［無機・分析化学基礎］

以下の問（１），（２）に答えよ．

（１）以下の問(a)～(c)に答えよ．

(a) 室温で, 酸化物 CaO および MgO はどちらも希塩酸に容易に溶けるが, 中性の水に対しては一方の酸化物はほとんど溶けない. 溶解度の低い酸化物がどちらかを答え，その理由を 150 字程度で記せ.

(b) H_2O，$[Co(H_2O)_6]^{3+}$，$[Co(H_2O)_6]^{2+}$について，Brønsted 酸として酸性度の強い順に不等号(>)を用いてならべ, その理由を 150 字程度で記せ.

(c) 室温，嫌気下で，Fe^{II} と Fe^{III} の混在した水溶液中の Fe^{II} と Fe^{III} の比率を決定する手法を一つ挙げ，その原理を 150 字程度で記せ.

（２）Ni^{II} は次ページの図 1 に示すように，四面体，平面四角形，八面体など多様な配位構造をとる．以下の問(d)～(i)に答えよ．

(d) Ni は原子番号 28 である. Ni^{II} の電子配置を以下の例にならって記せ. 例：C の電子配置は $1s^2 2s^2 2p^2$ である.

(e) $[NiCl_4]^{2-}$は四面体構造をとる(図 1(A))．この錯体の結晶場における d 軌道の分裂図，および Hund 則に基づいた電子配置を模式的に図示せよ.

(f) 問(e)の分裂した d 軌道間のエネルギー差を Δ_T とする．$[NiCl_4]^{2-}$の結晶場安定化エネルギーを Δ_T を用いて，導出過程とともに記せ.

(g) $[Ni(CN)_4]^{2-}$は平面四角形構造をとる(図 1(B))．この錯体の結晶場における d 軌道の分裂図，および Hund 則に基づいた電子配置を模式的に図示せよ.

(h) 問(e), (g)の電子配置に基づき，$[NiCl_4]^{2-}$，$[Ni(CN)_4]^{2-}$はそれぞれ常磁性か反磁性かを理由とともに 100 字程度で記せ.

(i) 八面体構造をとる$[Ni(H_2O)_6]^{2+}$(図 1(C))と$[Ni(NH_3)_6]^{2+}$(図 1(D))の光吸収スペクトルを比較する．d-d 遷移に由来する光吸収を，より長波長側に示す Ni^{II} 錯体はどちらと考えられるか．理由とともに 100 字程度で記せ．

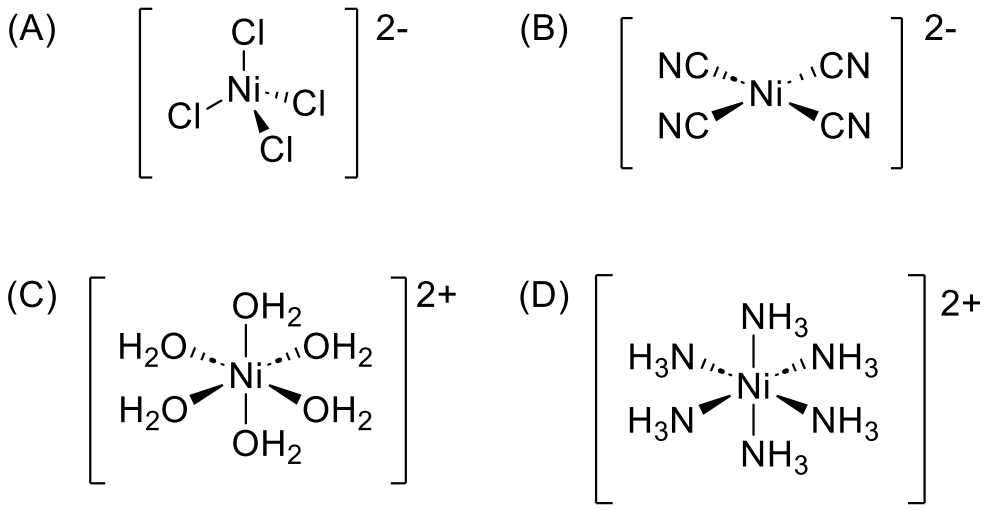

図 1. (A) $[NiCl_4]^{2-}$の構造．(B) $[Ni(CN)_4]^{2-}$の構造．(C) $[Ni(H_2O)_6]^{2+}$の構造．(D) $[Ni(NH_3)_6]^{2+}$の構造．

[Inorganic and analytical chemistry: basic]

Answer the following problems (1) and (2).

(1) Answer the following problems (a) through (c).

(a) At room temperature, oxides CaO and MgO are soluble in dilute hydrochloric acid, but one of them is almost insoluble in neutral water. Answer which oxide has the lower solubility and explain the reason in approximately 75 words.

(b) Arrange H_2O, $[Co(H_2O)_6]^{3+}$, and $[Co(H_2O)_6]^{2+}$ in descending order of Brønsted acidity using an inequality sign (>), and explain the reason in approximately 75 words.

(c) Answer a method for determining the ratio of Fe^{II} and Fe^{III} in an aqueous solution containing both Fe^{II} and Fe^{III} at room temperature under anaerobic conditions, and explain the principle in approximately 75 words.

(2) As shown in Fig. 1 on the next page, Ni^{II} has various coordination structures such as tetrahedral, square planar, and octahedral geometries. Answer the following problems (d) through (i).

(d) Atomic number of Ni is 28. Show the electron configuration of Ni^{II} following the example.
Example: The electron configuration of C is $1s^2 2s^2 2p^2$.

(e) $[NiCl_4]^{2-}$ has a tetrahedral geometry (Fig. 1(A)). Schematically illustrate the d-orbital splitting diagram and the electron configuration based on Hund's rule.

(f) The d-orbital splitting energy in problem (e) is defined as Δ_T. Answer the crystal field stabilization energy of $[NiCl_4]^{2-}$ using Δ_T. Also show the calculation process.

(g) $[Ni(CN)_4]^{2-}$ has a square planar geometry (Fig. 1(B)). Schematically illustrate the d-orbital splitting diagram and the electron configuration based on Hund's rule.

(h) Based on the electron configurations of problems (e) and (g), answer whether $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic or diamagnetic, and explain the reason in approximately 50 words.

(i) Comparing the optical absorption spectra of $[Ni(H_2O)_6]^{2+}$ (Fig. 1(C)) and $[Ni(NH_3)_6]^{2+}$ (Fig. 1(D)) with octahedral geometry, answer which Ni^{II} complex exhibits longer wavelength absorption originating from d-d transition. Explain the reason in approximately 50 words.

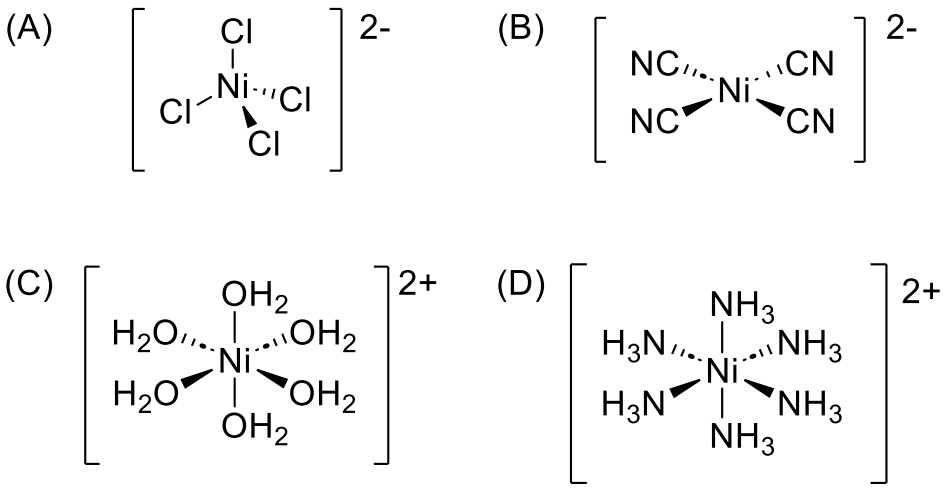

Fig 1. (A) Structure of $[NiCl_4]^{2-}$. (B) Structure of $[Ni(CN)_4]^{2-}$. (C) Structure of $[Ni(H_2O)_6]^{2+}$. (D) Structure of $[Ni(NH_3)_6]^{2+}$.