［無機・分析化学標準］

以下の問(１)〜(３)に答えよ.

（１） 金属錯体に関する以下の問(a), (b)に答えよ.

(a) 次の①と②について, 異性体の立体構造をすべて描け. もし異性体が存在しない場合は, 無しと記せ.

① $PtBrCl(CO)_2$　　② $[Ru(ethylenediamine)_3]^{2+}$

(b) 金属錯体の異性体を区別するための一般的な分析法を以下の③〜⑥から二つ選び, その原理と異性体の区別が可能な理由を 200 字程度で記せ.

③ 円二色性分光法　④ 電子スピン共鳴分光法
⑤ 赤外分光法　　⑥ 核磁気共鳴法

（２） 無機化合物の性質や分析手法に関する以下の問(c), (d)に答えよ.

(c) $MnCl_2$ 水溶液の光吸収は$[Mn(H_2O)_6]^{2+}$に由来し, 可視光領域に弱い光吸収を示す. $KMnO_4$ 水溶液の光吸収は$[MnO_4]^-$に由来し, 可視光領域に強い光吸収を示す. $MnCl_2$ と $KMnO_4$ の水溶液が異なる光吸収の強さを示す理由を, 光吸収と関係する電子遷移に注目して 150 字程度で記せ. 必要ならば図を用いてもよい. ただし, 図は字数に含めない.

(d) 金属水素化物の水素原子位置を精密に決定するには, X 線回折法よりも中性子回折法が適している. その理由と両手法の特徴を 150 字程度で記せ.

（３） ZnO の電気伝導に関する以下の問(e)〜(h)に答えよ.

(e) 化学量論組成の ZnO は絶縁体であり, その単結晶は可視光領域において高い光透過性を示す. その理由を, バンドギャップという言葉を用いて 50 字程度で記せ.

(f) ZnO 結晶に Al をドーピングすると n 型の電気伝導を示す. その理由を 50 字程度で記せ.

(g) 問(f)の結晶について, 温度上昇にともなう電気抵抗率のふるまいを, その理由とともに 50 字程度で記せ.

(h) 一辺の長さが 1.00 cm の正方形を底面とし, 厚さが 0.50 cm の ZnO 結晶の上下底面に電極をつけ, 電気抵抗 R を測定した. $R = 1.00 \times 10^3\ \Omega$ のとき, この試料の電気抵抗率 ρ (Ω cm)を有効数字に注意して答えよ. なお, 接触抵抗および R の測定誤差は無視できるとする.

[Inorganic and Analytical Chemistry: Standard]

Answer the following problems (1) through (3).

(1) Answer the following problems (a) and (b) concerning metal complexes.

(a) For each of the following ① and ②, draw the three-dimensional structure of all isomers. If there is no isomer, write "none."

① $PtBrCl(CO)_2$ ② $[Ru(ethylenediamine)_3]^{2+}$

(b) Select two analytical methods from ③ through ⑥ to distinguish isomers of metal complexes. Explain the principle of the method and how isomers can be distinguished in approximately 100 words for each method.

③ Circular dichroism spectroscopy ④ Electron spin resonance spectroscopy
⑤ Infrared spectroscopy ⑥ Nuclear magnetic resonance spectroscopy

(2) Answer the following problems (c) and (d) regarding the properties and analytical methods of inorganic compounds.

(c) The optical absorption of aqueous $MnCl_2$ solution originates from $[Mn(H_2O)_6]^{2+}$; a weak optical absorption is observed in the visible region. The optical absorption of aqueous $KMnO_4$ solution originates from $[MnO_4]^-$; a strong optical absorption is observed in the visible region. Explain the reason for the difference in the absorption intensity of these compounds based on the electron transition processes, in approximately 75 words. If needed, you can use a drawing for the explanation.

(d) To accurately determine the position of hydrogen atoms in metal hydrides, it is more appropriate to use neutron diffraction rather than using X-ray diffraction. Explain the reason for this in approximately 75 words, citing the characteristics of both methods.

(3) Answer the following problems (e) through (h) concerning the electrical conduction of ZnO.

(e) Stoichiometric ZnO is an insulator, and its single crystal is transparent to visible light. Explain the reason in approximately 25 words, using the term "band gap."

(f) ZnO crystals show n-type electrical conduction when doped with Al. Explain the reason in approximately 25 words.

(g) Explain the changes in the electrical resistivity of the crystal in problem (f) when the temperature is increased. Also, explain the reason in approximately 25 words.

(h) The electrical resistance R of a ZnO crystal with a square of 1.00 cm on a side and 0.50 cm in thickness is 1.00×10^3 Ω. The electrodes are attached to the top and bottom squares of the crystal. Calculate the electrical resistivity ρ (Ω cm). Assume that the contact resistance and the measurement

error of R are negligible. Note the significant figures.