CHEM-651: Inorganic Chemistry

Midterm I – September 30th, 2014

NAME Solution Set

This exam is comprised of 8 questions and is 11 pages in length. Please be sure that you have a complete exam and place your name on each page.

Answer each question to the best of your ability. Partial credit will be awarded where appropriate. You are not permitted to use any supplemental materials other than what is included in this test booklet. Calculators are not needed and are not permitted to be used. **PLEASE DO NOT REMOVE ANY PAGES FROM THIS EXAM.**

Write all your answers directly in this test booklet and show all work where necessary.

Good Luck!

1. _____ (20 points)
2. _____ (10 points)
3. _____ (8 points)
4. _____ (10 points)
5. _____ (20 points)
6. _____ (22 points)
7. _____ (10 points)
8. _____ (EC = 5 points)

Total _____

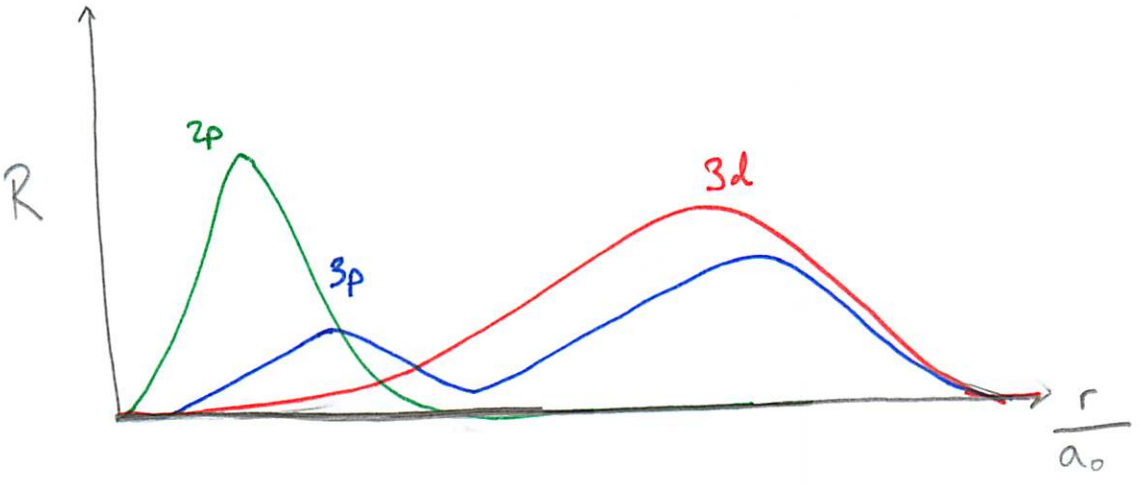
Name: _____

(d) (4 points) Account for the fact that Nb and Ta have very similar atomic radii.

Ta

Normally we would expect the 6th row element to have a larger radius than the 5th row homologue (Nb). However, in this case, the lanthanides come before Ta + the f-block e⁻ shield very poorly, which drives the Lanthanide Contraction. As such, the 6d e⁻ of Ta feel a similar Z^* to the 5d e⁻ of Nb.

(e) (6 points) Sketch radial distribution functions for the 2p, 3p, and 3d orbitals and, with reference to your diagrams, explain why a 3p orbital is lower in energy than a 3d orbital.



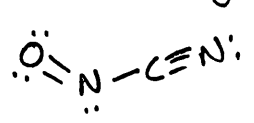
3p has some probability density that penetrates close to the nucleus. ∴ e⁻ spend some time close to the nucleus + 3p e⁻ is stabilized w/ respect to those in 3d.

Name: _____

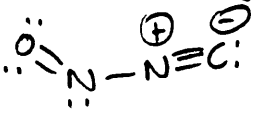
2. (10 total points) Three isomers having the empirical formula N_2CO are known: ONCN (Nitrosyl Cyanide), ONNC (nitrosyl isocyanide) and NOCN (isonitrosyl cyanide). See *Angew. Chem. Int. Ed.* **1997**, *36*, 1707. (10 pts)

   (a) (3 points) Draw *the most important resonance structure* for each of these isomers.
   (b) (3 points) Indicate the formal charges on each atom.

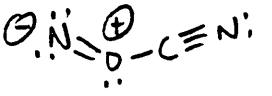
Nitrosyl Cyanide



Nitrosyl Isocyanide



Isonitrosyl Cyanide

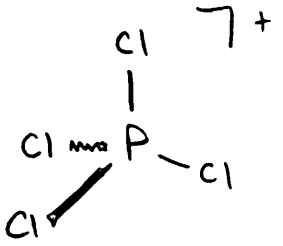


   (c) (4 points) Which of the three isomers do you predict to be most stable? Please provide a brief explanation for your reasoning.

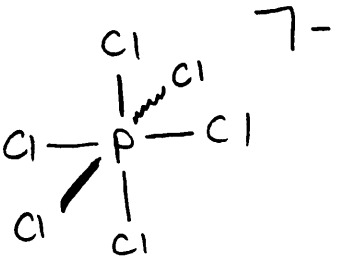
Nitrosyl cyanide is most stable because all formal charges are zero.

Name: _____

3. (8 total points; 4 points each) Solid phosphorus pentachloride is an ionic solid composed of PCl_4^+ cations and PCl_6^- anions. Please provide VSEPR structures for each of these ions? To what point group does each structure belong?



Td



O_h

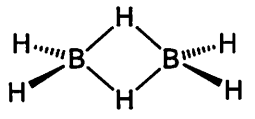
4. (10 total points; 1 point each) Please indicate the approximate hybridization and oxidation state of the central atom (**indicated in bold**) for each of the following species. Please place your answers in the boxes provided.

Compound	Hybridization	Oxidation State
NH_4^+	Sp^3	-3
BCl_3	Sp^2	+ 3
CO_2	SP	+ 4
NClO	Sp^2	+ 3
NO_2^-	Sp^2	+ 3

Name: _____

5. (20 total points; 2 points each) Determine the point groups of the following species. For structures that are not show, determine the lowest energy conformation of the molecule. Note: only answers placed in the empty boxes will be graded.

(a)

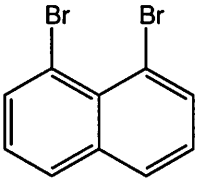


D_{2h}

(b) BF_4^-

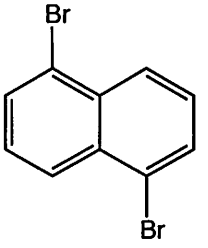
T_d

(c)



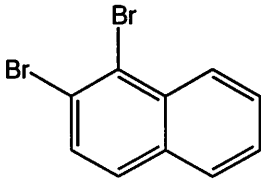
C_{2V}

(d)



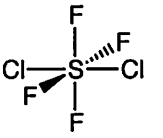
C_{2h}

(e)



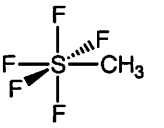
C_S

(f)



D_{4h}

(g)



C_S

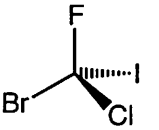
(h) H–C≡N

$C_{\infty V}$

(i) Acetylene

$D_{\infty h}$

(j)

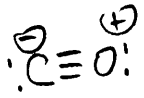


C_1

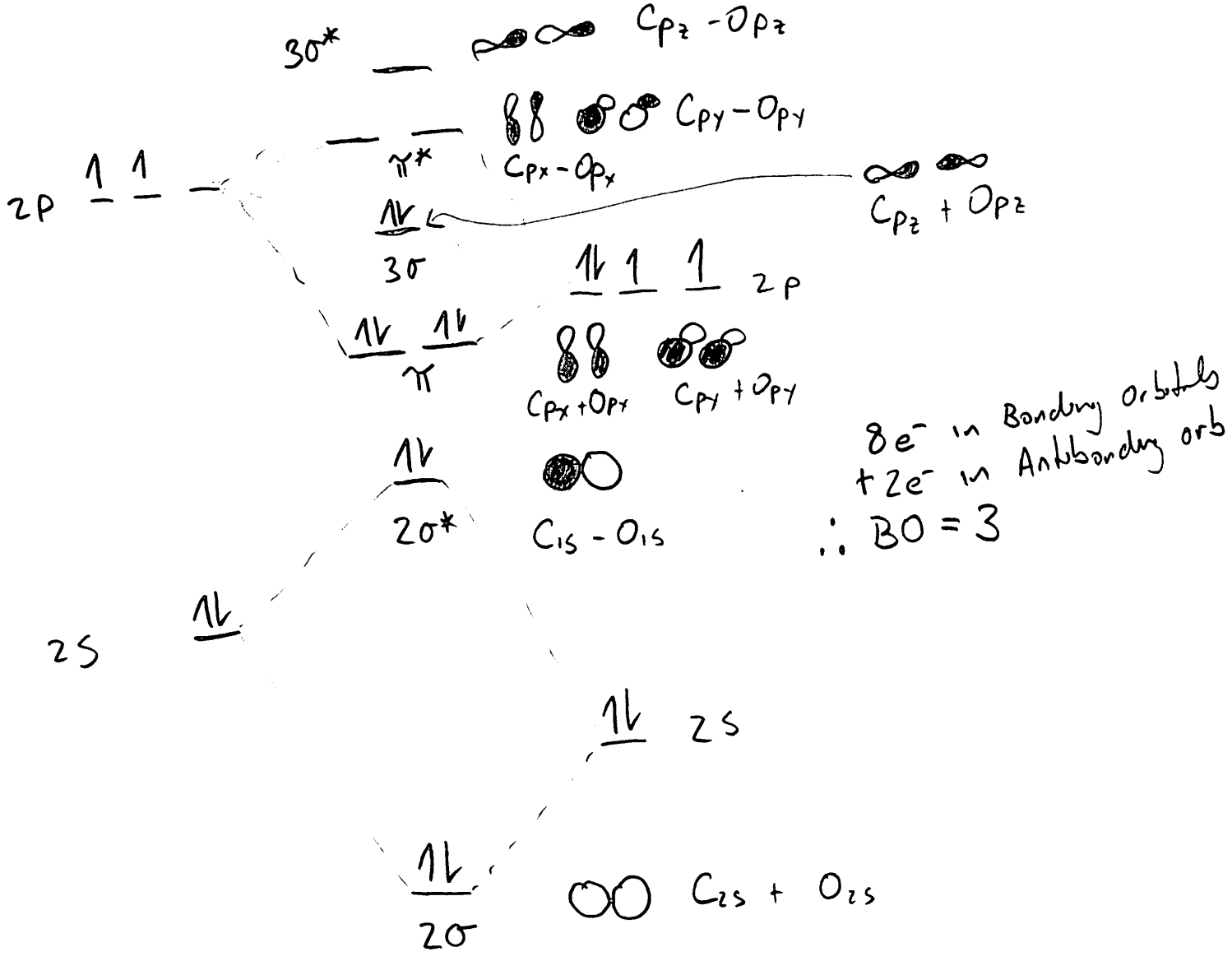
Name: _____

6. (22 total points) Carbon monoxide (CO) is a simple diatom that is an excellent ligand toward transition metals.

   (a) (2 points) Draw the Lewis structure of CO.

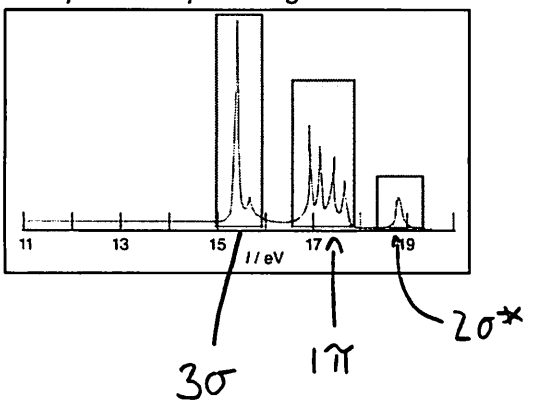


   (b) (10 points) Prepare a molecular orbital diagram for CO. Please be sure to label all atomic orbitals and all molecular orbitals. Please be sure to provide sketches that clearly show how the atomic orbitals interact to form MOs. What is the bond order of CO? (Note: you may find the table of *Atomic Orbital Ionization Energies* on page 11 of this exam to be useful in constructing your MO diagram).



Name: _____

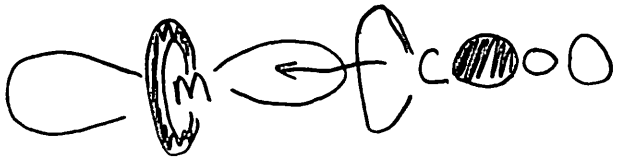
(c) (6 points) Based on the MO diagram that you developed in part (b), assign the 3 sets of lines in the UV photoelectron spectrum of CO, which is shown below. Please explain how you made your assignments.



More Stable orbitals correspond to higher I.
∴ the HOMO (3σ) will have the lowest Binding Energy of ~15 eV.

It makes sense that the HOMO-1 would be the π orbital as this band is highly structured suggesting that this orbital is highly populated + strongly contributes to the overall bonding of CO.

(d) (4 points) Although CO is a weak Brønsted base, it can serve as a strong Lewis base with transition metal centers. Based on the MO diagram you developed above, determine the types of interactions can CO form with a transition metal by drawing pictorial representations of the major bonding interactions between the frontier orbitals of CO and the relevant *d*-orbitals on a metal center. Please label all orbitals involved in the interactions you draw.

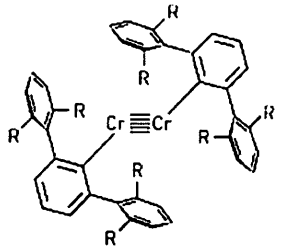


σ-donation

π-backbonding

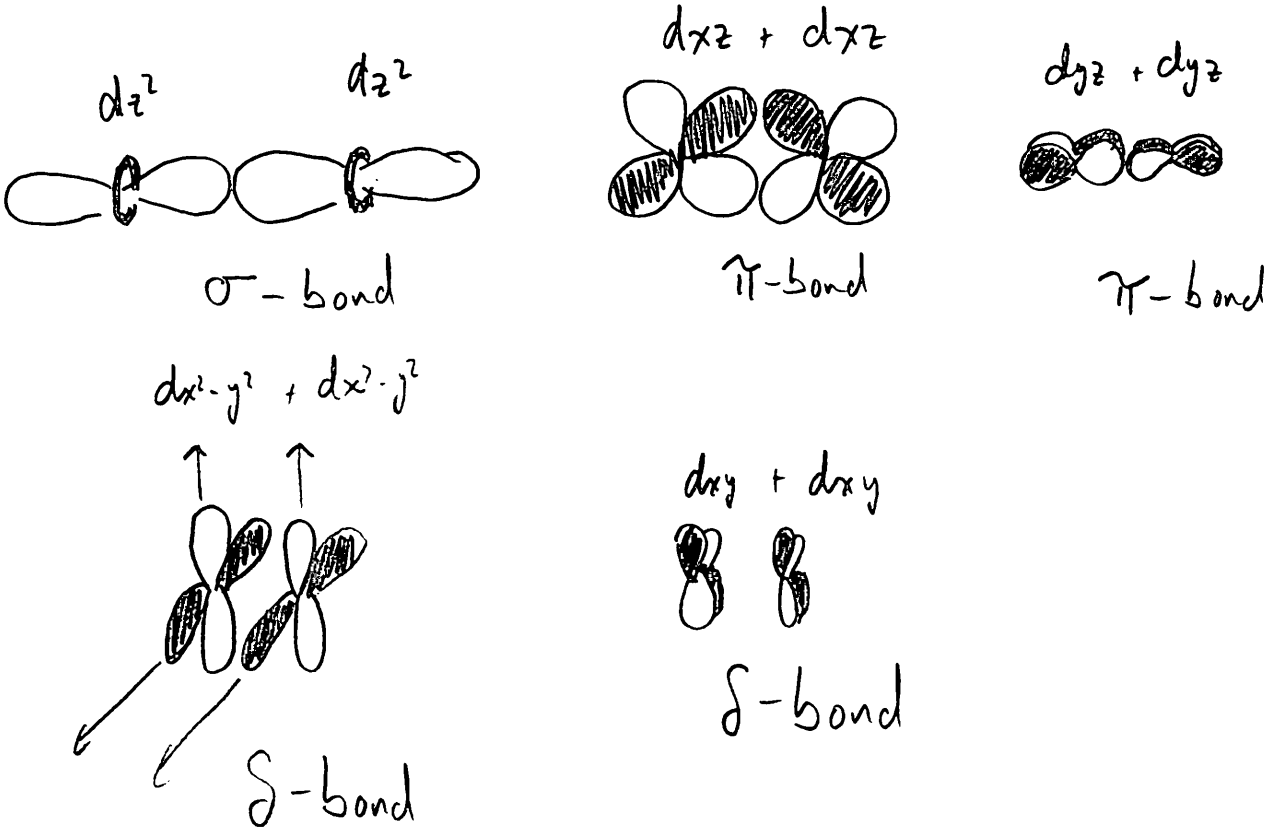
Name: _____

7. (10 total points) We saw in class that metals can be involved in multiple bonding with other metals. This was first demonstrated by F. A. Cotton and coworkers for $[Re_2Cl_8]^{2-}$ in which a metal-metal quadruple bond was observed. Phil Power's group described the chromium dimer shown below and proposed that this compound displays a M—M quintuple bond (*Science* **2005**, *310*, 844-847).



(a) (5 points) Sketch the five individual metal-metal bonding interactions that make up the quintuple bond. Please label the *d*-orbitals that you use for each case.

(b) (5 points) Label each interaction as being either a σ, π or δ bond.



Name: _____

8. Extra Credit: (5 total points) Provide the correct symbol for each of the missing elements below note: there are ten missing elements in total)

PERIODIC TABLE OF THE ELEMENTS

1 H 1.0079																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179
11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.08	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	Ga	32 Ge 72.59	33 As 74.9216	Se	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	Mo	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	Pd	47 Ag 107.868	48 Cd 112.41	49 In 114.82	Sn	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
Cs	Ba	57 La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	Os	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	Bi	84 Po (209)	At	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Name: _____

Atomic Orbital Ionization Energies (eV)

Valence Level	Element	1s	2s	2p	3s	3p	4s	4p
1	H	–13.6						
1	He	–24.5						
2	Li		–5.45					
2	Be		–9.30					
2	B		–14.0	–8.30				
2	C		–19.5	–10.7				
2	N		–25.5	–13.1				
2	O		–32.3	–15.9				
2	F		–46.4	–18.7				
2	Ne		–48.5	–21.5				
3	Na				–5.21			
3	Mg				–7.68			
3	Al				–11.3	–5.95		
3	Si				–15.0	–7.81		
3	P				–18.7	–10.2		
3	S				–20.7	–11.7		
3	Cl				–25.3	–13.8		
3	Ar				–29.2	–15.9		
4	K						–4.34	
4	Ca						–6.07	
4	Zn						–9.42	
4	Ga						–12.6	–5.95
4	Ge						–15.6	–7.56
4	As						–17.6	–9.05
4	Se						–20.8	–10.8
4	Br						–24.0	–12.5
4	Kr						–27.5	–14.3

Valence Level	Element	1s	2s	2p
4	Sc	–4.71	–5.70	–3.22
4	Ti	–5.58	–6.07	–3.35
4	V	–6.32	–6.32	–3.47
4	Cr	–7.19	–6.57	–3.47
4	Mn	–7.93	–6.82	–3.59
4	Fe	–8.68	–7.07	–3.72
4	Co	–9.42	–7.32	–3.84
4	Ni	–10.0	–7.56	–3.84
4	Cu	–10.7	–7.69	–3.97