

Solvation and Complexation Equilibria of Nickel(II) Thiocyanato Complexes in *N,N*-Dimethylacetamide

Makoto Koide

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

Shin-ichi Ishiguro*

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

The complexation of nickel(II) with thiocyanate (SCN^-) ions has been studied by titration spectrophotometry and calorimetry in *N,N*-dimethylacetamide (DMA) containing 0.2 mol dm^{-3} ($n\text{-C}_4\text{H}_9$) $_4\text{NBF}_4$ as a constant ionic medium at 298 K. All the experimental data were well explained in terms of the formation of four mononuclear $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ ($n = 1\text{--}4$) complexes and their formation constants, enthalpies and entropies were determined, together with their intrinsic electronic spectra. The intrinsic spectra were also extracted at 278 and 318 K, and their temperature dependence clearly demonstrated the presence of solvation equilibria, *i.e.* an equilibrium between two structural isomers with different numbers of bound solvent molecules. This is not the case for the $\text{Ni}^{II}\text{--SCN}^-$ system in *N,N*-dimethylformamide, where all the mono-, di-, tri- and tetra-thiocyanato complexes have a single structure of an octahedral six-coordination. These facts imply that the coordination of solvent molecules in the first solvation shell of the metal ion is strongly sterically hindered with DMA.

Metal ions are solvated and a specific solvation structure is developed around the metal ion in polar solvents. This applies particularly to multivalent metal ions and their structural parameters of solvation, such as coordination number and bond length, have been determined in aqueous solution by solution X-ray diffraction and EXAFS (extended X-ray absorption fine structure) methods.¹ Recently, the solvation structure in some polar organic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA) and tetramethylurea (TMU), has also been established.^{2–5} The solvation of metal ions in these aprotic O-donor solvents cannot simply be considered as an analogue to aqueous solution. Indeed, the nickel(II) ion is six-coordinated in DMF, DMA and DMSO as in water, while it is four- and five-coordinated in HMPA and TMU, respectively. The last two solvents are extremely bulky and the metal ion cannot simultaneously accommodate six solvent molecules due to steric hindrance. Such a solvation steric effect, as well as dielectric and donor–acceptor properties, play a key role in the complexation of metal ions in solution.

The divalent transition metal ions, except for the zinc(II) ion, are six-coordinated in DMA as well as in DMF. However, the complexation behaviour in these solvents is quite different, despite the fact that both the solvents have similar physicochemical solvent properties (relative permittivity $\epsilon_r = 37.8$, donor number $\text{DN} = 27.8$, acceptor number $\text{AN} = 13.6$ for DMA, and $\epsilon_r = 36.7$, $\text{DN} = 26.6$, $\text{AN} = 16.0$ for DMF).^{6,7} The complexation of the nickel(II) ion in DMA is of particular interest because the five-coordinate $[\text{NiX}(\text{DMA})_4]^+$ and $[\text{NiX}_2(\text{DMA})_3]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes are formed in equilibrium with six-coordinate $[\text{NiX}(\text{DMA})_5]^+$ and four-coordinate $[\text{NiX}_2(\text{DMA})_2]$ species, respectively.^{8,9} As the five-coordinate structure of the nickel(II) ion with sole monodentate ligands is scarce, the formation of such five-coordinate halogeno complexes in DMA suggests that a strong steric hindrance operates around the metal ion.

In the present work, to obtain further evidence for the solvation steric effect in DMA, we investigated the complexation of nickel(II) with thiocyanate ions in DMA. In DMF, the for-

mation of a series of four mononuclear nickel(II) thiocyanato complexes has been established.¹⁰ Note that all these complexes are octahedrally six-coordinated as $[\text{Ni}(\text{NCS})_n(\text{DMF})_{(6-n)}]^{(2-n)+}$ ($n = 1\text{--}4$) in DMF. Here, the spectrophotometric and thermodynamic results in DMA will be discussed in comparison with those in DMF.

Experimental

Materials

The DMA solvate of nickel(II) tetrafluoroborate, $\text{Ni}(\text{BF}_4)_2 \cdot n\text{DMA}$ ($n \approx 6$) was obtained by dissolving the corresponding hydrate in DMA. The solution was repeatedly concentrated by adding fresh DMA to remove water, and finally the green–yellow crystals were obtained. They were recrystallized twice from DMA and dried in a vacuum over P_2O_5 . Tetra-*n*-butylammonium tetrafluoroborate was prepared according to the literature.¹¹ Tetra-*n*-butylammonium thiocyanate (Fluka) was dried in a vacuum for one day and used without further purification. *N,N*-Dimethylacetamide was purified by distillation at 1200 Pa over BaO. All reagents were treated in a drybox over P_2O_5 .

Measurements

Spectrophotometric measurements were carried out by using a fully automatic titration- and spectral-data acquisition system combined with a 340 spectrophotometer (Hitachi). A nickel(II) tetrafluoroborate solution ($13\text{--}45 \text{ mmol dm}^{-3}$) was titrated with a 0.2 mol dm^{-3} ($n\text{-C}_4\text{H}_9$) $_4\text{NSCN}$ solution and electronic spectra were recorded over the range 410–840 nm. All the metal solutions contained 0.2 mol dm^{-3} ($n\text{-C}_4\text{H}_9$) $_4\text{NBF}_4$ as an inert ionic medium. The data at 278 K and 318 K were corrected for solution density.

Calorimetric measurements were performed by a fully automatic data acquisition system for titration and enthalpy data combined with a twin-type isoperibol calorimeter (Tokyo Riko) thermostatted at $(25.0 \pm 0.1)^\circ\text{C}$. Temperature fluctuation in the vessel was kept within $\pm 0.0001^\circ\text{C}$. A nickel(II) solution (30 cm^3 , $10\text{--}50 \text{ mmol dm}^{-3}$) was titrated

with a 0.2 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ solution. The details of measurements were described elsewhere.^{8,12}

Data Analysis

Spectrophotometric data $A(\lambda)$ at 50 selected wavelengths over the range 410–840 nm were analysed by a non-linear least-squares program, MQSPEC, by minimizing the error square sum, $U = \sum (A_{\text{calc}} - A_{\text{obs}})^2$ on the basis of the mass-balance equations with the metal ion and ligand. Formation constants and intrinsic electronic spectra of individual complexes were simultaneously optimized. Similarly, calorimetric data q obtained at each titration point were analysed by a non-linear least-squares program, MQCAL, by minimizing the error square sum, $U = \sum (q_{\text{calc}} - q_{\text{obs}})^2$ and formation constants and enthalpies were simultaneously optimized. The detailed procedure of data analysis was described elsewhere.^{8,12}

Results

Typical electronic spectra of solutions with varying ratios of total concentrations of SCN^- and Ni^{2+} ions, $C_{\text{SCN}} : C_{\text{Ni}}$, are depicted in Fig. 1(a). The initial nickel(II) tetrafluoroborate solution showed a weak absorption band at 427 nm.⁸ The solution changed from yellowish light-green to dark green upon addition of an $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ solution, and a broad band appeared ca. 600–700 nm. All spectral data measured were analysed by assuming the formation of varying sets of complexes and formation constants, and intrinsic electronic spectra of individual complexes were obtained. Among them, set (1, 2, 3), assuming the formation of the mono-, di- and trithiocyanato complexes, failed to give satisfactorily small R factors, as well as sets (2, 3, 4) and (1, 3, 4). On the other hand, set (1–4), assuming the formation of four mononuclear $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ ($n = 1\text{--}4$) complexes, reproduced well the experimental points with an R factor of 0.0040. We further examined the least-squares analyses by taking into account higher complexes, such as $[\text{Ni}(\text{NCS})_5]^{3-}$ and $[\text{Ni}(\text{NCS})_6]^{4-}$, in addition to those of set (1–4). However, the R factor was little improved, implying that the formation of these higher complexes was practically neglected. Thus, set (1–4) was adopted as a final choice. The extracted electronic spectra of individual $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ ($n = 1\text{--}4$) obtained at 298 K are shown in Fig. 1(b). Here, the molar absorption coefficients of all species were determined with accuracy $3\sigma = \pm 1/(10 \text{ mol}^{-1} \text{ dm}^2)$. Similarly, the spectrophotometric data obtained at 278 K and 318 K could be explained well in terms of set

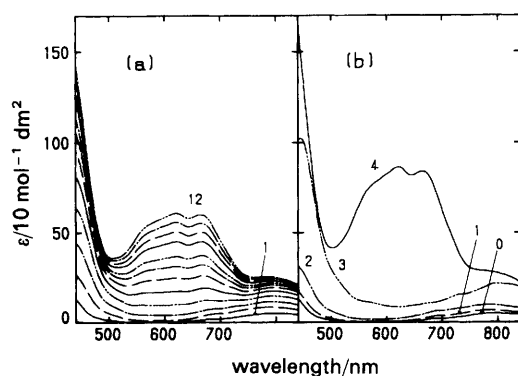


Fig. 1 (a) Electronic spectra of nickel(II)-thiocyanate-DMA solutions containing 0.2 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NBF}_4$ at 298 K. $C_{\text{SCN}} : C_{\text{Ni}}$ varied from 0 for solution 1 to 14.33 for solution 12. (b) Extracted intrinsic spectra of nickel(II) thiocyanate complexes in DMA at 298 K. Numbers represent n of $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$.

(1–4) with the R factors of 0.0062 and 0.0057, respectively. The electronic spectra of individual complexes thus obtained over the range 410–840 nm at different temperatures are shown in Fig. 2.

The broad band at 500–700 nm, which became more intense with increasing temperature, was ascribed to the $[\text{Ni}(\text{NCS})_4]^{2-}$ complex. To obtain further information on the $[\text{Ni}(\text{NCS})_4]^{2-}$ complex, electronic spectra were measured of: (a) DMA solution of $[\text{Ni}(\text{DMA})_6](\text{BF}_4)_2$ and $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ with $C_{\text{SCN}} : C_{\text{Ni}} = 38.5$ and (b) a nitromethane (NM) solution of $[\text{Ni}(\text{DMA})_6](\text{BF}_4)_2$ and $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ with $C_{\text{SCN}} : C_{\text{Ni}} = 5.0$; intensities of which were corrected for density change of solution. The spectra of solutions (a) and (b) at varying temperatures are shown in Fig. 3(a) and (b), respectively. In both cases, the intensity of the band at 500–700 nm increased with temperature, and the $\epsilon(615 \text{ nm})$ values reached up to 175 and 211 at 347 K in DMA and NM, respectively. On the basis of the formation constants obtained by analysing spectrophotometric data, it is estimated that ca. 85% of nickel(II) ions are present as $[\text{Ni}(\text{NCS})_4]^{2-}$ in the DMA solution. Although the formation constants have not been measured in NM, the $[\text{Ni}(\text{NCS})_4]^{2-}$ complex may also be predominant in the solvent. In NM, further addition of SCN^- to give $C_{\text{SCN}} : C_{\text{Ni}} > 10$, leads to a considerable intensity drop, which suggests the formation of a higher complex, $[\text{Ni}(\text{NCS})_5]^{3-}$ or $[\text{Ni}(\text{NCS})_6]^{4-}$.

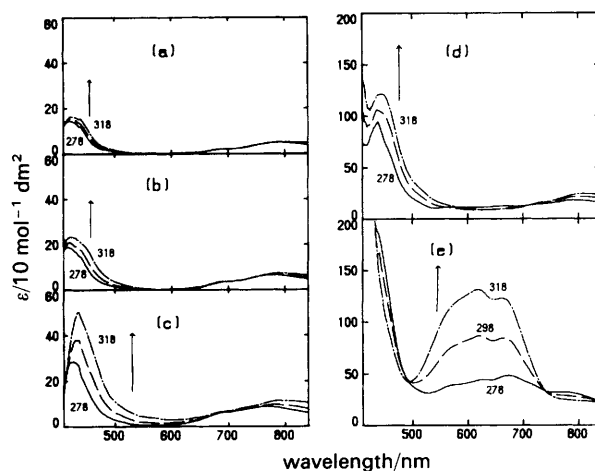


Fig. 2 Extracted intrinsic electronic spectra of (a) Ni^{2+} , (b) $[\text{Ni}(\text{NCS})]^{+}$, (c) $[\text{Ni}(\text{NCS})_2]$, (d) $[\text{Ni}(\text{NCS})_3]^{-}$ and (e) $[\text{Ni}(\text{NCS})_4]^{2-}$ at 278, 298 and 318 K. Arrows indicate increasing temperature.

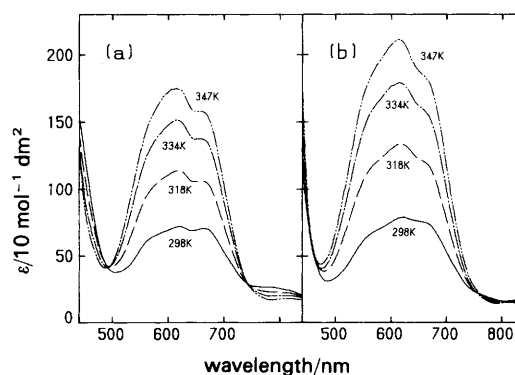


Fig. 3 Electronic spectra of nickel(II)-thiocyanate solution at 298, 318 and 347 K. (a) DMA solution containing $\text{Ni}(\text{BF}_4)_2$ and $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ in the ratio 1 : 38.5. (b) Nitromethane solution containing $\text{Ni}(\text{BF}_4)_2 \cdot n\text{DMA}$ and $(n\text{-C}_4\text{H}_9)_4\text{NCSN}$ in the ratio 1 : 5.

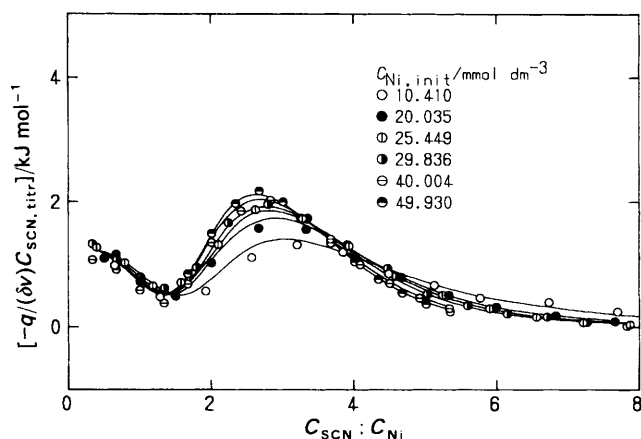


Fig. 4 Calorimetric titration curves for the nickel(II)-thiocyanate system in DMA containing 0.2 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{BF}_4$ at 298 K. Initial concentrations of nickel(II) ions: (○) 10.410, (●) 20.035, (◐) 25.449, (◑) 29.836, (⊖) 40.004 and (⊕) 49.930 mmol dm^{-3} . Solid lines show the curves calculated by using the constants in Table 1.

In Fig. 4, calorimetric titration curves for the $\text{Ni}^{\text{II}}\text{-SCN}^-$ system in DMA are shown, in which the $-q/[(\delta v)C_{\text{SCN, titr}}]$ values are plotted against the total concentration ratio of the ligand to the metal ion, $C_{\text{SCN}} : C_{\text{Ni}}$, where q , δv and $C_{\text{SCN, titr}}$ denote the measured heat of reaction, the volume of titrant added at each titration point and the concentration of SCN^- in the titrant, respectively. The reaction was slightly endothermic throughout titration. The data were analysed in two ways. First, both formation constants and enthalpies were optimized, and all the data were explained well in terms of set (1–4) with an R factor of 0.053. Secondly, the data were analysed on the basis of the formation constants obtained by spectrophotometry. The formation constants and enthalpies thus obtained are summarized in Table 1. Evidently, the formation constants determined by the procedures are the same within experimental error. The formation constants show little dependence upon temperature, which is consistent with small absolute ΔH° values, according to the van't Hoff equation.

Discussion

Fig. 5 shows the distribution of the $\text{Ni}^{\text{II}}\text{-SCN}^-$ system in DMA, along with that in DMF.¹⁰ Evidently, all the mono-, di-, tri- and tetra-thiocyanato complexes of nickel(II) are extensively formed in DMA, as well as in DMF. However, significant differences were found in their electronic spectra and thermodynamic parameters of complexation in the two solvents, as will be discussed below.

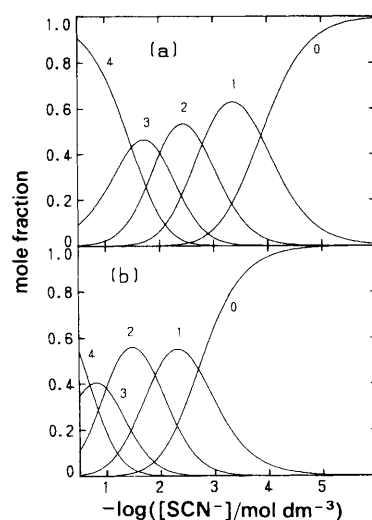


Fig. 5 Distribution of thiocyanato complexes of nickel(II) in (a) DMA and (b) DMF at 298 K. Numbers represent n in $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$.

Electronic Spectra

As seen in Fig. 2(a), the nickel(II) tetrafluoroborate solution shows a weak absorption band at 427 nm, typical of an octahedral nickel(II) chromophore, indicating that the metal ion is present mainly as $[\text{Ni}(\text{DMA})_6]^{2+}$.¹³ This is consistent with the conclusion drawn from our previous study by EXAFS.³ However, though small, the band is appreciably shifted to a longer wavelength with increasing temperature. The difference spectra, $\epsilon(318 \text{ K}) - \epsilon(278 \text{ K})$ in Fig. 6, show that a band at ca. 450 nm appears at elevated temperatures. This suggests that a solvation equilibrium is established between five- and six-coordinate isomers as



though the equilibrium is shifted far to the six-coordinate isomer. As the metal-solvent bond is ruptured upon formation of the five-coordinate isomer, reaction (1) may be more or less endothermic, and therefore the equilibrium shifts to the right at an elevated temperature. Lincoln *et al.*¹⁴ speculated the minor species to be $[\text{Ni}(\text{DMA})_4]^{2+}$ with either tetrahedral or square-planar structure. However, such a four-coordinate structure may be doubtful because a band at 600–800 nm, typical of a tetrahedral complex, is hardly observed.

Similarly to the full-solvate complex, the monothiocyanato complex shows a weak band at 400–500 nm, Fig. 2(b), which is shifted and simultaneously intensified at elevated temperatures. Again the difference spectrum demonstrates that a

Table 1 Overall formation constants, $\log(\beta_n/\text{mol}^{-n} \text{ dm}^{3n})$, and enthalpies, $\Delta H_{\beta_n}^\circ/\text{kJ mol}^{-1}$, for reactions, $\text{Ni}^{2+} + n\text{SCN}^- \rightarrow [\text{Ni}(\text{NCS})_n]^{(2-n)+}$ ($n = 1\text{--}4$) obtained by spectrophotometry and calorimetry in N,N -dimethylacetamide containing 0.2 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NiBF}_4$ as a constant ionic medium

temperature/K	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\Delta H_{\beta_1}^\circ$	$\Delta H_{\beta_2}^\circ$	$\Delta H_{\beta_3}^\circ$	$\Delta H_{\beta_4}^\circ$	N^a	R^b
	spectrophotometry									
278	3.8 (0.2)	6.6 (0.3)	8.6 (0.2)	10.0 (0.3)	—	—	—	—	2100	0.0062
298	3.88 (0.05)	6.68 (0.07)	8.70 (0.06)	10.20 (0.06)	—	—	—	—	2800	0.0040
318	3.93 (0.07)	6.73 (0.08)	8.74 (0.08)	10.34 (0.08)	—	—	—	—	2800	0.0057
	calorimetry (β optimised)									
298	3.9 (0.4)	6.7 (0.4)	8.6 (0.6)	10.4 (0.6)	1.3 (0.1)	0.7 (0.3)	7 (2)	6.3 (0.4)	85	0.053
	calorimetry (β fixed) ^c									
298	3.88	6.68	8.70	10.20	1.34 (0.08)	0.7 (0.1)	6.6 (0.2)	6.6 (0.3)	85	0.057

Values in parentheses refer to three standard deviations. ^a Total number of data points. ^b Hamilton R factor. ^c β values fixed to those obtained spectrophotometrically at 298 K.

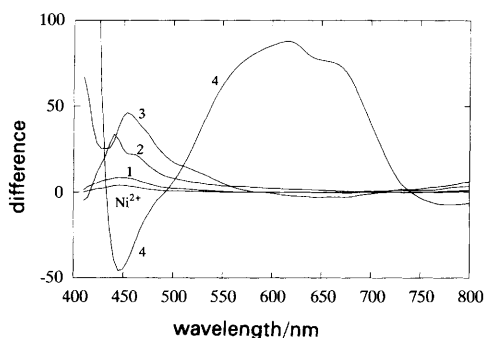
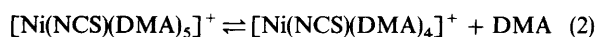


Fig. 6 Difference electronic spectra of the nickel(II)-thiocyanate-DMA solutions at 278 and 318 K. Numbers represent n in $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$.

new band at 450–460 nm grows with increasing temperature, suggesting that a solvation equilibrium is established. Also, it is plausible that the five-coordinate isomer is present partly in equilibrium with the six-coordinate isomer as:



and the five-coordinate isomer becomes more favourable at elevated temperatures. A similar five- and six-coordination equilibrium is also plausible for the dithiocyanato complex:



The temperature dependence is appreciably more marked for the dithiocyanato complexes than the monothiocyanato and full-solvate complexes.

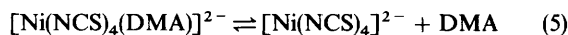
The intrinsic electronic spectra of the trithiocyanato complex show a significant temperature dependence, Fig. 2(d). This complex, unlike the mono- and di-thiocyanato complexes, exhibits a strong adsorption in the UV, probably due to a charge transfer (CT).^{15–17} As the CT band may be weakened monotonically at longer wavelength, a shoulder band at 450–460 nm is suggestive of the five-coordinate isomer. Therefore, we propose a solvation equilibrium:



and here, the equilibrium may be shifted to a larger extent to the five-coordination.

The intrinsic electronic spectra of the tetrathiocyanato complex, Fig. 2(e), show a distinct band at 500–700 nm,^{18–20} indicative of a tetrahedral four-coordinate structure. If the tetrahedral complex is fully formed, the ϵ_{max} at 620 nm may be 287/(10 mol⁻¹ dm²) in acetone, according to the literature.¹⁸ On the basis of this value, only 30% of nickel(II) ions are tetrahedrally coordinated in DMA at 298 K. Indeed, the band becomes more intensified at an elevated temperature, implying that the tetrahedral isomer is in equilibrium with, e.g., five-coordinate $[\text{Ni}(\text{NCS})_4(\text{DMA})]^{2-}$ or six-coordinate $[\text{Ni}(\text{NCS})_4(\text{DMA})_2]^{2-}$. The presence of isosbestic points at around 420, 490 and 740 nm is also indicative of a solvation equilibrium. Evidently, as the shoulder band at 450–460 nm on the CT band becomes weakened with increasing tem-

perature and the difference spectra exhibit a negative peak at 450–460 nm (Fig. 6), the band may be ascribed to the five-coordinate $[\text{Ni}(\text{NCS})_4(\text{DMA})]^{2-}$ isomer. We thus propose an equilibrium between the five- and four-coordination:



It is thus plausible that the band at 450–460 nm is typical for the five-coordinate $[\text{Ni}(\text{NCS})_n(\text{DMA})_{5-n}]^{(2-n)+}$ ($n = 1-4$) species. Note that the five-coordinate $[\text{NiX}(\text{DMA})_4]^+$ and $[\text{NiX}_2(\text{DMA})_3]$ ($X = \text{Cl}, \text{Br}$) isomers in DMA exhibit a typical band at ca. 460 nm also.

Thermodynamics

The stepwise formation constants, enthalpies and entropies for the Ni^{II}-SCN⁻ system in DMA are summarized in Table 2, along with those in DMF.¹⁰ The difference stepwise formation constants, enthalpies and entropies in these solvents are also listed. As seen in Fig. 5, the thiocyanato complexation is enhanced in DMA over DMF, though the extent of enhancement is relatively small compared with that for the halide (Cl, Br) ions.^{8,9} As the stepwise formation enthalpies of these complexes are more positive or less negative in DMA compared with those in DMF, the enhancement is solely due to the entropy effect. This applies particularly to the stepwise formation of the trithiocyanato complex, in which the enthalpy and entropy values are more positive by 8.9 kJ mol⁻¹ and 52 J K⁻¹ mol⁻¹, respectively, in DMA compared with the corresponding values in DMF. In contrast, the ΔH_n° and ΔS_n° values, 2.1 kJ mol⁻¹ and 29 J K⁻¹ mol⁻¹ for $n = 1$ and 1.1 kJ mol⁻¹ and 20 J K⁻¹ mol⁻¹ for $n = 2$, are much less positive. If we take into account that the metal ion is six-coordinated in all the $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ ($n = 1-4$) complexes in DMF, relatively large and positive difference enthalpy and entropy values for $[\text{Ni}(\text{NCS})_3]^-$ in DMA imply that an extensive liberation of solvent molecules occurs by accompanying the coordination geometry change in the solvent. This conclusion is consistent with that drawn from spectrophotometry. According to the extracted electronic spectra, the solvation equilibria is established, and the six-coordinate $[\text{Ni}(\text{NCS})_2(\text{DMA})_4]$ and the five-coordinate $[\text{Ni}(\text{NCS})_3(\text{DMA})_2]^-$ isomers are formed as predominant species in DMA. Therefore, the main reaction scheme at the third step may be expressed as follows:



and, here, the coordination number of the metal ion reduces from six to five upon complexation.

On the other hand, the ΔH_4° value is only slightly smaller, and the ΔS_4° value is slightly more positive in DMA relative to those in DMF. Therefore, the liberation of solvent molecules at the fourth step is expected to be moderate. Also, according to the electronic spectra, the main species of the tri- and tetra-thiocyanato complexes in DMA are suggested to be five-coordinated as $[\text{Ni}(\text{NCS})_3(\text{DMA})_2]^-$ and $[\text{Ni}(\text{NCS})_4(\text{DMA})]^{2-}$, respectively, and the main reaction

Table 2 Stepwise formation constants, $\log(K_n/\text{mol}^{-1} \text{ dm}^3)$, 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, $[\text{Ni}(\text{NCS})_n]^{(3-n)+} + \text{SCN}^- \rightarrow [\text{Ni}(\text{NCS})_{n+1}]^{(2-n)+}$ ($n = 1-4$) in *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylformamide (DMF) and their differences, Δ , between solvents at 298 K

solvent	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	ΔH_1°	ΔH_2°	ΔH_3°	ΔH_4°	ΔS_1°	ΔS_2°	ΔS_3°	ΔS_4°	$\Delta G_{\beta 4}^\circ$ ^a	$\Delta H_{\beta 4}^\circ$ ^a	$\Delta S_{\beta 4}^\circ$ ^a
DMA ^b	3.88	2.80	2.02	1.50	1.34	-0.7	5.9	0.0	79	51	58	29	-58	6.6	218
DMF ^c	2.7	1.9	0.8	0.8	-0.72	-1.8	-3.0	1.4	50	31	6	21	-36	-4.0	107
Δ ^d	1.18	0.9	1.22	0.7	2.06	1.1	8.9	-1.4	29	20	52	8	-22	10.6	111

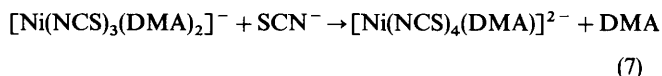
^a For the overall formation of $[\text{Ni}(\text{NCS})_4]^{2-}$. ^b This study. ^c Ref. 10. ^d Δ denotes $P(\text{DMA}) - P(\text{DMF})$, where $P = \log K_n, \Delta H_n^\circ, \Delta S_n^\circ$.

Table 3 Enthalpies of transfer, $\Delta_t H^\circ$ (DMF \rightarrow DMA) of nickel(II) complexes, $[\text{NiCl}_n]^{(2-n)+}$ and $[\text{Ni}(\text{NCS})_n]^{(2-n)+}$ complexes ($n = 1-4$), at 298 K on the basis of the tetraphenylarsonium tetraphenylborate (TATB) assumption

	n				
	0	1	2	3	4
$[\text{NiCl}_n]^{(2-n)+}$	+17.4 ^a	+43.4 ^a	+52.5 ^a	-7.5 ^a	+5.7 ^a
$[\text{Ni}(\text{NCS})_n]^{(2-n)+}$	+17.4 ^a	+21.3	+24.2	+34.9	+35.1

^a Ref. 21.

scheme at the fourth step may be represented as follows:



and therefore, there is no change in the coordination number upon complexation in this case.

In DMA, as discussed above, all the thiocyanato complexes of nickel(II) are under the solvation isomerism, and thus the complexation at each consecutive step may proceed through both isomers. However, as the determination of equilibrium constants for reactions (1)–(5) is unsuccessful at the present stage, we cannot deconvolute the observed stepwise enthalpy and entropy values into the contribution of each isomer. Furthermore, the solvation isomerism may lead to an appreciable temperature dependence of the reaction enthalpies and entropies. This is in fact observed in the case for the $\text{Ni}^{\text{II}}-\text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}$) system.⁸ However, in the present $\text{Ni}^{\text{II}}-\text{SCN}^-$ system, the reaction heats measured were too small to obtain reliable temperature dependence of the enthalpies and entropies.

Enthalpies of Transfer

Steric solvent effects do not always lead to the change in the direct coordination structure. Indeed, practically no change was found on the structural parameters in DMA and DMF, *i.e.* according to our EXAFS study,³ the $\text{Ni}^{\text{II}}-\text{O}$ bond lengths are 204 and 205 pm for DMA and DMF, respectively, and the coordination number is close to six in both the solvents. However, the enthalpies of transfer, $\Delta_t H^\circ$, are more sensitive to the solvent effect. The $\Delta_t H^\circ$ values of the thiocyanato complexes from DMF to DMA are summarized in Table 3, along with those for the chloro complexes.²¹ To evaluate these $\Delta_t H^\circ$ values, the values of $\Delta_t H^\circ(\text{Ni}^{2+}) = +17.4 \text{ kJ mol}^{-1}$ and $\Delta_t H^\circ(\text{SCN}^-) = +1.8 \text{ kJ mol}^{-1}$ were used, which have been obtained previously on the basis of an extrathermodynamic tetraphenylarsonium tetraphenylborate (TATB) assumption.²¹ Here, the positive value of $\Delta_t H^\circ(\text{Ni}^{2+})$ indicates that the $\text{Ni}^{\text{II}}-\text{solvent}$ interaction is weakened in DMA relative to DMF. This may be due to the solvation steric effect. The $\Delta_t H^\circ$ values for $[\text{Ni}(\text{NCS})]^{2+}$ and $[\text{Ni}(\text{NCS})_2]^{+}$ are 21.3 and 24.2 kJ mol^{-1} , respectively, only slightly larger than the corresponding value for Ni^{2+} . On the other hand, the $\Delta_t H^\circ$ values for $[\text{Ni}(\text{NCS})_3]^{-}$ and $[\text{Ni}(\text{NCS})_4]^{2-}$ are 34.9 and 35.1 kJ mol^{-1} , respectively. These values are significantly larger and an even larger $\Delta_t H^\circ$ value of 43.4 kJ mol^{-1} has been obtained for $[\text{NiCl}]^{2+}$.²¹ The nickel(II) ion within the $[\text{NiCl}]^{2+}$ complex is six-coordinated in DMF,¹⁰ while it is five-coordinated to a larger extent, and a solvation equilibrium between five- and six-coordination is

established, in DMA.⁸ This implies that, also with $[\text{Ni}(\text{NCS})_3]^{-}$, the coordination number around the nickel(II) ion changes from six to five upon transfer from DMF to DMA. This is consistent with the conclusion from titration calorimetry and spectrophotometry.

Conclusion

It is suggested from both thermodynamic and spectrophotometric data that, with each of the four nickel(II) thiocyanato complexes, the coordination number is more or less reduced upon transfer from DMF to DMA. Solvation equilibria between two structural isomers are established for all the metal thiocyanato complexes in DMA unlike DMF, in which all the complexes are six-coordinated. As physicochemical properties of DMF and DMA as solvents are similar, a significant solvent effect may not be ascribed to an electronic origin. As DMA involves an acetylmethyl group next to the carbonyl oxygen atom that binds to the metal ion, the simultaneous accommodation of six DMA molecules around the metal ion may be strongly sterically hindered. To avoid the steric hindrance between solvent molecules, the coordination structure may be deformed or, in an extreme case, the coordination number may be reduced.

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