Inorganic Chemistry I

【Total 2 pages】

Ⅰ－a

Answer the following questions about homonuclear diatomic molecules such as nitrogen molecules (N≡N) and oxygen molecules (O=O).

（1）Write the atomic orbital diagrams of nitrogen and oxygen atoms. Electrons are described using the arrows ↑↓ considering the electronic spins.

（2）Explain bonding σ and π orbitals and antibonding σ* and π* orbitals from the overlaps of atomic orbitals.

（3）Write the molecular orbital diagrams of nitrogen and oxygen molecules.

（4）Answer the reason that the nitrogen molecule has a triple bond and the oxygen molecule has a double bond.

（5）Answer with the reason which molecule has paramagnetism, the nitrogen or oxygen molecules.

（6）Answer the reason why the bond length of the nitrogen molecule becomes longer by the cationization, whereas that of the oxygen molecule becomes shorter.

Ⅰ－b

In the NaCl structure, answer the following questions.

（1）An anion is considered to be in contact with its six nearest cations. When the anion is also in contact with the anion that is closest to it, find the ratio r/R of the radius r of the cation to the radius R of the anion with the two-digit accuracy.

（2）For NaF, NaCl and NaBr, list them in order of the increasing melting point, using the inequality symbol, and explain why they are in that order.

（3） Both KCl and NaCl form face-centered cubic crystals. When the powder X-ray diffraction patterns are measured, the diffraction lines from the (200) plane appear at different angles θ. Explain why this is the case. The lattice constants are 5.63 Å for NaCl and 6.28 Å for KCl.

（4） When the powder X-ray diffraction patterns are measured, the diffraction line from the (111) plane is not observed in KCl, unlike NaCl. Explain why.

(The end)

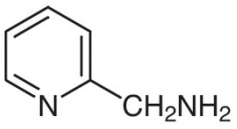
Inorganic Chemistry Ⅱ

【Total 2 pages】

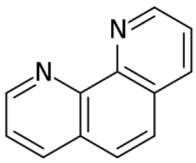
Ⅱ－a Read the following sentences and answer the questions.

Fe^{2+} ions exhibit interesting temperature-dependent properties originating from the number of d electrons. $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$ (2-pic: 2-picolylamine, see below left) shows paramagnetism around room temperature with an effective magnetic moment of ~5 μ_B, while it becomes diamagnetic by cooling down to ~110 K. On the other hand, $[Fe(phen)_2(NCS\text{-}N)_2]^{2+}$ (phen: 1,10-phenanthroline, see below right; NCS-*N*: the N atom is coordinated to Fe) gives a similar phase transition also around ~110 K, while $[Fe(phen)_3]^{2+}$ or $[FeI_2(phen)_2]$ do not.

Molecular structure of 2-pic



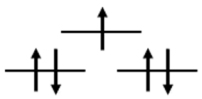
Molecular structure of phen



（1） Answer the name of the phase transition.

（2） Assuming the octahedral ligand field around Fe^{2+}, answer the Fe 3d electronic configuration in $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$ at room temperature. For the description of the electronic configuration, see the example at the right side.

Example of electronic configuration



（3） Assuming similarly the octahedral ligand field around Fe^{2+}, answer the Fe 3d electronic configuration in $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$ at low temperature (<110 K).

（4） Is this phase transition the first or second order? Answer together with a concise reason.

（5） Is the effective magnetic moment of the free Fe^{2+} ion greater or smaller than that of $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$ at room temperature? Answer together with a reason concisely.

（6） It is known that $[Fe(phen)_3]^{2+}$ and $[FeI_2(phen)_2]$ have different numbers of unpaired electrons. Answer the numbers of unpaired electrons in $[Fe(phen)_3]^{2+}$ and $[FeI_2(phen)_2]$, respectively.

（7） Answer the spectrochemical series for the four ligands of NCS-*N*, phen, 2-pic, and I^- in the sequential order of the crystal-field splitting from small to large.

Ⅱ－b　Answer the following questions about metal complexes. (Ph = phenyl)

(1) Draw the three-dimensional structure of the following complexes. Also, answer the formal oxidation number of each transition metal and the number of valence electrons based on the 18-electron rule.

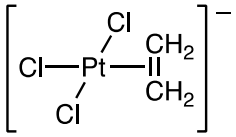
(a) [*trans*-$PdCl_2(PPh_3)_2$]

(b) [*fac*-$CoCl_3(NH_3)_3$]

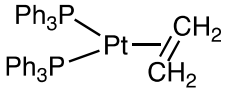
(c) $[Ag(NH_3)_2]^+$

(d) [$W(\eta^6$-benzene$)(CO)_3$]

(2) In the following platinum complexes, the carbon-carbon double bond distance of the ethylene ligand is **A**: 1.35 Å, **B**: 1.43 Å. Explain why the carbon-carbon distance is longer in **B** compared to **A**.

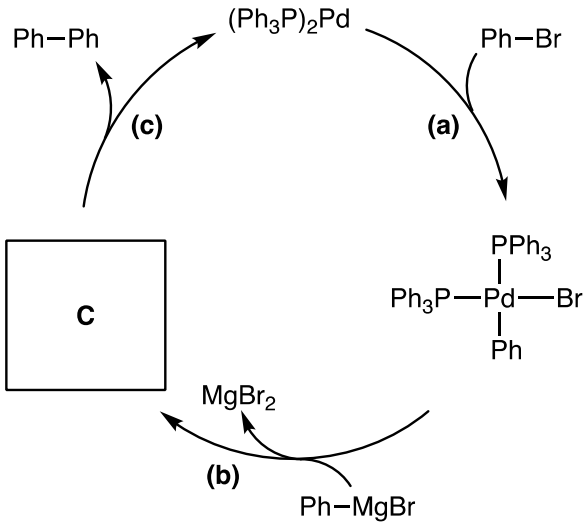


A



B

Ⅱ－c　Answer the following questions about catalytic reactions. (Ph = phenyl)



(1) Choose the names for reactions **(a)**, **(b)**, and **(c)** from the following list.

transmetalation　oxidative addition　insertion　cycloaddition

β-hydride elimination　reductive elimination

(2) Draw the structure of complex **C**.

(The end)