{x^2-y^2}$
   d) all of the above
   e) *a* and *c* only
   f) none of the above

3. Which of the following is **true** about the symmetry of the following SALC? (wrt = with respect to…)

   a) antisymmetric wrt *E*
   b) symmetric wrt C_4
   c) gerade
   d) ungerade
   e) antisymmetric wrt *i*
   f) none of the above



4. What is the appropriate hybridization of the underlined atom in $CH_3\underline{C}N$ (acetonitrile)?

   a) the atom should not be hybridized
   b) sp
   c) sp^2
   d) sp^3
   e) d^3s
   f) none of the above

5. Which of the following is the best description each of the O-N σ bond in NO_2^- ?

   a) $\sigma_{ON} = O\ sp + N\ sp^2$ for both NO bonds
   b) $\sigma_{ON} = O\ sp^2 + N\ sp^2$ for both NO bonds
   c) $\sigma_{ON} = O\ sp^3 + N\ sp^3$ for both NO bonds
   d) $\sigma_{ON} = O\ sp + N\ sp$ for both NO bonds
   e) $\sigma_{ON} = O\ sp^2 + N\ sp$ for both NO bonds
   f) each σ_{ON} bond is different

6. Which of the following complexes should have the largest Δ_o (assume all are low-spin)?

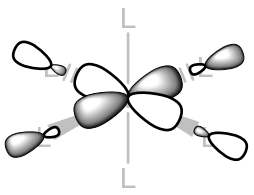
   a) $[Mn(NH_3)_6)]^{2+}$
   b) $[Mn(BF_3)_6)]^{2+}$
   c) $[Mn(OH_2)_6)]^{2+}$
   d) $[Mn(CH_3)_6)]^{4-}$
   e) $[Mn(N(CH_3)_3)_6)]^{2+}$
   f) it is impossible to tell

7. Which of the following statements is **false** about octahedral and tetrahedral complexes with σ-donor ligands?

   a) only 2 metal d orbitals mix with ligand σ orbitals in O_h symmetry
   b) Δ_t is typically about $\left(\frac{4}{9}\right)\Delta_o$
   c) the metal d orbitals are responsible for more M-L bonds in octahedral complexes
   d) the valence metal d_{xy} orbital is non-bonding in O_h symmetry
   e) T_d are more likely to be high spin
   f) none of the above

8. What is the most appropriate description of the following molecular orbital from an O_h complex?

   a) metal-based σ_b orbital
   b) metal-based σ* orbital
   c) non-bonding orbital
   d) ligand-based σ_b orbital
   e) ligand-based σ* orbital
   f) none of the above



Part 2. ***(30 marks total)***

In this part of the exam, your answers will also be in the form of a multiple choice response. However, a series of questions will all share the same series of possible answers. These are listed at the beginning of the question.

Q9-16. (1 mark each) The following species can all serve as ligands in transition metal complexes. Identify the properties of each of these ligands by selecting the appropriate answer from the list below. When necessary, **the underlined atom represents the atom which is being used to form the bond to the metal.** In each case, select a single answer.

9. $N(CH_3)_3$

10. $\underline{Br}^-$

11. $CH_3C\underline{N}$

12. $\underline{O}CN^-$

13. $AlCl_3$

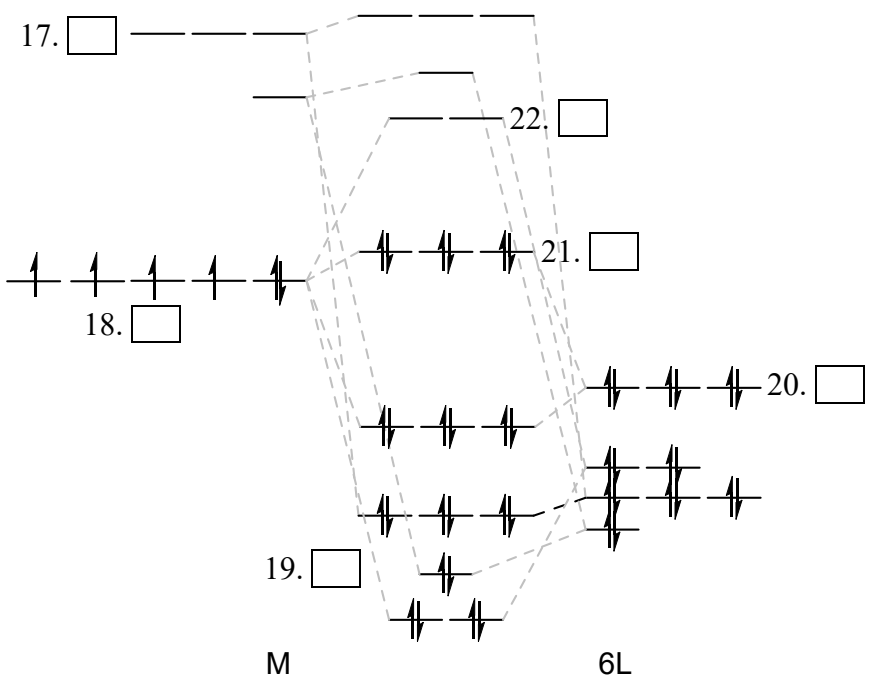
14. $\underline{C}N^-$

15. $N\underline{O}_3^-$

16. 2,2'-bipyridine

a) σ-donor only
b) σ-donor + σ-acceptor
c) σ-donor + π-donor
d) σ-donor + π-acceptor
e) σ-acceptor only
f) π-donor only
g) π-acceptor only
h) cannot bind through this atom

Q17-22. (2 mark each) The following MO diagram is a partial valence MO diagram for a low-spin d^6 complex with *π donor ligands*. Identify the most accurate description for each of the orbitals identified. The number corresponds to the question number. **Each answer can only be used once.**



a) σ* MO
b) σ_b MO
c) non-bonding MO
d) π* MO
e) π_b MO
f) metal d orbitals
g) metal s orbitals
h) metal p orbitals
i) ligand σ SALCs
j) ligand π SALCs

Q23-27. (2 marks each) Select the appropriate electronic configuration that corresponds to the properties described AND identify the appropriate spin state. **For each question, you MUST select two bubbles: one for the d^n configuration (a-j) and the other for the spin state (k-m).**

a) d^0
b) d^1
c) d^2
d) d^3
e) d^4
f) d^5
g) d^6
h) d^7
i) d^8
j) d^{10}

k) high spin
l) low spin
m) high-spin/low-spin not applicable

23. An octahedral complex with the largest possible *LFSE.*

24. An octahedral complex with a ***very small*** Δ_o formally having 5 σ bonds and 1 π bond.

25. An octahedral complex with a ***very large*** Δ_o where $LFSE = 0$ and formally having 3 π bonds.

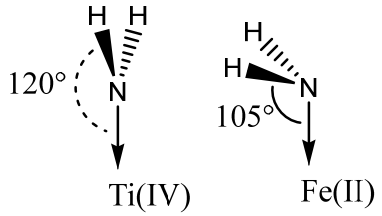
26. An octahedral complex with $S = 3/2$ that cannot have any other spin states.

27. A tetrahedral complex with a total spin of $S = 5/2$.

Part 3. ***(22 marks total)***

In this last part of the exam, your answers should be **written clearly on the back page of the answer sheet in the appropriate box**. Only answers within the box will be considered while marking.

28. **(12 marks)** Two complexes with amido ligands (NH_2^-) show different M-NH_2 bonding geometries. The geometries of the M-N bonds in the two complexes are shown on the right. Importantly, for the Ti(IV) complex, all of the atoms shown are in the same plane ($TiNH_2$), which is not true for the Fe(II) complex. **Both complexes have no unpaired electrons.**



a) In which complex is the amido ligand acting "normally", *i.e.*, purely as a σ-donor?

b) Draw the correct ligand field splitting diagram for the Ti(IV) complex using the correct symmetry labels assuming pseudo-O_h symmetry. Be sure to include metal *d* electrons where appropriate.

c) Draw the correct ligand field splitting diagram for the Fe(II) complex using the correct symmetry labels assuming pseudo-O_h symmetry. Be sure to include metal *d* electrons where appropriate.

d) What is the difference between the amido ligand in the Ti(IV) complex and the one in the the Fe(II) complex?

e) Draw the localized M-N antibonding interaction that is *unique* to the Ti(IV) complex? (focus on a single M-N interaction, don't worry about any other ligands)

f) What difference in the metal ions creates this change in the ligand behaviour?

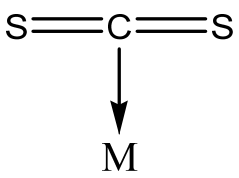
29. **(10 marks)** Carbon disulfide (CS_2) is not typically a ligand in transition metal complexes, mostly because it decomposes easily. However, several transition metal complexes with this ligand have been isolated.

a) Draw the appropriate Lewis structures that properly describe the bonding in CS_2.

b) In what types of orbitals do each of the *four lone pairs* reside? (*e.g.* the lone pair in NH_3 is in an sp^3 orbital)

c) Draw a representation of one of each of the bonding, non-bonding, and antibonding molecular orbitals that describe the π delocalization in this molecule. *Show the internuclear nodes if applicable. Use the relative sizes of the components to identify the amount each of the atoms is contributing to each orbital* – if all atoms contribute evenly, they should all have the same "size".

d) In complexes where CS_2 acts as a ligand, it sometimes binds in a so-called "side-on" geometry (shown below) and is positioned such that it is closest to the central carbon atom. Why is this unexpected? Which orbital would have to be used to form the σ bond? **CS_2 is acting as a pure σ donor in this situation.**



e) How would you expect CS_2 to bind to a metal centre if it were acting as both a σ-donor and a π-donor? Which orbitals on the ligand would be used to form each of these bonds?

END OF EXAM

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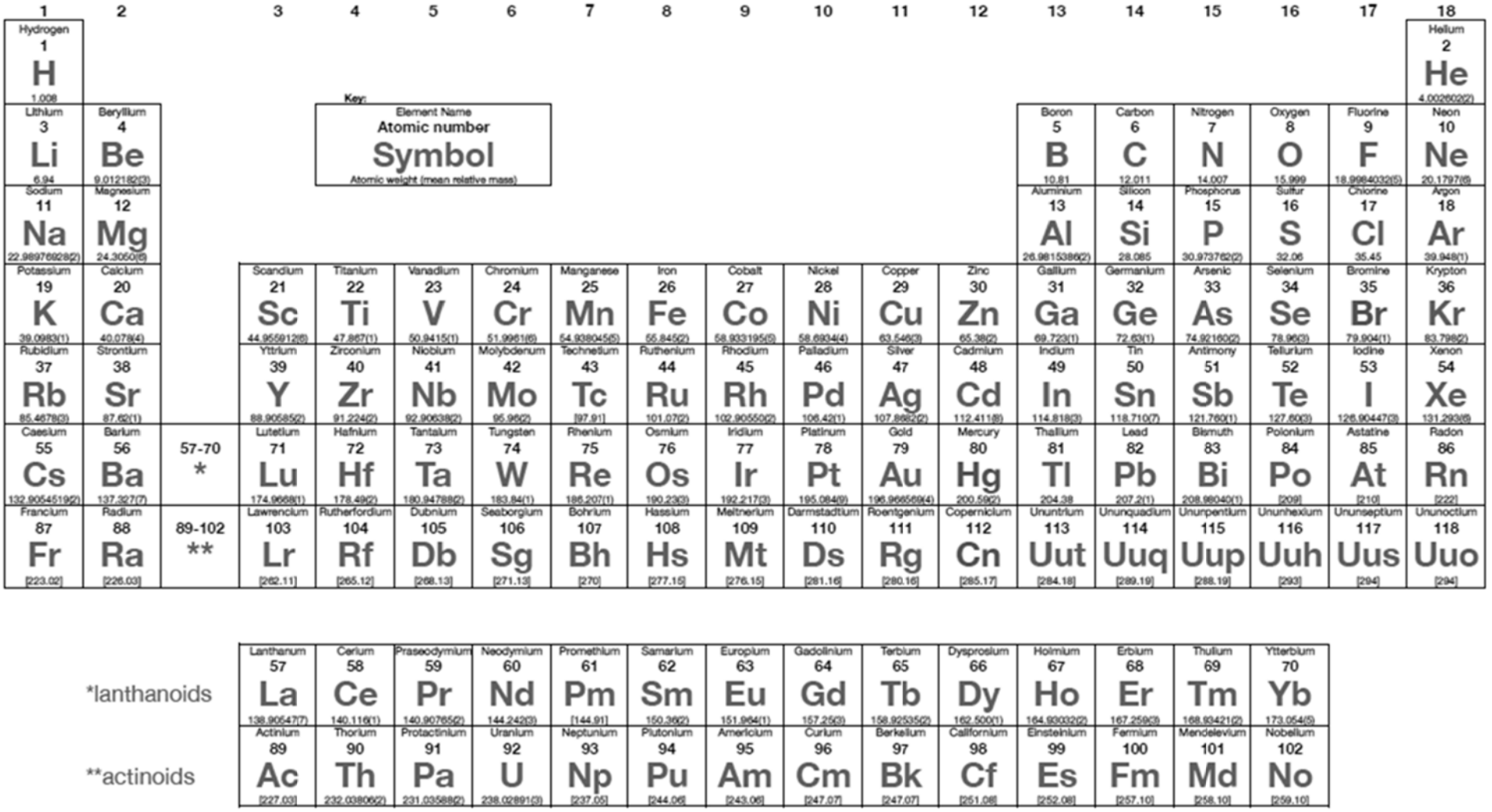
This page is available in case you need extra space to work on problems


1
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15
16
17
18
Hydrogen 1 H 1.008
Helium 2 He 4.002602(2)
Key:
Element Name
Atomic number
Symbol
Atomic weight (mean relative mass)
Lithium 3 Li 6.94
Beryllium 4 Be 9.012182(3)
Boron 5 B 10.81
Carbon 6 C 12.011
Nitrogen 7 N 14.007
Oxygen 8 O 15.999
Fluorine 9 F 18.9984032(5)
Neon 10 Ne 20.1797(6)
Sodium 11 Na 22.98976928(2)
Magnesium 12 Mg 24.3050(6)
Aluminium 13 Al 26.9815386(2)
Silicon 14 Si 28.085
Phosphorus 15 P 30.973762(2)
Sulfur 16 S 32.06
Chlorine 17 Cl 35.45
Argon 18 Ar 39.948(1)
Potassium 19 K 39.0983(1)
Calcium 20 Ca 40.078(4)
Scandium 21 Sc 44.955912(6)
Titanium 22 Ti 47.867(1)
Vanadium 23 V 50.9415(1)
Chromium 24 Cr 51.9961(6)
Manganese 25 Mn 54.938045(5)
Iron 26 Fe 55.845(2)
Cobalt 27 Co 58.933195(5)
Nickel 28 Ni 58.6934(4)
Copper 29 Cu 63.546(3)
Zinc 30 Zn 65.38(2)
Gallium 31 Ga 69.723(1)
Germanium 32 Ge 72.63(1)
Arsenic 33 As 74.92160(2)
Selenium 34 Se 78.96(3)
Bromine 35 Br 79.904(1)
Krypton 36 Kr 83.798(2)
Rubidium 37 Rb 85.4678(3)
Strontium 38 Sr 87.62(1)
Yttrium 39 Y 88.90585(2)
Zirconium 40 Zr 91.224(2)
Niobium 41 Nb 92.90638(2)
Molybdenum 42 Mo 95.96(2)
Technetium 43 Tc [97.91]
Ruthenium 44 Ru 101.07(2)
Rhodium 45 Rh 102.90550(2)
Palladium 46 Pd 106.42(1)
Silver 47 Ag 107.8682(2)
Cadmium 48 Cd 112.411(8)
Indium 49 In 114.818(3)
Tin 50 Sn 118.710(7)
Antimony 51 Sb 121.760(1)
Tellurium 52 Te 127.60(3)
Iodine 53 I 126.90447(3)
Xenon 54 Xe 131.293(6)
Caesium 55 Cs 132.90545192(2)
Barium 56 Ba 137.327(7)
57-70 *
Lutetium 71 Lu 174.9668(1)
Hafnium 72 Hf 178.49(2)
Tantalum 73 Ta 180.94788(2)
Tungsten 74 W 183.84(1)
Rhenium 75 Re 186.207(1)
Osmium 76 Os 190.23(3)
Iridium 77 Ir 192.217(3)
Platinum 78 Pt 195.084(9)
Gold 79 Au 196.966569(4)
Mercury 80 Hg 200.59(2)
Thallium 81 Tl 204.38
Lead 82 Pb 207.2(1)
Bismuth 83 Bi 208.98040(1)
Polonium 84 Po [209]
Astatine 85 At [210]
Radon 86 Rn [222]
Francium 87 Fr [223.02]
Radium 88 Ra [226.03]
89-102 **
Lawrencium 103 Lr [262.11]
Rutherfordium 104 Rf [265.12]
Dubnium 105 Db [268.13]
Seaborgium 106 Sg [271.13]
Bohrium 107 Bh [270]
Hassium 108 Hs [277.15]
Meitnerium 109 Mt [276.15]
Darmstadtium 110 Ds [281.16]
Roentgenium 111 Rg [280.16]
Copernicium 112 Cn [285.17]
Ununtrium 113 Uut [284.18]
Ununquadium 114 Uuq [289.19]
Ununpentium 115 Uup [288.19]
Ununhexium 116 Uuh [293]
Ununseptium 117 Uus [294]
Ununoctium 118 Uuo [294]
*lanthanoids
Lanthanum 57 La 138.90547(7)
Cerium 58 Ce 140.116(1)
Praseodymium 59 Pr 140.90765(2)
Neodymium 60 Nd 144.242(3)
Promethium 61 Pm [144.91]
Samarium 62 Sm 150.36(2)
Europium 63 Eu 151.964(1)
Gadolinium 64 Gd 157.25(3)
Terbium 65 Tb 158.92535(2)
Dysprosium 66 Dy 162.500(1)
Holmium 67 Ho 164.93032(2)
Erbium 68 Er 167.259(3)
Thulium 69 Tm 168.93421(2)
Ytterbium 70 Yb 173.054(5)
**actinoids
Actinium 89 Ac [227.03]
Thorium 90 Th 232.038062(2)
Protactinium 91 Pa 231.03588(2)
Uranium 92 U 238.02891(3)
Neptunium 93 Np [237.05]
Plutonium 94 Pu [244.06]
Americium 95 Am [243.06]
Curium 96 Cm [247.07]
Berkelium 97 Bk [247.07]
Californium 98 Cf [251.08]
Einsteinium 99 Es [252.08]
Fermium 100 Fm [257.10]
Mendelevium 101 Md [258.10]
Nobelium 102 No [259.10]

D_{2h}	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	functions
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	functions
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(xz, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0	(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1	
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0	

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	functions	
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		($2z^2$-x^2-y^2, x^2-y^2)
T_1	3	0	-1	1	-1		
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	functions
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	($2z^2$-x^2-y^2, x^2-y^2)
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	