

Contribution from the Department of Electronic Chemistry,
Tokyo Institute of Technology at Nagatsuta, Midori-ku, Yokohama 227, Japan

Thermodynamics and Structure of Isothiocyanato Complexes of Manganese(II), Cobalt(II), and Nickel(II) Ions in *N,N*-Dimethylformamide

Shin-ichi Ishiguro* and Kazuhiko Ozutsumi†

Received August 4, 1989

The formation of isothiocyanato complexes of manganese(II), cobalt(II), and nickel(II) has been studied by calorimetry and spectrophotometry in *N,N*-dimethylformamide (DMF) containing 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ as an ionic medium at 25°C . The formation of a series of mononuclear $[\text{M}(\text{NCS})]^+$, $[\text{M}(\text{NCS})_2]^+$, $[\text{M}(\text{NCS})_3]^-$, and $[\text{M}(\text{NCS})_4]^{2-}$ ($\text{M} = \text{Mn, Co, Ni}$) complexes is proposed for all the metal ions examined. It is demonstrated that, for Co(II), an octahedral (O_h) to tetrahedral (T_d) geometry change occurs extensively at the third consecutive step, i.e. $[\text{Co}(\text{NCS})_2(\text{DMF})_4] (O_h) + \text{NCS}^- \rightarrow [\text{Co}(\text{NCS})_3(\text{DMF})]^- (T_d) + 3\text{DMF}$. On the other hand, with Ni(II), no geometry change does occur throughout steps of complexation, so that octahedral, six-coordinate geometry may be preserved for all the complexes, including $[\text{Ni}(\text{NCS})_3(\text{DMF})_3]^-$ and $[\text{Ni}(\text{NCS})_4(\text{DMF})_2]^{2-}$. With Mn(II), although there is no spectroscopic evidence, the thermodynamic parameters suggest that an octahedral to tetrahedral geometry change occurs at either the third step or the fourth, and the tetrahedral $[\text{Mn}(\text{NCS})_4]^{2-}$ complex is finally formed. This implies that an octahedral-tetrahedral equilibrium, $[\text{Mn}(\text{NCS})_3(\text{DMF})_3]^- (O_h) = [\text{Mn}(\text{NCS})_3(\text{DMF})]^- (T_d) + 2\text{DMF}$, is established. These results for the $\text{M}^{\text{II}}-\text{NCS}^-$ ($\text{M} = \text{Mn, Co, Ni}$) systems are in contrast to those for the $\text{M}^{\text{II}}-\text{Cl}^-$ systems, in which an octahedral to tetrahedral geometry change occurs at the second step for Mn(II) and Co(II), and at the third for Ni(II), in the same solvent.

Introduction

The extent of complexation of bivalent metal with halide and pseudohalide ions in aprotic donor solvents, such as acetonitrile (AN), propylene carbonate (PC), dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF), is remarkably enhanced over water.¹⁻⁸ For example, the formation of $[\text{CuCl}_4]^{(2-n)+}$ in these solvents is promoted in the order water < DMSO < DMF < AN < PC. Evidently, this is not the order of decreasing relative dielectric constants of solvents,⁹ water (78.39) > PC (64.92) > DMSO (46.45) > DMF (36.71) > AN (35.94) at 25°C . It should, therefore, be stressed that the dielectric constant of solvent is not the main factor controlling the ease of metal complexation in these solutions. Even more important and essential solvent properties may be those reflecting short-range interactions at the molecular level. The electron-pair donating and accepting abilities of solvents are especially emphasized,¹⁰⁻¹² as ions are solvated in solution. Also, the role of solvent-solvent interactions in the bulk must be emphasized. This effect is especially important for solvents such as water,¹³ possessing strong hydrogen-bonding ability, and DMSO, in which specific dipole-dipole interactions operate between solvent molecules.^{3,14-16} However, a universal measure for the strength of solvent-solvent interactions has still not been established.

As a metal ion can accommodate simultaneously a number of ligands as well as solvent molecules in the primary coordination spheres, interactions between ligating ions and molecules may also play a significant role in complexation behavior of metal ions. For bulky organic solvent molecules, a sort of rotational motion must be sterically hindered to an appreciable extent. In aprotic solvents such as AN, DMF, and DMSO, bivalent transition-metal ions are six-coordinated and octahedral geometry is established as in water.¹⁷⁻²⁷ In *N,N*-dimethylacetamide (DMA), an equilibrium between six- and four-coordination is suggested for cobalt(II) and nickel(II) ions.^{22,23} In an extreme case, the coordination number of bivalent transition-metal ions is reduced, indeed to 4 in hexamethylphosphoramide (HMPA), which is especially bulky.²⁴⁻²⁸ It has been pointed out in our previous works^{1-3,29,30} that an octahedral to tetrahedral geometry change occurs upon complexation of a bivalent transition metal with halide ions in AN, DMF, and DMSO, and such geometry changes have been verified by electronic spectra as well as by direct solution X-ray diffraction.²⁹⁻³¹ In HMPA, in which metal ions are four-coordinated, unusual thermodynamic behavior has been observed for the complexation of cobalt(II) with halide ions.³² These observations evidently indicate that not only thermodynamic but also kinetic

behavior of metal ions in solution cannot be understood without taking into account the coordination geometry of metal ions and its change upon complexation.

Interestingly, with Zn(II) and Cd(II), an octahedral to tetrahedral geometry change occurs at a later step for the thiocyanato complexes than for the halide complexes.³³⁻³⁵ For the thiocyanato

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† Present address: Department of Chemistry, University of Tsukuba, Ibaragi 305, Japan.

complexes of Co(II) in aqueous methanol,³⁶ the geometry change occurs on the formation of $[\text{Co}(\text{NCS})_4]^{2-}$. These imply that the thiocyanate ion behaves rather differently from halide ions. Although various metal(II)-thiocyanate systems have so far been studied in solution,³⁷⁻⁴² quantitative thermodynamic studies aiming at obtaining reaction enthalpies and entropies are scarce, especially in nonaqueous solution. Comprehensive works for various kinds of metal ions are therefore indispensable. In this work we investigated the complexation of manganese(II), cobalt(II), and nickel(II) with thiocyanate ions in DMF by calorimetry⁴³ and spectrophotometry. This paper presents sets of reliable thermodynamic parameters for the formation of isothiocyanato complexes of Mn(II), Co(II), and Ni(II) in DMF, probably for the first time in nonaqueous solution, along with the extracted electronic spectra of individual complexes.

Experimental Section

Reagents. All chemicals used were of reagent grade. The DMF solvates of manganese(II), cobalt(II), and nickel(II) perchlorates were prepared as described elsewhere.^{29,30} *N,N*-Dimethylformamide was dried for several weeks over 4A 1/16 molecular sieves and then distilled under reduced pressure and stored with molecular sieves in a dark bottle with a P_2O_5 drying tube.

Measurements. Calorimetric measurements were carried out by using a fully automatic on-line calorimetry system, consisting of a twin-type calorimeter (Tokyo Riko), in a room thermostated at 25 ± 0.2 °C. All metal(II) perchlorate solutions contained 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ as an ionic medium. $\text{M}(\text{ClO}_4)_2$ ($\text{M} = \text{Mn, Co, Ni}$) solutions were titrated with a 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NSCN}$ solution. A solution (40 cm^3) containing a metal(II) perchlorate was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying tube, was inserted in an aluminum block thermostated at 25.0 ± 0.0001 °C in an air bath. Portions of the $(\text{C}_2\text{H}_5)_4\text{NSCN}$ solution were added to this solution from an autoburet (APB-118, Kyoto Electronics). Heats of complexation at each titration point were measured with a certainty of $\pm 0.02 \text{ J}$ and corrected for heat of dilution of the titrant. The heat of dilution had been determined in advance by separate experiments and was found to be very small.

Spectrophotometric measurements were carried out by using an automatic spectrophotometric titration system, which includes a Shimadzu MPS-2000 spectrophotometer. The system, along with a computer program for device control and data acquisition, was developed in our laboratory. A flow cell with a path length of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. A test solution thermostated at 25 °C was circulated, passing through a flow cell, by using a Teflon pump. Initially, an $\text{M}(\text{ClO}_4)_2$ ($\text{M} = \text{Co, Ni}$) solution (25 cm^3) was placed in a vessel under a dry nitrogen atmosphere, and the solution was then titrated with 0.05 or 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NSCN}$ solution. Measured electronic spectra were recorded in 1-nm intervals over the wavelength range 300–850 nm. Spectrophotometric data thus obtained at 50 selected wavelengths, over the ranges 450–700 nm for Co(II) and 350–850 nm for Ni(II), were employed for the least-squares calculation of formation constants.

Data Analysis. If the formation of only mononuclear complexes is assumed, the overall formation of the $[\text{M}(\text{NCS})_n]^{(2-n)+}$ ($\text{M} = \text{Mn, Co, Ni}$) complex can be defined as in eqs 1 and 2. A heat q_i measured at



$$\beta_n = [\text{M}(\text{NCS})_n^{(2-n)+}] / [\text{M}^{2+}][\text{NCS}^-]^n \quad (2)$$

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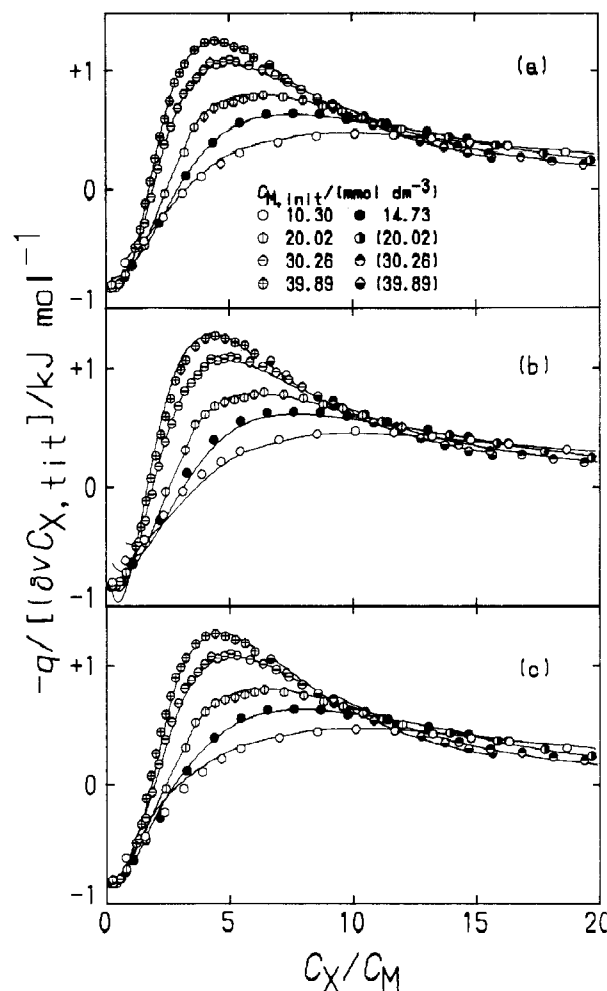


Figure 1. Calorimetric titration curves for the $\text{Mn}^{\text{II}}-\text{NCS}^-$ system obtained in *N,N*-dimethylformamide containing 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ at 25 °C. Concentrations of Mn(II) ion in initial test solutions, $C_{\text{Mn,init}}/(\text{mmol dm}^{-3})$, are given. The solid lines are calculated by using constants in Table I: (a) set (1,2,3,4); (b) set (1,2,3); (c) set (1,2,4).

the i th titration point is expressed by formation constants β_n and overall enthalpies $\Delta H^\circ_{\beta_n}$ as in eq 3, where V_i denotes the volume of the test solution.

$$q_i = -(V_i \sum \beta_n (\Delta H^\circ_{\beta_n}) [\text{M}^{2+}]_i [\text{NCS}^-]_i^n - V_{i-1} \sum \beta_n (\Delta H^\circ_{\beta_n}) [\text{M}^{2+}]_{i-1} [\text{NCS}^-]_{i-1}^n) \quad (3)$$

Similarly, the absorbance A_{ij} for a given solution i and wavelength λ_j is represented by using the formation constant β_n and molar extinction coefficient $\epsilon_n(\lambda_j)$ of the $[\text{M}(\text{NCS})_n]^{(2-n)+}$ complex as in eq 4. The

$$A_{ij} = \sum \epsilon_n(\lambda_j) \beta_n [\text{M}^{2+}]_i [\text{NCS}^-]_i^n + \epsilon_{\text{M}}(\lambda_j) [\text{M}^{2+}]_i + \epsilon_{\text{NCS}}(\lambda_j) [\text{NCS}^-]_i \quad (4)$$

concentrations of free M^{2+} and NCS^- ions are related to their total concentrations, $C_{\text{M},i}$ and $C_{\text{X},i}$, respectively, according to the mass-balance equations (5) and (6).

$$C_{\text{M},i} = [\text{M}^{2+}]_i + \sum \beta_n [\text{M}^{2+}]_i [\text{NCS}^-]_i^n \quad (5)$$

$$C_{\text{X},i} = [\text{NCS}^-]_i + \sum n \beta_n [\text{M}^{2+}]_i [\text{NCS}^-]_i^n \quad (6)$$

Formation constants and enthalpies were obtained simultaneously by minimizing $U = \sum (q_{i,\text{obsd}} - q_{i,\text{calcd}})^2$, and formation constants and molar absorption coefficients by $U = \sum (A_{i,\text{obsd}} - A_{i,\text{calcd}})^2$; a nonlinear least-squares program according to an algorithm proposed by Marquardt⁴⁴ was used.

Results

The calorimetric titration curves obtained for the manganese(II), cobalt(II), and nickel(II) thiocyanate systems are de-

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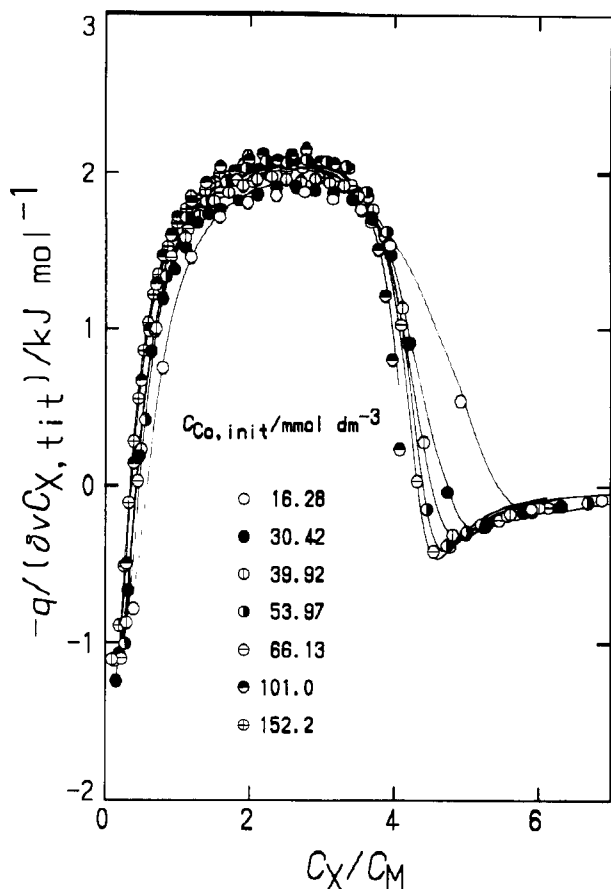


Figure 2. Calorimetric titration curves for the Co^{II}-NCS⁻ system obtained in *N,N*-dimethylformamide containing 0.4 mol dm⁻³ (C₂H₅)₄N-ClO₄ at 25 °C. Concentrations of Co(II) ion in initial test solutions, C_{Co,init}/(mmol dm⁻³), are given. The solid lines are calculated by using constants in Table II.

Table I. Overall Formation Constants log (β_{*n*}/(mol^{-*n*} dm^{3*n*})) and Reaction Enthalpies Δ*H*^o_{β_{*n*}/(kJ mol⁻¹) for Sets of [Mn(NCS)_{*n*}]^{(2-*n*)+} Obtained by Analyzing Calorimetric Data in *N,N*-Dimethylformamide Containing 0.4 mol dm⁻³ (C₂H₅)₄NClO₄ as an Ionic Medium at 25 °C^a}

	(1,2,3,4)	(1,2,3)	(1,2,4)
log β ₁	2.3 (0.1) ^b	1.7 (0.3)	2.9 (0.5)
log β ₂	3.8 (0.2)	3.0 (0.2)	4.9 (0.6)
log β ₃	4.6 (0.2)	3.9 (0.1)	
log β ₄	5.6 (0.2)		6.8 (0.6)
Δ <i>H</i> ^o _{β₁}	-1.0 (0.1)	-1.1 (0.2)	-0.9 (0.2)
Δ <i>H</i> ^o _{β₂}	-2.6 (0.4)	-6 (2)	-1.2 (0.2)
Δ <i>H</i> ^o _{β₃}	7 (4)	21 (3)	
Δ <i>H</i> ^o _{β₄}	15.2 (1.3)		12.5 (0.4)
R ^c	0.0192	0.0483	0.0456

^aThe total number of calorimetric data points is 128. ^bValues in parentheses refer to three standard deviations. ^cThe Hamilton *R* factor.

pictured in Figures 1-3, respectively. The heat of reaction *q*_{*i*} measured at each titration point was normalized with the volume of the titrant added δ*v*_{*i*} and the concentration of the thiocyanate ion in the titrant C_{X,tit}, and the term -*q*_{*i*}/[(δ*v*_{*i*})C_{X,tit}] was plotted against C_{X,*i*}/C_{M,*i*} in solution (*i* is omitted in the figures). These experimental data were analyzed by assuming various sets of mononuclear complexes, as have performed previously in the analysis of binary metal-halide systems.}

In the Mn^{II}-NCS⁻ system, among various sets examined, set (1,2,3,4), assuming the formation of [Mn(NCS)]⁺, [Mn(NCS)₂], [Mn(NCS)₃]⁻, and [Mn(NCS)₄]²⁻, exhibited the minimum Hamilton *R* factor [$[\sum (q_{i,obsd} - q_{i,calcd})^2 / \sum (q_{i,obsd})^2]^{1/2}$]. Also, set (1,2,3), eliminating [Mn(NCS)₄]²⁻ from set (1,2,3,4), and set (1,2,4) show small values of the *R* factor. The overall formation constants log β_{*n*} and enthalpies Δ*H*^o_{β_{*n*}} obtained for these sets are

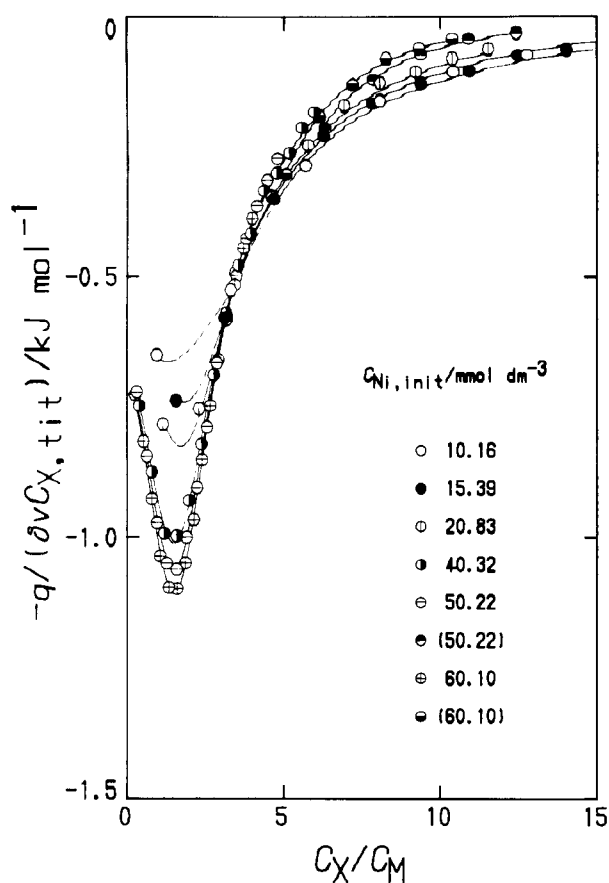


Figure 3. Calorimetric titration curves for the Ni^{II}-NCS⁻ system obtained in *N,N*-dimethylformamide containing 0.4 mol dm⁻³ (C₂H₅)₄N-ClO₄ at 25 °C. Concentrations of Ni(II) ion in initial test solutions, C_{Ni,init}/(mmol cm⁻³), are given. The solid lines are calculated by using constants in Table II.

Table II. Overall Formation Constants log (β_{*n*}/(mol^{-*n*} dm^{3*n*})) and Reaction Enthalpies Δ*H*^o_{β_{*n*}}/(kJ mol⁻¹) for the Formation of [M(NCS)_{*n*}]^{(2-*n*)+} (M = Co, Ni) Obtained by Analyzing Calorimetric Data in *N,N*-Dimethylformamide Containing 0.4 mol dm⁻³ (C₂H₅)₄NClO₄ as an Ionic Medium at 25 °C

	Co ^{II}	Ni ^{II}
log β ₁	2.4 (0.1)	2.7 (0.1)
log β ₂	4.2 (0.6)	4.6 (0.1)
log β ₃	6.6 (0.5)	5.6 (0.2)
log β ₄	9.9 (0.2)	6.3 (0.4)
Δ <i>H</i> ^o _{β₁}	-0.9 (0.4)	-0.72 (0.02)
Δ <i>H</i> ^o _{β₂}	-16 (24)	-2.5 (0.1)
Δ <i>H</i> ^o _{β₃}	34 (37)	-5.5 (1.1)
Δ <i>H</i> ^o _{β₄}	5.7 (0.1)	-4.0 (0.5)
R ^b	0.0417	0.0177
N ^c	174	85

^aValues in parentheses refer to three standard deviations. ^bThe Hamilton *R* factor. ^cThe number of calorimetric data points.

listed in Table I. In Figure 1, the solid curves, calculated by using constants in Table I, are compared with the experimental curves. Evidently, the calculated curves for case (1,2,3) ill reproduce the experimental points in the range of small C_X/C_M, implying that the formation of the [Mn(NCS)₄]²⁻ complex cannot be neglected. Although the calculated curves of both sets (1,2,3,4) and (1,2,4) seem to reproduce well the experimental points, the estimated uncertainties of formation constants for case (1,2,4) are appreciably larger than those for case (1,2,3,4). This implies that the [Mn(NCS)₃]⁻ complex also cannot be eliminated, and thus case (1,2,3,4) is proposed as a final choice.

Similarly, for the Co^{II}-NCS⁻ and Ni^{II}-NCS⁻ systems, the *R* factors for various sets are compared, and finally, calorimetric data for both metal systems are best explained in terms of set (1,2,3,4). The overall formation constants log β_{*n*} and enthalpies Δ*H*^o_{β_{*n*}} of these complexes are listed in Table II. The solid lines

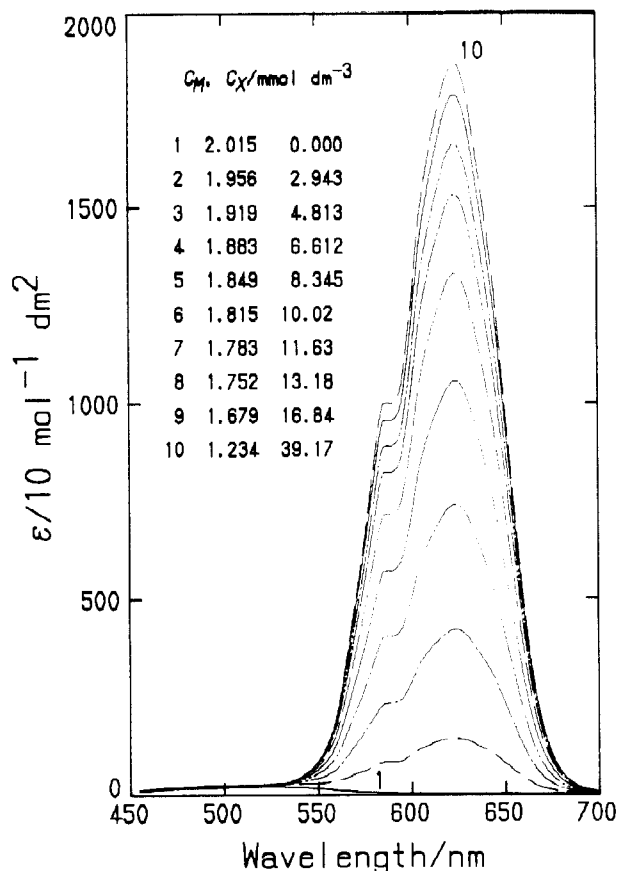


Figure 4. Typical measured electronic spectra of cobalt(II) thiocyanate-DMF solutions in the range 450–700 nm. Intensities are normalized with a unit concentration of the metal ion in solution. The total concentrations of metal and ligand ions, $C_M/(\text{mmol dm}^{-3})$ and $C_X/(\text{mmol dm}^{-3})$, in measured solutions are given.

Table III. Overall Formation Constants $\log(\beta_n/(\text{mol}^{-n} \text{dm}^{3n}))$ and Reaction Enthalpies $\Delta H^\circ_{\beta_n}/(\text{kJ mol}^{-1})$ for the Formation of $[\text{Co}(\text{NCS})_n]^{(2-n)+}$ in *N,N*-Dimethylformamide Containing 0.4 mol dm^{-3} $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ as an Ionic Medium at 25 °C^a

	(1,2,3,4)	(1,3,4)	(1,2,4)	(1,2,3)
$\log \beta_1$	2.70 (0.01) ^b	2.72 (0.01)	2.66 (0.01)	2.73 (0.02)
$\log \beta_2$	4.10 (0.14)		4.43 (0.04)	4.90 (0.06)
$\log \beta_3$	7.32 (0.05)	7.40 (0.02)		7.70 (0.02)
$\log \beta_4$	10.34 (0.02)	10.37 (0.01)	10.38 (0.01)	
R^c	0.0107	0.0112	0.0137	0.0473
$\Delta H^\circ_{\beta_1}$	-1.0 (0.2)	-1.5 (0.1)	-2.1 (0.3)	
$\Delta H^\circ_{\beta_2}$	-23 (6)		13 (3)	
$\Delta H^\circ_{\beta_3}$	13 (1)	8.7 (0.6)		
$\Delta H^\circ_{\beta_4}$	5.9 (0.1)	6.1 (0.1)	6.4 (0.2)	
R^c	0.0627	0.0869	0.143	

^a The ΔH° values are evaluated on the basis of the formation constants obtained from spectrophotometric data. The number of spectrophotometric and calorimetric data points are 4850 and 174, respectively. ^b Values in parentheses refer to three standard deviations. ^c The Hamilton R factor.

in Figures 2 and 3, calculated by using the constants in Table II, reproduce well the experimental points.

The variation of electronic spectra of Co(II) solutions on the addition of a $(\text{C}_2\text{H}_5)_4\text{NCSN}$ solution are shown in Figure 4. A drastic spectral change obviously indicates the formation of tetrahedral species. The result of the least-squares analysis assuming various sets of complexes is shown in Table III. Set (1,2,3), assuming the formation of $[\text{Co}(\text{NCS})]^+$, $[\text{Co}(\text{NCS})_2]$, and $[\text{Co}(\text{NCS})_3]^-$, exhibits a large R factor relative to sets (1,2,4), (1,3,4), and (1,2,3,4). This indicates that the formation of $[\text{Co}(\text{NCS})_4]^{2-}$ cannot be neglected. The R factors for sets (1,3,4) and (1,2,4) are small, implying that the extent of formation of either $[\text{Co}(\text{NCS})_2]$ or $[\text{Co}(\text{NCS})_3]^-$ is very much suppressed. However, they

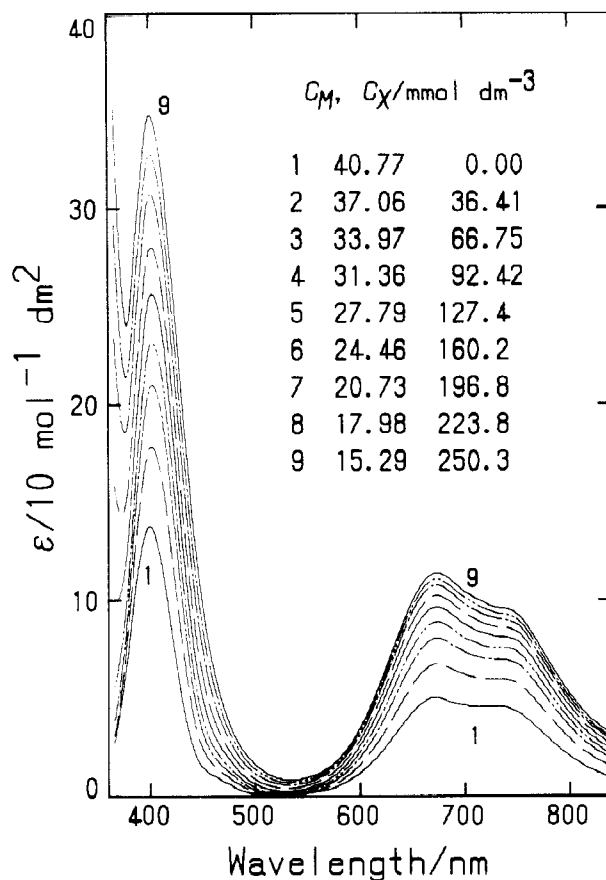


Figure 5. Typical measured electronic spectra of nickel(II) thiocyanate-DMF solutions in the range 350–850 nm. Intensities are normalized with a unit concentration of the metal ion in solution. The total concentrations of metal and ligand ions, $C_M/(\text{mmol dm}^{-3})$ and $C_X/(\text{mmol dm}^{-3})$, in measured solutions are given.

cannot be eliminated. Consequently, set (1,2,3,4), is the most plausible one. As the formation constants from spectrophotometry could be determined with small standard deviations, calorimetric data were then treated by regarding these formation constants as known parameters. In Table III are also listed the enthalpy values thus obtained. Note that uncertainties of the enthalpy values lessened to a considerable extent as compared with those in Table II. Along with the formation constants, electronic spectra of individual cobalt(II) thiocyanato complexes were extracted by analyzing spectrophotometric data, which will be discussed in a later section.

On the other hand, the variation of electronic spectra of Ni(II) solutions on the addition of a $(\text{C}_2\text{H}_5)_4\text{NCSN}$ solution is very small, as seen in Figure 5. This does not mean that the complexation of Ni(II) with NCS^- ions hardly occurs in DMF, because significant exothermicity is in fact observed for the reaction. The nonlinear least-squares analysis was then applied for the spectrophotometric data. However, it turned out that the spectral change is too small to obtain reliable formation constants. Therefore, electronic spectra of individual nickel(II) thiocyanato complexes were extracted on the basis of the formation constants determined by calorimetry.

Discussion

Thiocyanate ions can bind to metal ions through either the N or the S end. They bind to the soft Hg(II) ion through the soft S end and to the Cd(II) ion, possessing medium hard and soft character, in fact through either the S or the N end.¹⁸ On the other hand, for the Zn(II) ion, SCN^- ions bind through the N end, as has been proved by solution X-ray diffraction in water and DMSO.^{45,46} The mode of SCN^- bonding to Mn(II), Co(II),

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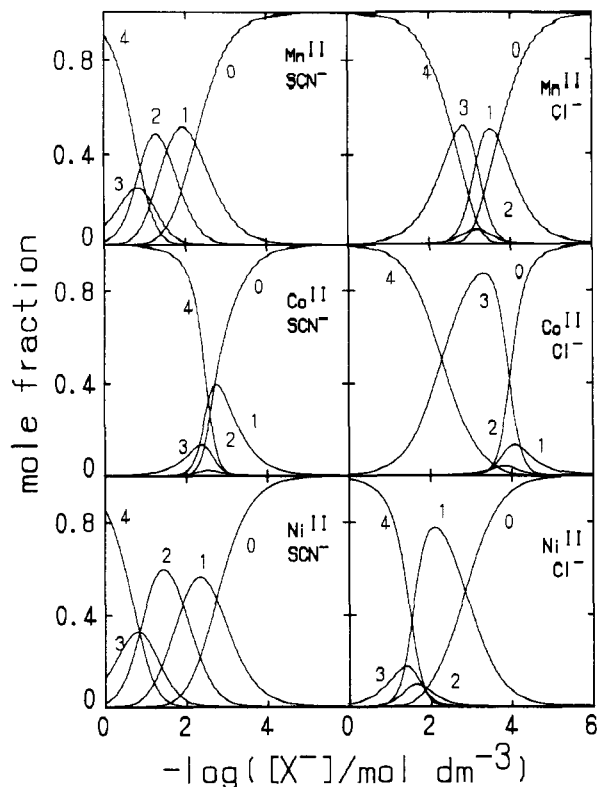


Figure 6. Distribution of species in the $M^{II}-X^{-}$ ($M = \text{Mn, Co, Ni}$; $X = \text{NCS, Cl}$) systems in N,N -dimethylformamide at 25 °C. The $[\text{MX}_n]^{(2-n)+}$ complexes are represented by n values.

Table IV. Stepwise Formation Constants $\log(K_n/(\text{mol}^{-1} \text{dm}^3))$ and Reaction Enthalpies $\Delta H_n^\circ/(\text{kJ mol}^{-1})$ and Entropies $\Delta S_n^\circ/(\text{J K}^{-1} \text{mol}^{-1})$ for the Reaction $[\text{MX}_{n-1}]^{(3-n)+} + X^{-} = [\text{MX}_n]^{(2-n)+}$ ($M = \text{Mn, Co, Ni}$; $X = \text{NCS, Cl}$) in N,N -Dimethylformamide at 25 °C^a

	X = NCS			X = Cl		
	Mn ^{II}	Co ^{II}	Ni ^{II}	Mn ^{II}	Co ^{II}	Ni ^{II}
$\log K_1$	2.3	2.4 (2.7)	2.7	3.7	3.4	2.9
$\log K_2$	1.6	1.8 (1.4)	1.9	2.4	3.4	0.9
$\log K_3$	0.8	2.4 (3.2)	0.8	3.9	5.0	1.8
$\log K_4$	1.0	3.3 (3.0)	0.8	2.6	2.3	1.9
ΔH_1°	-1.0	-0.9 (-1.0)	-0.7	1.1	6.3	8.6
ΔH_2°	-1.6	-15 (-22)	-1.8	26	52	19
ΔH_3°	9.3	50 (35)	-3.0	5	-25	63
ΔH_4°	8.6	-29 (-7.0)	1.4	-10.5	-6.1	-13
ΔS_1°	40	43 (49)	50	74	87	84
ΔS_2°	24	-16 (-45)	31	131	241	82
ΔS_3°	46	211 (180)	6	89	12	245
ΔS_4°	49	-30 (34)	21	15	23	-9
$\log \beta_4$	5.6	9.9 (10.3)	6.3	12.6	14.1	7.5
$\Delta H_{\beta_4}^\circ$	15.2	5.7 (5.9)	-4.0	21.3	27.6	77.2
$\Delta S_{\beta_4}^\circ$	159	209 (218)	107	313	363	401

^a The $\log \beta_4$, $\Delta H_{\beta_4}^\circ$, and $\Delta S_{\beta_4}^\circ$ values refer to the overall formation of $[\text{MX}_4]^{2-}$. Values for $[\text{Co}(\text{NCS})_n]^{(2-n)+}$ in parentheses are calculated by using the constants obtained on the basis of the $\log K_n$ values from spectrophotometry.

and Ni(II) ions in solution may be the same as that to the Zn(II) ion. The distribution of the thiocyanato complexes of Mn(II), Co(II), and Ni(II) ions is depicted in Figure 6, along with that of the chloro complexes for comparison. It is stressed that, for any metal system, the profile of the distribution of species for the NCS⁻ ligand is very much different from that for the Cl⁻ ligand. The difference is especially marked for Mn(II) and Ni(II). This remarkable difference between thiocyanato and chloro complexes cannot be understood, without taking into account the coordination geometry change around metal ion, as will be described below.

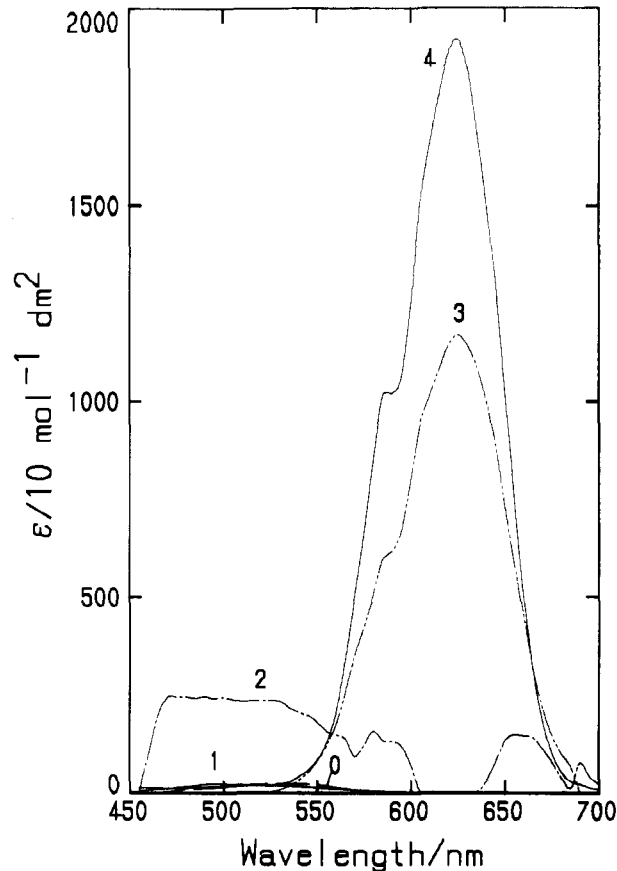
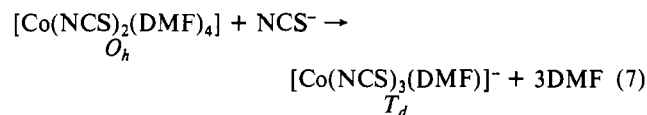


Figure 7. Extracted electronic spectra of individual cobalt(II) thiocyanato complexes in DMF. The $[\text{Co}(\text{NCS})_n]^{(2-n)+}$ complexes are represented by n values. The spectrum of $[\text{Co}(\text{NCS})_2]$ involves large uncertainties.

The stepwise formation constants and reaction enthalpies and entropies for the thiocyanato complexes of Mn(II), Co(II), and Ni(II) are summarized in Table IV, together with those for the chloro complexes for comparison.

The Co^{II}-NCS⁻ System. In the Co^{II}-NCS⁻ system, the metal solutions change color from pink to blue on the addition of a $(\text{C}_2\text{H}_5)_4\text{NCSN}$ solution, suggesting a coordination geometry change around the metal ion. Electronic spectra of individual cobalt(II) thiocyanato complexes provide further information regarding the geometry change. As seen in Figure 7, the electronic spectrum of $[\text{Co}(\text{NCS})]^{+}$, showing a sole weak band over the range 450–650 nm, is similar to that of the octahedral $[\text{Co}(\text{DMF})_6]^{2+}$ complex, while the $[\text{Co}(\text{NCS})_3]^{-}$ and $[\text{Co}(\text{NCS})_4]^{2-}$ complexes exhibit an intense band around 625 nm, which is typical for a tetrahedral complex. With $[\text{Co}(\text{NCS})_2]$, we propose octahedral geometry, as its electronic spectrum is distinct from that of $[\text{Co}(\text{NCS})_4]^{2-}$, although the intensities involve rather large uncertainties. These evidently indicate that an octahedral to tetrahedral geometry change does occur at the third consecutive step, as in eq 7. The same conclusion is deduced from reaction enthalpy



and entropy values. Looking at the stepwise $\log K_n$, ΔH_n° , and ΔS_n° values, one sees that they irregularly vary with n . The stepwise ΔH_n° and ΔS_n° quantities for the NCS⁻ ligand exhibit especially large and positive values at $n = 3$, although the values involve large uncertainties owing to the suppressed formation of both $[\text{Co}(\text{NCS})_2]$ and $[\text{Co}(\text{NCS})_3]^{-}$ complexes, as shown in Figure 6. This indicates an extensive liberation of solvent molecules, i.e. an octahedral to tetrahedral geometry change, at $n = 3$. Note that the geometry change occurs at the second consecutive step for the Cl⁻ ligand in DMF³⁰ and at the fourth step for the NCS⁻

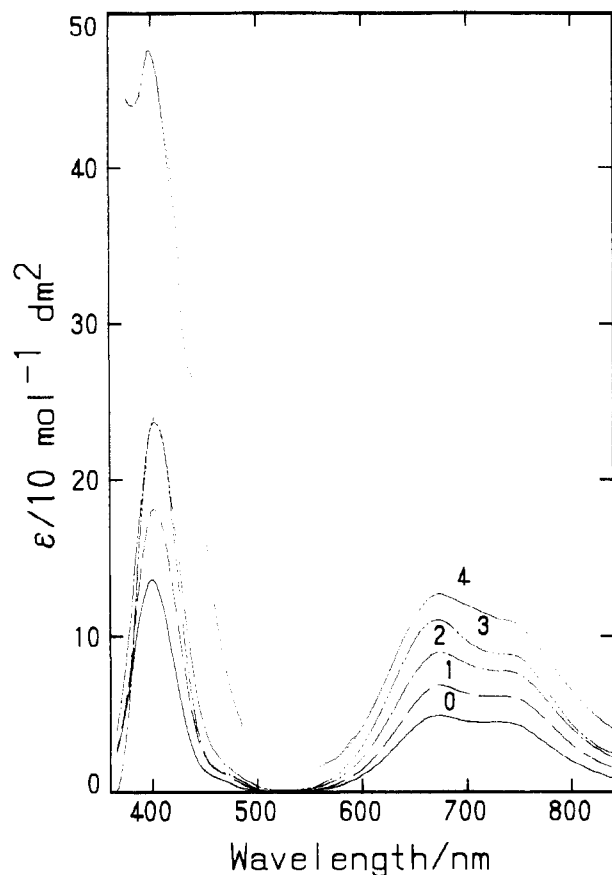


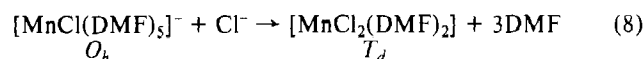
Figure 8. Extracted electronic spectra of individual nickel(II) thiocyanato complexes in DMF. The $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ complexes are represented by n values.

ligand in aqueous methanol.³⁶ The step of an octahedral to tetrahedral geometry change for the cobalt(II) ion thus depends on the nature of ligating ions and molecules. This may not be unexpected because, for Co(II), since the difference between octahedral and tetrahedral ligand field stabilization energies (LFSE) is relatively small,⁴⁷ interligand steric interactions may play an important role in determining the coordination geometry.

The Ni^{II}-NCS⁻ System. In the Ni^{II}-NCS⁻ system, the color of an initial metal solution remained green on the addition of a $(\text{C}_2\text{H}_5)_4\text{NCSN}$ solution, in contrast to the Ni^{II}-Cl⁻ system, where the geometry change does occur at the third step to lead to a blue solution of the tri- and tetrachloro complexes in DMF.²⁹ Evidence of unvarying coordination geometry of the SCN complexes is provided by their electronic spectra in Figure 8, which are all similar to the spectrum of $[\text{Ni}(\text{DMF})_6]^{2+}$ solvate ion. This is further supported by the fact that no irregularity in the ΔH°_n and ΔS°_n quantities appears at any consecutive step. For Ni(II), octahedral geometry is preferred to tetrahedral in view of the LFSE.⁴⁷ Besides, as the NCS⁻ ion may bind to the nickel(II) ion through the N end, which is as small as the oxygen atom, maintaining an almost linear Ni-N-CS configuration, six-coordination may not be sterically unfavored in the isothiocyanato complexes. The formation of the $[\text{Ni}(\text{NCS})_4(\text{DMF})_2]^{2-}$ complex is thus proposed.

The Mn^{II}-NCS⁻ System. As seen in Table IV, the variation of stepwise formation constants, enthalpies, and entropies for the NCS⁻ ligand is remarkably different from that for the Cl⁻ ligand. In the Cl⁻ system relatively large and positive ΔH°_n and ΔS°_n values are observed at $n = 2$, clearly demonstrating that an oc-

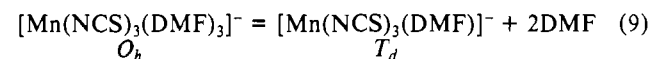
tahedral to tetrahedral geometry change occurs, and more than one DMF molecules is desolvated at the second step, as in eq 8.



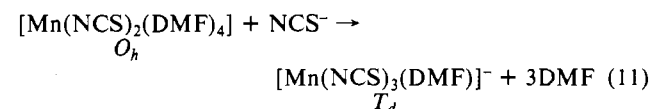
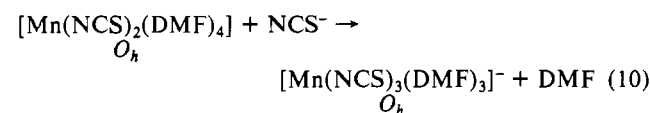
The log K_2 value for the Cl⁻ ligand is appreciably smaller than the log K_1 value, as well as log K_3 , and consequently the extent of formation of $[\text{MnCl}_2]$ is very much suppressed (Figure 6). On the other hand, in the case of the NCS⁻ ligand, the formation constant decreases in the normal order $K_1 > K_2 > K_3 \approx K_4$, as is the case for the Ni^{II}-NCS⁻ system, resulting in a very similar profile of the distribution of species for both metal systems. This is surprising if we consider the difference between LFSEs of manganese(II) and nickel(II) ions. Furthermore, the distribution of species for the Mn^{II}-NCS⁻ system is very much different from that for the Zn^{II}-NCS⁻ system in DMF.⁴⁸ This is also surprising, as both the metal ions have zero LFSEs. In the Zn^{II}-NCS⁻ system, the tetrahedral $[\text{Zn}(\text{NCS})_n]^{(2-n)+}$ complexes are successively formed, except for the octahedral $[\text{Zn}(\text{NCS})_3\text{S}_3]^{-}$ (S = H₂O, DMF, DMSO, etc.) complex.^{33,48,49} It is thus supposed that the coordination geometries of the thiocyanato complexes of Mn(II) are different from those of Zn(II), owing probably to a slightly larger ionic radius of the manganese(II) ion compared to the zinc(II) ion.²⁴

In the Mn^{II}-NCS⁻ system, the ΔH°_1 and ΔH°_2 values are slightly negative, the ΔH°_3 and ΔH°_4 values are positive, and the ΔS°_n ($n = 1-4$) values are all positive and similar. No striking values for the reaction enthalpy and entropy are observed throughout the steps. Such a feature is in contrast to that in the Mn^{II}-Cl⁻ system, in which irregular reaction enthalpy and entropy values, indicative of the coordination geometry change, appear at the second step. This might indicate that the geometry change hardly occurs in the Mn^{II}-NCS⁻ system. However, the ΔH°_n and ΔS°_n ($n = 3, 4$) values for the Mn^{II}-NCS⁻ system are evidently larger than those for the Ni^{II}-NCS⁻ system, so that an extensive liberation of solvent molecules may occur at the third step and/or the fourth.

If the geometry change occurs at the third step (i.e., the formation of $[\text{Mn}(\text{NCS})_2(\text{DMF})_4] (O_h)$, $[\text{Mn}(\text{NCS})_3(\text{DMF})]^{-} (T_d)$, and $[\text{Mn}(\text{NCS})_4]^{2-} (T_d)$ is assumed), we expect the relationships $\Delta H^\circ_3 \gg \Delta H^\circ_4$ and $\Delta S^\circ_3 \gg \Delta S^\circ_4$. On the other hand, if the geometry change occurs at the fourth step (i.e., the formation of $[\text{Mn}(\text{NCS})_2(\text{DMF})_4] (O_h)$, $[\text{Mn}(\text{NCS})_3(\text{DMF})_3]^{-} (O_h)$, and $[\text{Mn}(\text{NCS})_4]^{2-} (T_d)$ is assumed), opposite relationships, $\Delta H^\circ_3 \ll \Delta H^\circ_4$ and $\Delta S^\circ_3 \ll \Delta S^\circ_4$, may result. In fact, the ΔH°_3 value is similar to the ΔH°_4 value, and the ΔS°_3 value is also similar to the ΔS°_4 value, implying that the geometry change occurs at both the steps. We thus propose the formation of both $[\text{Mn}(\text{NCS})_3(\text{DMF})]^{-} (T_d)$ and $[\text{Mn}(\text{NCS})_3(\text{DMF})_3]^{-} (O_h)$ complexes at the third step, which is followed by the formation of $[\text{Mn}(\text{NCS})_4]^{2-} (T_d)$ at the fourth. This leads to the conclusion that an octahedral (O_h)-tetrahedral (T_d) equilibrium, as shown in eq 9, is established. If such an octahedral-tetrahedral equilibrium

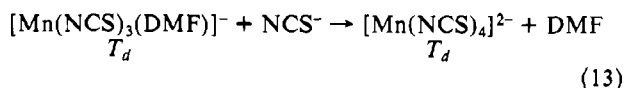
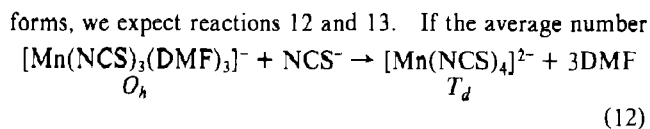


occurs, the number of solvent molecules liberated at the third step may be averaged with respect to the two reactions (10) and (11).



Subsequently, at the fourth step, as the $[\text{Mn}(\text{NCS})_4]^{2-}$ complex

(47) For high-spin bivalent transition-metal ions, in general, the Δ_{O_h} value for an octahedral complex is larger than the Δ_{T_d} value for a tetrahedral complex. Here, we adopt the relationship $\Delta_{T_d} = (4/9)\Delta_{O_h}$. Then, for the d⁷ cobalt(II) ion, the LFSE for an octahedral complex, $8\Delta_{O_h}$, is similar to that for a tetrahedral complex, $12\Delta_{T_d}$. On the other hand, for the d⁸ nickel(II) ion, the LFSE for an octahedral complex, $12\Delta_{O_h}$, is significantly larger than that for a tetrahedral complex, $8\Delta_{T_d}$.



of solvent molecules liberated at the third and fourth steps is almost the same, similar and moderate ΔS°_3 and ΔS°_4 values may result. Therefore, this may apply for the $\text{Mn}^{\text{II}}\text{-NCS}^-$ system in DMF.

Such an octahedral–tetrahedral equilibrium may not be unexpected, because an octahedral–tetrahedral equilibrium has in fact been suggested for the $\text{Cd}^{\text{II}}\text{-X}^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) system.⁵⁰

Acknowledgment. This work was financially supported by Grant-in-Aid for Scientific Research No. 1540503 from the Ministry of Education, Science and Culture of Japan.

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Contribution from the Department of Chemistry II, Faculty of Science,
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One-Electron-Transfer Reactions of Molybdenum(V) and Manganese(III) Porphyrins with Solvated Electrons and Solvent Radicals in 2-Methyltetrahydrofuran¹

T. Suzuki,[†] T. Imamura,^{*†} T. Sumiyoshi,[‡] M. Katayama,[‡] and M. Fujimoto[†]

Received August 17, 1989

The reactions of the six-coordinate molybdenum(V) tetraphenylporphyrins $\text{Mo}^{\text{VO}}(\text{TPP})\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{F}, \text{NCS}, \text{N}_3, \text{OCH}_3, \text{OC}(\text{CH}_3)_3$) with solvated electrons and solvent radicals were studied pulse-radiolytically, focusing on effects of the axial ligand X on the rates. Electron-pulse irradiation of the 2-methyltetrahydrofuran (MeTHF) solution dissolving $\text{Mo}^{\text{VO}}(\text{TPP})\text{X}$, which possess neutral charge and are almost all the same size, causes the reduction of the central molybdenum atom, yielding $\text{Mo}^{\text{IV}}(\text{TPP})$ at room temperature. The constrained complexes $[\text{Mo}^{\text{IV}}(\text{TPP})\text{X}]^-$, formed at 77 K by γ -irradiation, are not stable intermediates in the reactions at room temperature. The reduction proceeds by an outer-sphere mechanism competitively between the reactions with the solvated electron and with the MeTHF neutral radical (MeTHF[•]). The second-order rate constants of the reactions with the solvated electron and with MeTHF[•] are in the range of 10^{10} and $10^9\text{--}10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively, and depend on the axial ligand X. The orders of the constants are $\text{NCS} > \text{Br} > \text{Cl}$ for the reductions by the solvated electron and $\text{NCS} > \text{Br} > \text{Cl} \approx \text{N}_3 > \text{F} > \text{OCH}_3 > \text{OC}(\text{CH}_3)_3$ for the reductions by MeTHF[•]. The effects of the axial ligand on the redox potentials of $\text{Mo}^{\text{VO}}(\text{TPP})\text{X}$ were also studied electrochemically. The redox half-wave potentials of the central molybdenum atom, $\text{Mo}(\text{V})/\text{Mo}(\text{IV})$, depend on the axial ligand and are in the order $\text{Br} > \text{Cl} > \text{NCS} > \text{N}_3 > \text{F} > \text{OCH}_3 > \text{OC}(\text{CH}_3)_3$. The orders of magnitude of the radiolytic reaction rate constants almost parallel the order of the anodic shift in the redox potentials of $\text{Mo}(\text{V})/\text{Mo}(\text{IV})$, as suggested by the Marcus–Hush theory; i.e., the displacement of the axial ligand X mainly reflects on the redox potentials of the central molybdenum that causes the variation in the rates for these outer-sphere redox reactions. Manganese(III) porphyrin systems were also reported in comparison with the $\text{Mo}^{\text{VO}}(\text{TPP})\text{X}$ systems.

Introduction

In the last quarter of a century, extensive kinetic studies of radiation-induced redox reactions of metal complex ions^{2–6} and metalloporphyrins⁷ with solvated electrons or inorganic and organic radicals have been carried out with widespread physicochemical and biochemical interests. These studies revealed that various metal ions and metalloporphyrins react with solvated electrons with rates close to the diffusion-controlled limit.

Anbar and Hart indicated a profound effect of ligand on the reactivity of metal complexes toward hydrated electrons in the order $\text{I} > \text{Cl} > \text{F} > \text{H}_2\text{O} > \text{NH}_3 > \text{CN} > \text{OH}$.² On the other hand, Marcus and Hush predicted a correlation between the rates in outer-sphere redox reactions and the rates in electrochemical reactions.^{8–11} The correlation was observed for the reaction systems $\text{V}^{2+}\text{-Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Cr}(\text{bpy})_3^{2+}\text{-Co}(\text{NH}_3)_5\text{X}^{2+}$.¹² The correlation between chemical reaction rates and redox potentials has also been observed for the reactions of zinc porphyrins with $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ in the order $\text{Zn}(\text{TMpyP}) > \text{Zn}(\text{TAPP}) > \text{Zn}(\text{TPPS})$ ^{7b} and for the reactions of lanthanoid elements with the hydrated electron in the order $\text{Eu}^{3+} > \text{Yb}^{3+} > \text{Sm}^{3+}$ but has not been observed for the reaction systems of actinide ions.^{4,5} However, in the redox reactions of metal complexes possessing the same charge and size, no systematic studies on the effects of ligands and redox potentials on rates have been reported so far. Are there really ligand effects on the rates in the outer-sphere reactions that proceed with rates close to the diffusion-controlled limit? If so,

what kinds of effects are caused?

Recently, we reported that γ -ray irradiation of oxomolybdenum(V) tetraphenylporphyrins $\text{Mo}^{\text{VO}}(\text{TPP})\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{F}, \text{NCS}$)¹³ in the glassy matrix of 2-methyltetrahydrofuran

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[†] Department of Chemistry II.

[‡] Department of Nuclear Engineering.