

学位請求論文

および参考論文

題目

Studies on Solute-solvent Interactions Using the Macrocyclic Tetramine
Nickel Complex as a Probe

(環状テトラミンニッケル錯体を用いた溶質-溶媒相互作用
に関する研究)

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主 論 文

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Nickel Complex as a Probe

(環状テトラミンニッケル錯体を用いた溶質-溶媒相互作用
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1. Coordination of Dialkyl Sulfoxides in Square-Planar Solvents Using
1,4,7,10-Tetraazacyclododecane(12) and 1,4,7,11-Tetraazacyclododecane(11) as
Probes

S. Yamaguchi, E. Iwamoto, and T. Yamamoto
J. Chem. Soc., Faraday Trans. 2, 86, 1027 (1990).

2. Spectroscopic Coordination of Acetylacetonate in Square-Planar
1,4,7,10-Tetraazacyclododecane(12) and 1,4,7,11-Tetraazacyclododecane(11) as
Probes

S. Yamaguchi, E. Iwamoto, and T. Yamamoto
J. Chem. Soc., Chem. Commun., 64 (1991).

3. Synthesis and Ion-Exchange of 1,4,7,10,13,16-Hexamethyloctadecane(18)
and 1,4,7,11,14,17-Hexamethyloctadecane(17) with Chloride as Well as Effects of
Cationic Exchange

S. Yamaguchi, E. Iwamoto, and T. Yamamoto
J. Chem. Soc., Chem. Commun., 64 (1991).

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主論文の基礎となった原著論文

1. Axial Co-ordination and Ion-pair Formation for R,S,R,S-1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) Perchlorate in Various Mixed Solvents with Nitrobenzene

E. Iwamoto, T. Yokoyama, S. Yamasaki, T. Yabe, T. Kumamaru, and Y. Yamamoto;
J. Chem. Soc., Dalton Trans., 1935 (1988).

2. Dimerisation of Dimethyl Sulphoxide in Dipolar Aprotic Solvents using R,S,R,S-1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) as a Probe

T. Yokoyama, E. Iwamoto, and T. Kumamaru;
J. Chem. Soc., Faraday Trans., **86**, 2937 (1990).

3. Extraordinary Coordination of Acetonitrile to Square-Planar 1,4,8,11-Tetraazacyclotetradecanenickel(II) and [(1R,4R,8S,11S)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Cations

T. Yokoyama, E. Iwamoto, and T. Kumamaru;
Bull. Chem. Soc. Jpn., **64** (1991).

4. Solvation and Ionic Association of (1R,4S,8R,11S)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate in Mixed Solvents of N,N-Dimethylformamide and N,N-Dimethylacetamide with Nitrobenzene and 1,2-Dichloroethane

T. Yokoyama, E. Iwamoto, and T. Kumamaru;
Bull. Chem. Soc. Jpn., **64** (1991).

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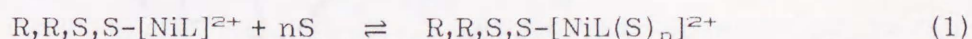
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Introduction

It is very important to investigate the solute-solvent interactions with respect to the properties of solvents, because most solvents are the essential species for chemical reactions in solutions. Generally, a metal ion of the acid property in solution is strongly solvated by some basic solvent molecules and the solvation phenomena well reflect the basicity of the solvent. However, simple salts of metal ions of high charges hardly dissolve in organic solvents. When the metal ion reacts with some organic ligands to form complex salts, it becomes soluble in organic solvents. Therefore, the complex ions can be a useful probe to examine the solute-solvent interaction in organic solvents. A complex ion which has the only one coordination site is more useful for investigation of the solute-solvent interactions since a simple 1:1 metal-solvent reaction is expected. In this connection, the square-planar and macrocyclic tetramine nickel complex is just a complex ion for this purpose.

It is well known that 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) (henceforth $[\text{NiL}]^{2+}$) has two stable isomers, R,S,R,S- and R,R,S,S-nitrogen configurations, depending on the method of synthesis.^{1,2} Figure 1 shows the geometries of $[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane). There have been a number of studies concerning the kinetic and thermodynamic aspects of these complexes. In some pure solvents, the thermodynamic parameters ΔH° , ΔS° , and ΔV° were determined by means of the chemical shifts of ^1H NMR and ^{13}C NMR of R,R,S,S- $[\text{NiL}]^{2+}$,³⁻⁵ for the equilibrium (1)



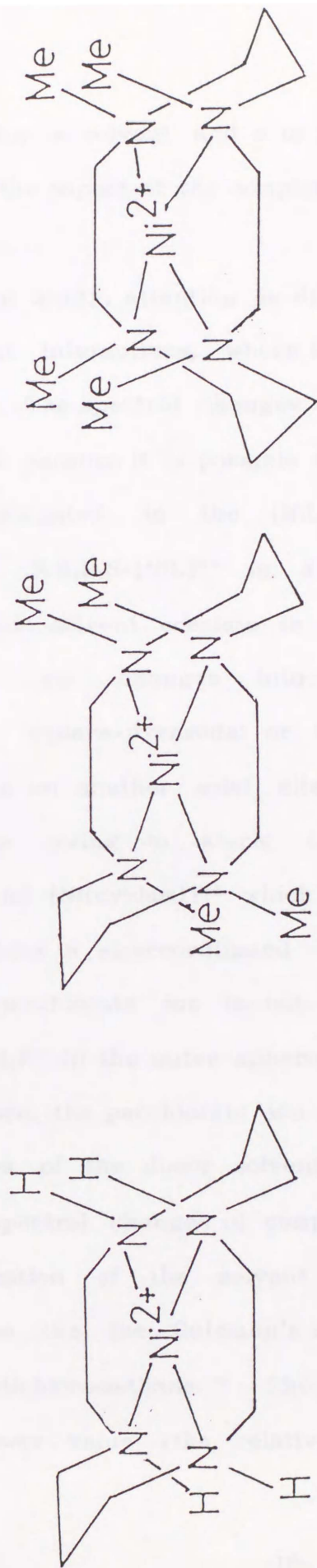


Fig. 1 Macrocyclic tetramine nickel complexes: (a) $[\text{Ni}(\text{cyclam})]^{2+}$; (b) $\text{R,R,S,S-}[\text{NiL}]^{2+}$; (c) $\text{R,S,R,S-}[\text{NiL}]^{2+}$.

where S stands for a solvent and n is 1, 2, 3, These works have been concentrated on the aspect of the complex itself but not of the coordinating solvent.

In the present study, attention is directed towards the solvent-solvent and solute-solvent interactions, where this square-planar complex is being used as a probe. The spectral changes due to d-d transition in the visible range are helpful because it is possible to judge visually whether the donor solvent is coordinated to the $[\text{NiL}]^{2+}$ or not. The square-planar four-coordinated $\text{R,S,R,S-}[\text{NiL}]^{2+}$ is a red colored low-spin complex. However, if a basic solvent coexists in the solution of $\text{R,S,R,S-}[\text{NiL}]^{2+}$, the nickel complex ion changes into a green colored, high-spin, five-coordinated, square-pyramidal or trigonal-bipyramidal complex. The methylene groups on another axial site hinder an approach of the sixth solvent molecule owing to steric crowding.¹³ On the other hand, $\text{R,R,S,S-}[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ which are of the same square-planar as $\text{R,S,R,S-}[\text{NiL}]^{2+}$ form a six-coordinated complex by ligation of two donor solvents. The perchlorate ion is not coordinated to $[\text{NiL}]^{2+}$, forms the ion-pair with $[\text{NiL}]^{2+}$ in the outer sphere, and less interacts with the donor solvent. Therefore, the perchlorate ion was chosen as a counter ion.

The basicities of the donor solvents have ever been correlated with enthalpies and spectral changes of complexation. The former is enthalpies of adduct formation of the solvent with antimony pentachloride in 1,2-dichloroethane (i.e. the Gutmann's donor number, DN)¹⁴ and with boron trifluoride in dichloromethane.¹⁵ The latter is the dependence of the coordination power value (the relative Gibbs free energy change for

solvation of nickel ion, CP) for pure solvent⁹⁾ and with the coordination of a donor solvent at the sixth site to bis(acetylacetonato)vanadyl (VO(acac)₂) altering the position of two absorption bands (D_{11,1}) for pure solvent.^{10), 11)} These correlations give a good linear relationship between the basicities and the measured values, although some solvents deviate from it. It is considered that the deviation refers to steric factors and self-association of the donor solvents.

The basicities of donor solvents are also characterized from the equilibrium constants obtained by the variation of the visible spectra for R,S,R,S-[NiL]²⁺ in various mixed solvents. The equilibrium of R,S,R,S-[NiL]²⁺ with the donor solvent is written in equation (2)



where K_{NiS} is the coordination constant. Table 1 gives the donor solvents examined and their abbreviations together with DN.⁷⁾

The donor solvents in Table 1 can be classified by the coordinating atom into two classes: the one is oxygen coordinate (Ac, FA, NMF, DMF, DMA, DMP, DMAc, DMBz, DEF, DEA, TMU, DMSO, MeOH, EtOH, H₂O, TBP, HMPA, NB, NM, and PC) and the other is nitrogen coordinate (AN, PN, n-BuN, BzN, and Py). The specific interaction of the complex cations with these solvents is investigated by spectrometry and conductometry. This will be discussed on the basicities, steric hindrance and self-association of the donor solvents.

Chapter 1 assesses the basicity of the donor solvents using the

Table 1. Donor solvents with DN

Solvent	Abbreviation	DN
1,2-Dichloroethane	(DCE)	0
Nitromethane	(NM)	2.7
Nitrobenzene	(NB)	4.4
Benzonitrile	(BzN)	11.9
Acetonitrile	(AN)	14.1
Propylene carbonate	(PC)	15.1
Propionitrile	(PN)	16.1
n-Butylonitrile	(n-BuN)	16.6
Acetone	(Ac)	17.0
Water	(H ₂ O)	18.0
Methanol	(MeOH)	19
Ethanol	(EtOH)	20
Tributyl phosphate	(TBP)	23.7
Formamide	(FA)	24
N,N-Dimethylpropionamide	(DMP)	24.0
N,N-Dimethylformamide	(DMF)	26.6
N,N-Dimethylacetamide	(DMA)	27.8
N,N-Dimethylacrylamide	(DMAc)	28.9
Dimethyl sulphoxide	(DMSO)	29.8
N,N-Diethylformamide	(DEF)	30.9
Tetramethylurea	(TMU)	31
N,N-Dimethylbenzamide	(DMBz)	31.2
N,N-Diethylacetamide	(DEA)	32.2
Pyridine	(Py)	33.1
Hexamethylphosphoric triamide	(HMPA)	38.8
N-methylformamide	(NMF)	49

coordination constant (K_{NIS}) of the donor solvents to R,S,R,S-[NiL]²⁺ in NB. Chapters 2, 3, and 4 clarify the origin of deviating from the linear relationship between DN and K_{NIS} . The difference between solvation by DMF and by DMA is described in Chapter 2. The dimerization of DMSO with the K_{NIS} values of various donor solvents is described in Chapter 3. The π -back donation of nitriles is described in Chapter 4.

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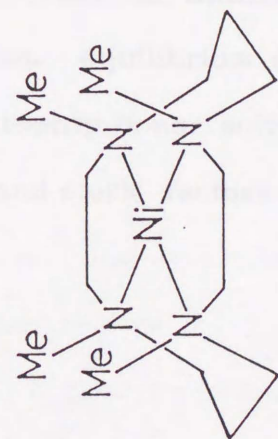
Chapter 1

Axial Coordination to R,S,R,S-[NiL]²⁺ of Donor Solvents in Nitrobenzene

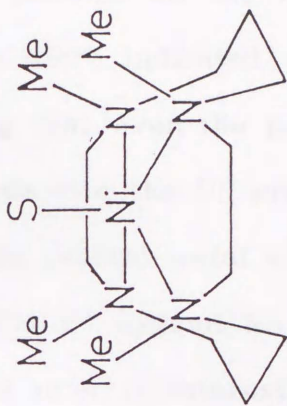
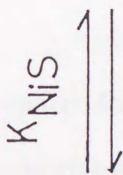
1. Introduction

It is well known that $[\text{NiL}]^{2+}$ has two stable isomers, R,S,R,S and R,R,S,S configurations at nitrogen, depending on the method of synthesis, and in coordinating solvents or in the presence of unidentate anions the former and latter isomers readily form five- and six-coordinate complexes, respectively.¹⁻⁴⁾ This is one of the reasons why there have been a number of studies concerning the kinetic and thermodynamic aspects of this complex.⁴⁻¹⁵⁾ For the R,S,R,S isomer, red, low-spin, square-planar and green, high-spin, square-pyramidal species coexist in solution according to the Reaction (1) where S is a donor solvent and K_{NiS} is the equilibrium constant. Equilibrium of the reaction (1) has been studied in water, DMF, DMSO, and AN by spectrometry^{4, 8-12)} and the n.m.r. method.^{4, 11)} In water at 25 °C, ca. 50 % of the complex is square pyramidal.⁴⁾ Recently it was reported¹⁶⁾ that NB and DMA solutions of R,S,R,S- $[\text{NiL}]^{2+}$ are red, showing that both of those solvents are not coordinated; water dissolved in NB is not coordinated to the complex cation, but when dissolved in DMA it is easily coordinated to give green solutions. These phenomena suggest that R,S,R,S- $[\text{NiL}]^{2+}$ exhibits unique axial interactions with solvents.

The axial interactions of square-planar complexes have been examined with respect to the coordinating and solvating ability of solvents: $[\text{Ni}(\text{cyclam})]^{2+}$,^{17, 18)} C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II),¹⁸⁾ bis(dimethylglyoximate) cobalt(III),¹⁹⁾ and mixed-ligand copper(II) complexes of ethylenediamine and β diketones.^{20, 21)} The complex $[\text{Ni}(\text{cyclam})]^{2+}$ readily undergoes axial attack of counter ions as well as basic solvents.^{17, 18, 22, 23)} It was reported that the relative stability



+ S



(1)

Reaction (1)

order of adducts formed by the axial coordination was DMF>AN>DMSO>water.^{1,7)} This order was not predicted by the basicity of the solvents and it was suggested that, compared to water, rod-like AN molecules would more effectively enter into the first coordination sphere due to weak interaction with NH protons on the ligand. Conductance measurements of [Ni(cyclam)](ClO₄)₂ in NB^{2,4)} indicated exceedingly large ion-pair formation constants, suggesting that even the perchlorate ion of much lower basicity formed hydrogen-bonds with the NH protons. Thus, the cyclam complex has two reactive sites, the central metal and the NH protons. In this connection the complex R,S,R,S-[NiL]²⁺ without NH protons possesses only a single free coordination site and so it is interesting to investigate systematically its axial interactions.

In this study the ion-pair formation constant of R,S,R,S-[NiL]²⁺ with the perchlorate ion were determined by conductance measurements and are discussed in relation to the axial coordination of solvents. The perchlorate salt was selected in order to minimize specific anionic interactions with solvents and the cation. Equilibrium (1) in NB as a non-coordinating diluent was also studied for twenty donor solvents, and is discussed in terms of the basicity of solvents and steric factors involving the four methyl groups and donor solvents.

2. Experimental

The salts [NiL](ClO₄)₂ with R,S,R,S and R,R,S,S nitrogen configurations were prepared by the published methods,^{1,2,25,26)} and were recrystallized from Ac-diethyl ether mixtures, and water, respectively. Infrared spectra

for these salts showed that no NH absorptions are present (Found: C, 32.80; H, 6.55; N, 10.95%. Calc. for R,S,R,S-[NiL](ClO₄)₂: C, 32.70; H, 6.25; N, 11.00%. Found for R,R,S,S-[NiL](ClO₄)₂: C, 32.80; H, 6.50; N, 11.10%). The salt R,R,S,S-[NiL(N₃)]ClO₄ was prepared by adding sodium azide to an aqueous R,S,R,S-[NiL](ClO₄)₂ solution²⁶⁾ and recrystallized from MeOH-diethyl ether mixtures (Found: C, 36.80; H, 7.35; N, 21.70%. Calc. for R,S,R,S-[NiL(N₃)]ClO₄: C, 36.85; H, 7.05; N, 21.45%).

NB (reagent grade, Wako Pure Chemical Industries Ltd.) was purified by fractional distillation under reduced pressure through a 1.2-m column, after washing with sulphuric acid, sodium carbonate, and distilled water, successively. NM, DMF, DMSO, HMPA, DMA, PC, and Py (reagent grade, Wako) were purified by fractional distillation under reduced pressure. AN, Ac, and MeOH were purified by fractional distillation. BzN, PN, n-BuN, and DMP (reagent grade, Tokyo Kasei Kogyo Co., Ltd.), and DEF, DEA, DMAc, and DMBz (Aldrich Chemical Co.) were used after standing over molecular sieves (type 4A) for 1 week. The conductances (S cm⁻¹) of the solvents are $1.6 \times 10^{-9} - 3 \times 10^{-7}$ for NB-AN mixtures, $1.6 \times 10^{-9} - 3 \times 10^{-7}$ for NB-DMA, 4.5×10^{-8} for PC, 2.1×10^{-7} for DMSO, 3.7×10^{-7} for DMF, 8.3×10^{-8} for Ac, and 6.6×10^{-7} for NM.

The instrumentation and procedure used for the measurements of viscosity and conductance were the same as described previously,²⁷⁾ except that in place of the dilution technique a burette allowing a concentrated solution of salt to be added to the conductance cell was used for conductance measurements.²⁸⁾ The relative permittivities (D) of the solvent mixtures were measured using a Shibayama model SS-208A dielectric constant

cell shielded with wire netting in a water-bath thermostatted to 25 ± 0.01 °C. Carbon tetrachloride, NB, AN, DCE, and DMA were used as reference solvents for the calibration of dielectric constant. The instrumentation and the procedure used for measurements of spectra and water contents were described previously.¹⁵⁾

3. Results and Discussion

The R,S,R,S, R,R,S,S, and R,S,R,R isomers of $[\text{NiL}]^{2+}$ have been reported.^{1-3, 14, 15)} Lincoln et al.¹⁵⁾ found that the published method^{1, 2)} for the preparation of the R,S,R,S isomer also gave small amounts of the R,S,R,R isomer but the latter isomerizes to the former with the high-spin species being more favoured for the R,S,R,S isomer. The visible spectra of R,S,R,S and R,R,S,S isomers in NB, AN, and DMF at 25 °C are shown in Fig. 1. The maximum wavelength λ_{max} in nm and the molar absorptivity ϵ_{max} in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ in parenthesis of the R,S,R,S isomer are 610 (37) and 382 (119) in AN, 660 (41) and 400 (131) in DMF, and 519 (224) in NB; literature values are 610 (39.6) and 386 (128),⁵⁾ and 610 (34) and 390 (118)²⁾ in AN. The corresponding values for the R,R,S,S isomer are 543 (6.0) and 349 (14) in AN, 503 (21) and 373 (20) in DMF, and 498 (92) in NB; literature values in AN are 540 (5.9) and 340 (14.0).⁵⁾ The absorption peaks at 519 and 498 nm in NB and 503 nm in DMF are assigned to the low-spin species and the other peaks to the high-spin species. The spectra for both isomers in AN and DMF indicate complete and almost complete conversion of the low-spin into the high-spin species, respectively, and those in NB indicate no conversion. A blue shift of the absorption peaks occurs for the AN adduct compared to the DMF adduct.

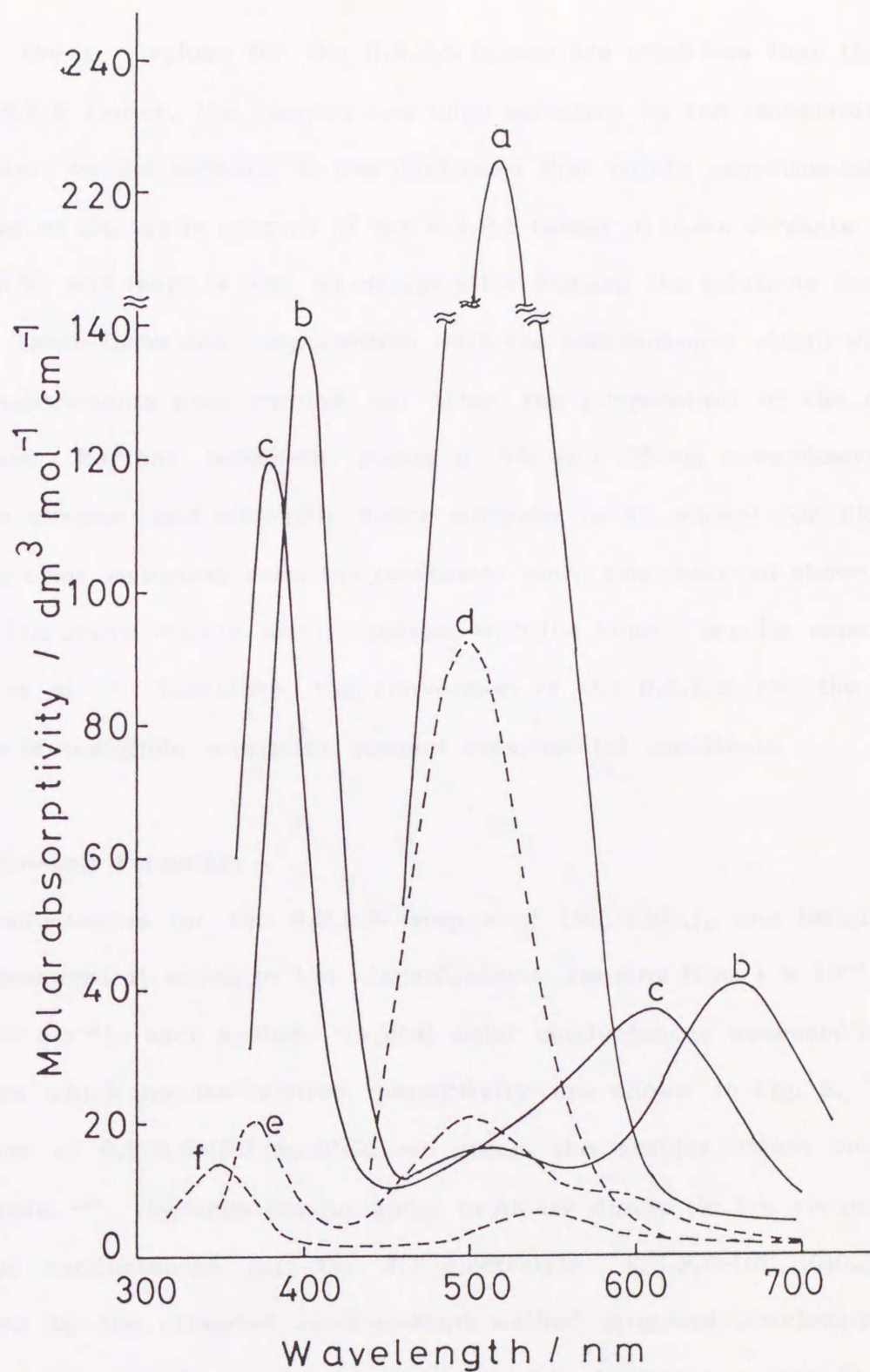


Fig. 1 Visible absorption spectra for the R,S,R,S and R,R,S,S isomers of $[\text{NiL}](\text{ClO}_4)_2$ in some organic solvents at 25 °C. For the R,S,R,S isomer: (a) NB; (b) DMF; (c) AN. For the R,R,S,S isomer: (d) NB; (e) DMF; (f) AN

As the ϵ_{max} values for the R,R,S,S isomer are much less than those for the R,S,R,S isomer, the spectra are very sensitive to the isomerization of the latter to the former. It was confirmed that within experimental error there is no change in spectra of the R,S,R,S isomer in these solvents over 40 h at 25 °C and there is also no change after heating the solutions for 2 h at 40 °C. These times and temperatures were the maximum ones within which all the measurements were carried out after the preparation of the complex solutions. Further, isosbestic points at 596 and 585 nm were observed for all the oxygen- and nitrogen- donor solvents in NB, except for HMPA for which a clear deviation from the isosbestic point was observed above 0.3 mol dm⁻³. The above results are compatible with the kinetic results reported by Moore et al.¹⁴⁾ Therefore, the conversion of the R,S,R,S into the R,R,S,S isomers is negligible under the present experimental conditions.

3. 1. Ion-pair Formation

Conductances for the R,S,R,S isomers of [NiL](ClO₄)₂ and [NiL(N₃)]ClO₄ were measured at seven to ten concentrations ranging from 1 × 10⁻⁴ to 4 × 10⁻³ mol dm⁻³ in each system. Typical molar conductances measured in NB-AN mixtures which are iso-relative permittivity are shown in Fig. 2. All the solutions of R,S,R,S-[NiL(N₃)]ClO₄ are green, the complex cation being five coordinate.²⁶⁾ The large conductances in AN are due to its low viscosity.

The conductances for the 2:1 electrolyte R,S,R,S-[NiL](ClO₄)₂ were analyzed by the extended Jenkins-Monk method proposed previously,²⁷⁾ to get the first (K_{a1}) and second (K_{a2}) ion-pair formation constants in the reactions (2) and (3) where the

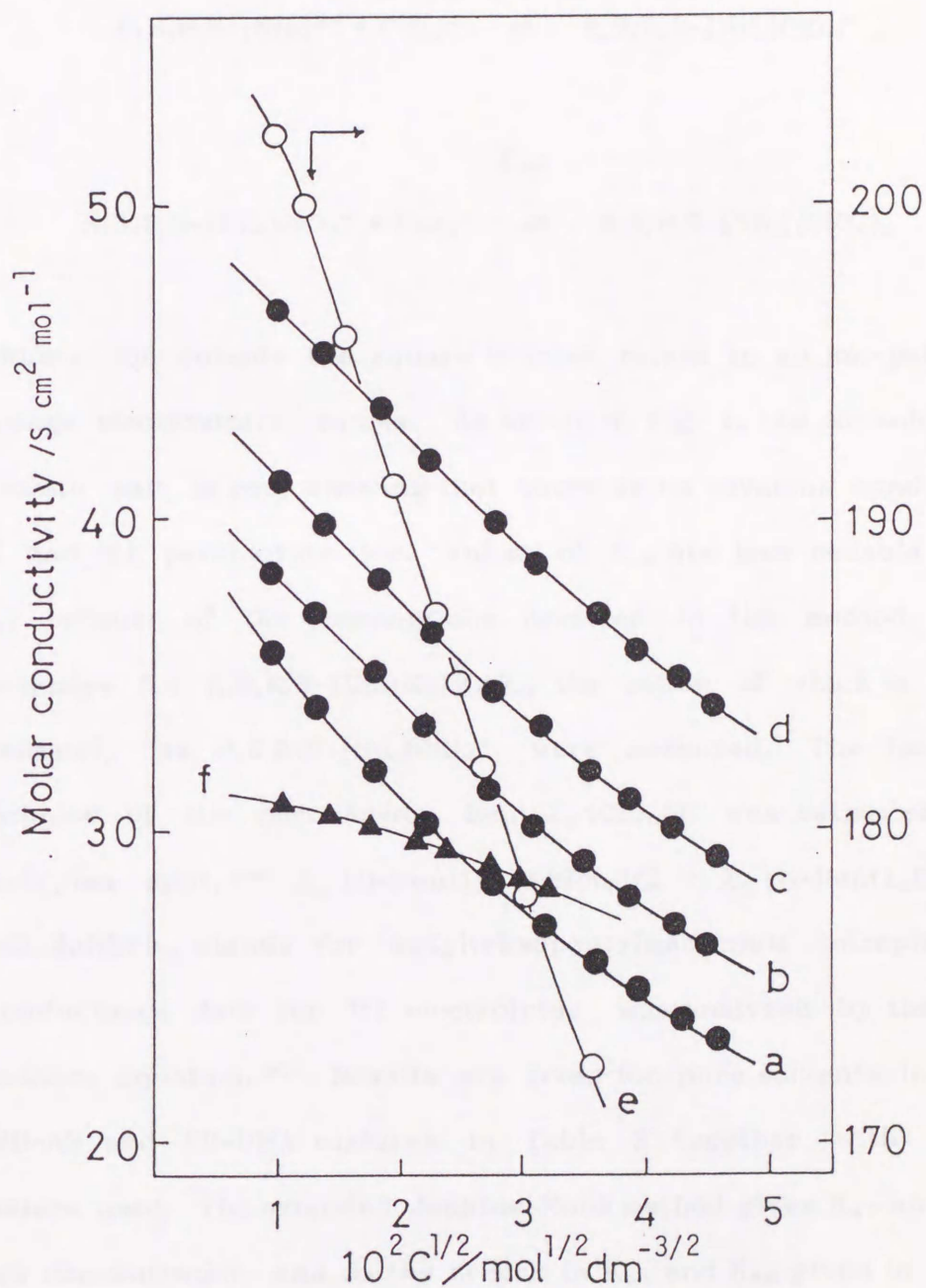
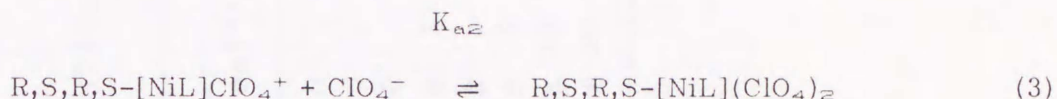
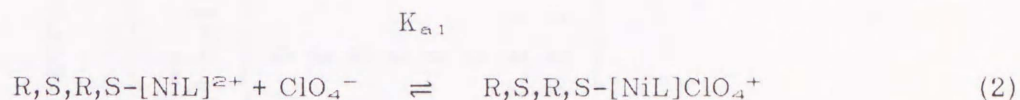


Fig. 2 Plots of the molar conductivities of $1/2$ R,S,R,S-[NiL](ClO₄)₂ and R,S,R,S-[NiL(N₃)]ClO₄ against the square root of the concentration in NB-AN mixtures at 25 °C. AN fraction: for R,S,R,S-[NiL](ClO₄)₂, (a) 0.0, (b) 0.038, (c) 0.0093, (d) 0.178, (e) 1.0; for R,S,R,S-[NiL(N₃)]ClO₄, (f) 0.0



perchlorate ion outside the square bracket refers to an ion-pair formed by long-range electrostatic forces. As shown in Fig. 1, the NB solution of the perchlorate salt is red, showing that there is no covalent bond between the nickel and the perchlorate ion. Values of K_{a2} are less reliable than those of K_{a1} because of the assumptions involved in the method. Therefore, conductances for $R,S,R,S-[NiL(N_3)]ClO_4$, the cation of which is regarded as approximately as $R,S,R,S-[NiL]ClO_4^+$, were measured. The limiting molar conductance of the perchlorate ion, $\lambda_0(ClO_4^-)$, was estimated using the Fuoss-Coplan split,²⁹⁾ $\Lambda_0[(i-Pent)_3BuNBPh_4]/2 = \lambda_0[(i-Pent)_3BuN^+]$, where $(i-Pent)_3BuNBPh_4$ stands for butyltriisopentylammonium tetraphenylborate. The conductance data for 1:1 electrolytes was analyzed by the Fuoss-Hsia conductance equation.³⁰⁾ Results are given for pure solvents in Table 1 and for NB-AN and NB-DMA mixtures in Table 2 together with the solvent parameters used. The extended Jenkins-Monk method gives K_{a1} and K_{a2} values at each concentration and so the errors in K_{a1} and K_{a2} given in Tables 1 and 2 are ascribed to the standard deviations of the K_{a1} and K_{a2} values, respectively. Although conductances for $R,S,R,S-[NiL](ClO_4)_2$ in Py were measured in the concentration range $1.4 \times 10^{-4} - 4.2 \times 10^{-3}$ mol dm⁻³, they

Table 1. Solvent parameters and conductances for R,S,R,S-[NiL](ClO₄)₂ in pure solvents at 25 °C

Solvent D	$10^2 \eta$ / Pa s	$\lambda_0(\text{ClO}_4^-)$ / S cm ² mol ⁻¹	$\Lambda_0(1/2\text{MX}_2)$ / S cm ² mol ⁻¹	$r_s^{a)}$ / nm	K_{a1} / dm ³ mol ⁻¹	K_{a2} / dm ³ mol ⁻¹
PC	64.4	2.530	18.4	33.98	0.42	0
DMSO	46.68	1.996	24.4	42.87	0.44	0
DMA	37.78	0.919	43.5	76.72	0.54	0
DMF	36.71	0.802	51.7	92.76	0.50	0
NM	36.67	0.627	53.8	104.2	0.52	0
AN	36.0	0.344	103.7 ^{b)}	212.2	0.44	0
NB	34.82	1.842	21.1	39.2	0.49	12 ± 1
Ac	20.7	0.304	118.35 ^{c)}	217.0	0.55	155 ± 1

a) Stokes' radii. b) Ref. 48. c) Ref. 49.

Table 2. Solvent parameters and conductances for R,S,R,S isomers of $[\text{NiL}](\text{ClO}_4)_2$ and $[\text{NiL}(\text{N}_3)]\text{ClO}_4$ in mixed solvents of AN and DMA with NB at 25 °C

Solvent	D	$10^2 \eta$ /Pa s	$\lambda_0(\text{ClO}_4^-)$ /Scm ² mol ⁻¹	R,S,R,S- $[\text{NiL}](\text{ClO}_4)_2$			R,S,R,S- $[\text{NiL}(\text{N}_3)]\text{ClO}_4$				
				$\Lambda_0(1/2\text{MX}_2)$ /Scm ² mol ⁻¹	$r_s^a)$ /nm	K_{a1} /dm ³ mol ⁻¹	K_{a2} /dm ³ mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	$r_s^a)$ /nm	K_a /dm ³ mol ⁻¹	
$X_{\text{AN}}^{b)}$	0.0	34.82	1.8415	21.1	39.2	0.49	1190 ± 10	12 ± 1	31.72	0.42	83 ± 8
	0.038	34.85	1.756	22.1	44.1	0.42	760 ± 10	86 ± 1	33.39	0.41	74 ± 7
	0.093	34.90	1.637	24.1	44.3	0.50	630 ± 5	74 ± 1	35.88	0.42	60 ± 4
	0.178	34.97	1.469	26.9	49.9	0.48	490 ± 5	77 ± 1	39.92	0.43	42 ± 7
	1.0	36.0	0.344	103.7	212.2	0.44	190 ± 5	0	162.8	0.40	27 ± 5
$X_{\text{DMA}}^{b)}$	0.0	34.82	1.8415	21.1	39.2	0.49	1190 ± 10	12 ± 1	31.72	0.42	83 ± 8
	0.026	35.0	1.808	21.2	39.9	0.48	510 ± 5	68 ± 1	32.67	0.40	78 ± 1
	0.109	35.26	1.754	22.1	41.2	0.49	290 ± 5	45 ± 1	33.73	0.40	62 ± 1
	0.216	35.63	1.664	23.4	43.4	0.49	150 ± 5	21 ± 1	35.71	0.40	48 ± 3
	1.0	37.78	0.919	43.5	76.72	0.54	0	0	64.68	0.42	20 ± 2

a) Stokes' radii. b) Mole fraction.

could not be reasonably analyzed by any method.

The five solvents, i.e. DMA, DMF, NM, AN, and NB, have nearly the same relative permittivity although different basicities. When the distance of closest approach between the nickel ion and the perchlorate ion is 0.5 nm, the Bjerrum equation of electrostatic association²¹⁾ predicts $K_{a1} = 20$ and $K_{a2} = 0$ for PC, 80 and 2 for DMSO, 200 and 8 for DMF, 250 and 10 for AN, 300 and 12 for NB, and 8400 and 130 $\text{dm}^3 \text{mol}^{-1}$ for Ac. The results obtained show that the complex forms ion pairs more readily in NB and less so in DMA and DMF than expected from electrostatic theory. Since K_{a1} and K_{a2} for $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ in NB are 11000 and 620 $\text{dm}^3 \text{mol}^{-1}$, respectively,²⁴⁾ the marked decrease in ion-pair formation constants for the present complex upon substitution of its methyl groups by protons provides evidence for hydrogen-bonding interactions of the perchlorate ion.

In the iso-relative permittivity systems in Table 2 it is seen that K_{a1} decreases with increasing fraction of the basic solvents, AN and DMA. As shown in Fig. 1, since AN is bonded to the nickel on the same side as the four methyl groups, the decrease in K_{a1} indicates that the site of ion pairing is mainly the axial pocket in the second coordination sphere surrounded by the four nitrogen substituents, and the axially associated perchlorate ions are easily displaced by basic molecules because the perchlorate ion is attracted mainly by electrostatic forces.

On the other hand, it is interesting that although DMA is more weakly coordinated in NB compared to AN as will be shown later, DMA has the same effect on ion-pair formation as AN; also DMA molecules in neat DMA are hardly bonded to the nickel but result in complete dissociation of the

perchlorate ion. Since this cannot be explained by electrostatic theory based on relative permittivity, it seems that solvation of the axial pocket by DMA without coordination plays an important role. A similar effect is observed for R,S,R,S-[NiL(N₃)]ClO₄ for which K_a slightly decreases with increasing AN and DMA contents. This means that the main site of ion pairing for K_a or K_{a2} is the other axial site opposite to the N₃ group; although both the perchlorate ion and donor solvents cannot be bonded to the nickel due to steric hindrance by the folded alkyl backbone of the ligand, the perchlorate ion which is weakly ion-paired in the second coordination sphere is easily displaced by solvating donor solvents. However, such as solvation is too weak to be reflected in the Stokes radii.

3. 2. Coordination of Donor Solvents

Properties required for the diluents are to be able to dissolve the complex salt sufficiently so as to permit spectrometric measurement of the chromophore, not to coordinate to the nickel, and to interact as little as possible with donor solvents added. Therefore, dipolar aprotic solvents, i. e. NB, NM, and PC, were examined as diluents. NB (DN⁽³²⁾ = 4.4) and NM (DN = 2.7) are of low basicity and do not coordinate, although in NB the complex forms ion pairs; PC is not coordinated in spite of its higher basicity (DN = 15.1) and the complex does not form ion pairs in this solvent.

Typical variations of the visible spectra of R,S,R,S-[NiL](ClO₄)₂ in NB with DMF content are shown in Fig. 3. The amount of the five-coordinate species increases as the DMF content increases. The absorbance at 519 nm can be taken as a measure of the ability of donor solvents to bond to the

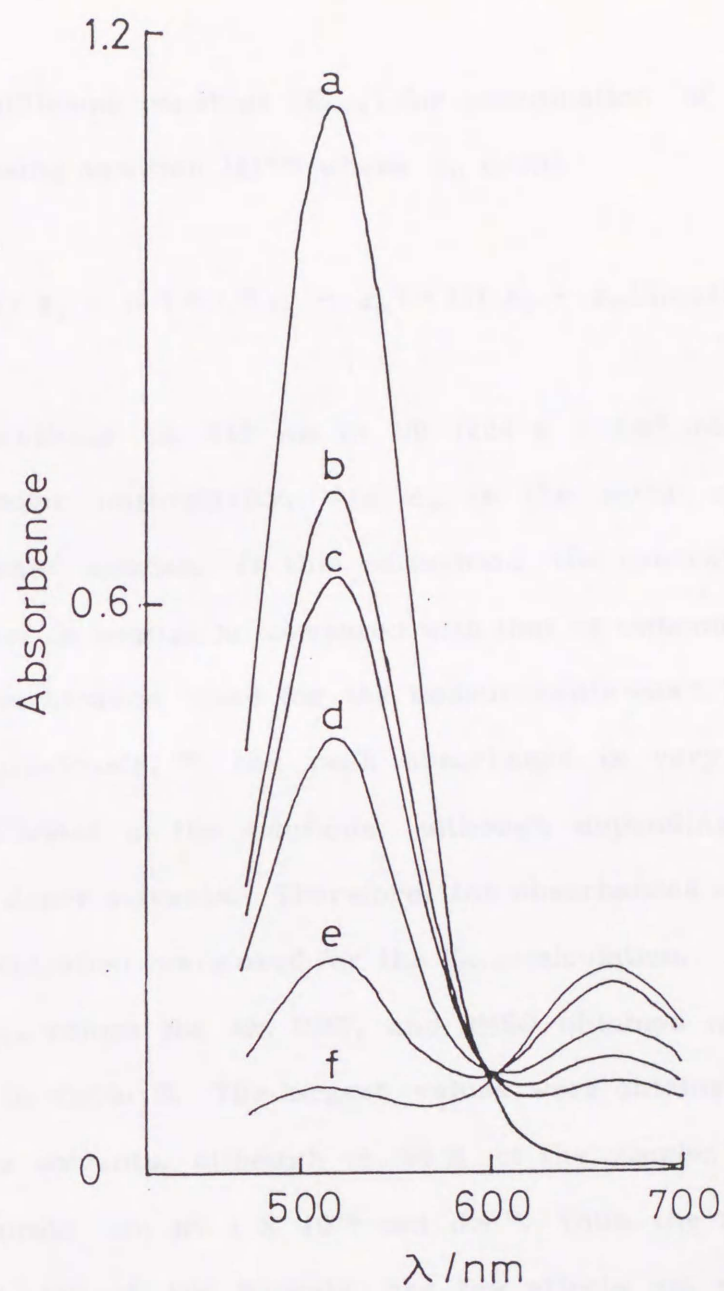


Fig. 3 Variation of the visible spectrum with the DMF concentration for a 1.0×10^{-3} mol dm^{-3} solution of $\text{R,S,R,S-[NiL](ClO}_4)_2$ in NB at 25°C . DMF concentration (mol dm^{-3}): (a) 0.00, (b) 0.102, (c) 0.151, (d) 0.301, (e) 1.01, and (f) neat.

nickel(II).

The equilibrium constant (K_{NiS}) for coordination of donor solvents was evaluated using equation (4)⁽³³⁾ where ϵ_0 is the

$$1/(\epsilon_0 - \epsilon) = 1/(\epsilon_0 - \epsilon_S) + 1/(\epsilon_0 - \epsilon_S)K_{NiS}[S] \quad (4)$$

molar absorptivity at 519 nm in NB ($224 \pm 1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), ϵ is the apparent molar absorptivity, and ϵ_S is the molar absorptivity of the five-coordinate species. In this calculation the concentration of S bonded to the cation is negligible compared with that of unbonded S since the metal chelate concentration used for the measurements was $1 \times 10^{-3} \text{ mol dm}^{-3}$. As reported previously,¹⁶⁾ the peak absorbance is very sensitive to small amounts of water in the solutions, although depending on the basicity of coexisting donor solvents. Therefore, the absorbances extrapolated to zero water concentration were used for the K_{NiS} calculation.

The K_{NiS} values for AN, DMF, and DMSO obtained in the three diluents are given in Table 3. The largest values were obtained in NB for all the three donor solvents, although ca. 50 % of the complex forms ion pairs with the perchlorate ion at $1 \times 10^{-3} \text{ mol dm}^{-3}$. Thus, the ion pairing with the perchlorate ion of low basicity has few effects on equilibrium (1). The lower K_{NiS} values for NM and PC may be attributed to their higher acidities (NM, acceptor number,⁽³⁴⁾ AcN = 20.5; PC, AcN = 18.3), while for NB AcN = 14.8. Therefore, NB was selected as diluent throughout the coordination study.

The effects of donor solvents on absorbances were examined at the concentrations 0.1, 0.15, 0.3, and 1 mol dm^{-3} , except for 0.003, 0.009, 0.01,

Table 3. Coordination constants $K_{N:IS}$ [equation (4)] in NB, NM, and PC at 25 °C

Donor solvent	NB	NM	PC
AN	3.4 ± 0.2	1.2 ± 0.1	1.1 ± 0.2
DMF	6.3 ± 0.6	1.4 ± 0.2	1.7 ± 0.1
DMSO	4.4 ± 0.2	1.0 ± 0.1	1.0 ± 0.2

and 0.03 mol dm⁻³ for HMPA. Fig. 4 shows the variation of ϵ at 519 nm with the concentration of S, together with the molar absorptivity in neat solvents. It should be noted that the decreasing effect of DMA, DMP, and DEA on ϵ is less than that of the homologous amides DMF and DEF, and the ϵ values in the neat solvent remain almost unchanged, compared with ϵ_0 , showing that DMA, DMP, and DEA are hardly coordinated.

These absorbance data were plotted according to equation (4) (Fig. 5). In all cases good linear relationships were obtained: all the coefficients of correlation are larger than 0.997, except for ca. 0.988 for DMA and DEA. Two points for DMA are not plotted because they are off scale. In some cases negative ϵ_S values were obtained from the intercept, e.g. -1.6 for DEF and -55 dm³ mol⁻¹ cm⁻¹ for BzN. Thus, this equation is very sensitive to the data uncertainty and assumptions.^(35,36) Therefore, K_{NIS} values were also evaluated by equation (5) with a constant value of $\epsilon_S = 10$ dm³ mol⁻¹ cm⁻¹ obtained in neat DEF. In the case of strongly basic HMPA, equation (4) gave a negative intercept and equation (5) increasing K_{NIS} with

$$K_{NIS} = (\epsilon_0 - \epsilon) / (\epsilon - \epsilon_S)[S] \quad (5)$$

increasing concentration of HMPA. In Table 4 the K_{NIS} values obtained in these two ways are listed in increasing order of solvent donor number. Each method gave nearly the same values. The donor numbers of DMP, DMAc, and DMBz were estimated from a relationship between the ¹H chemical shift of MeOH in various donor solvents with the DN values of the solvents.⁽³⁷⁾

The equilibrium constants show three main trends: (a) there is no

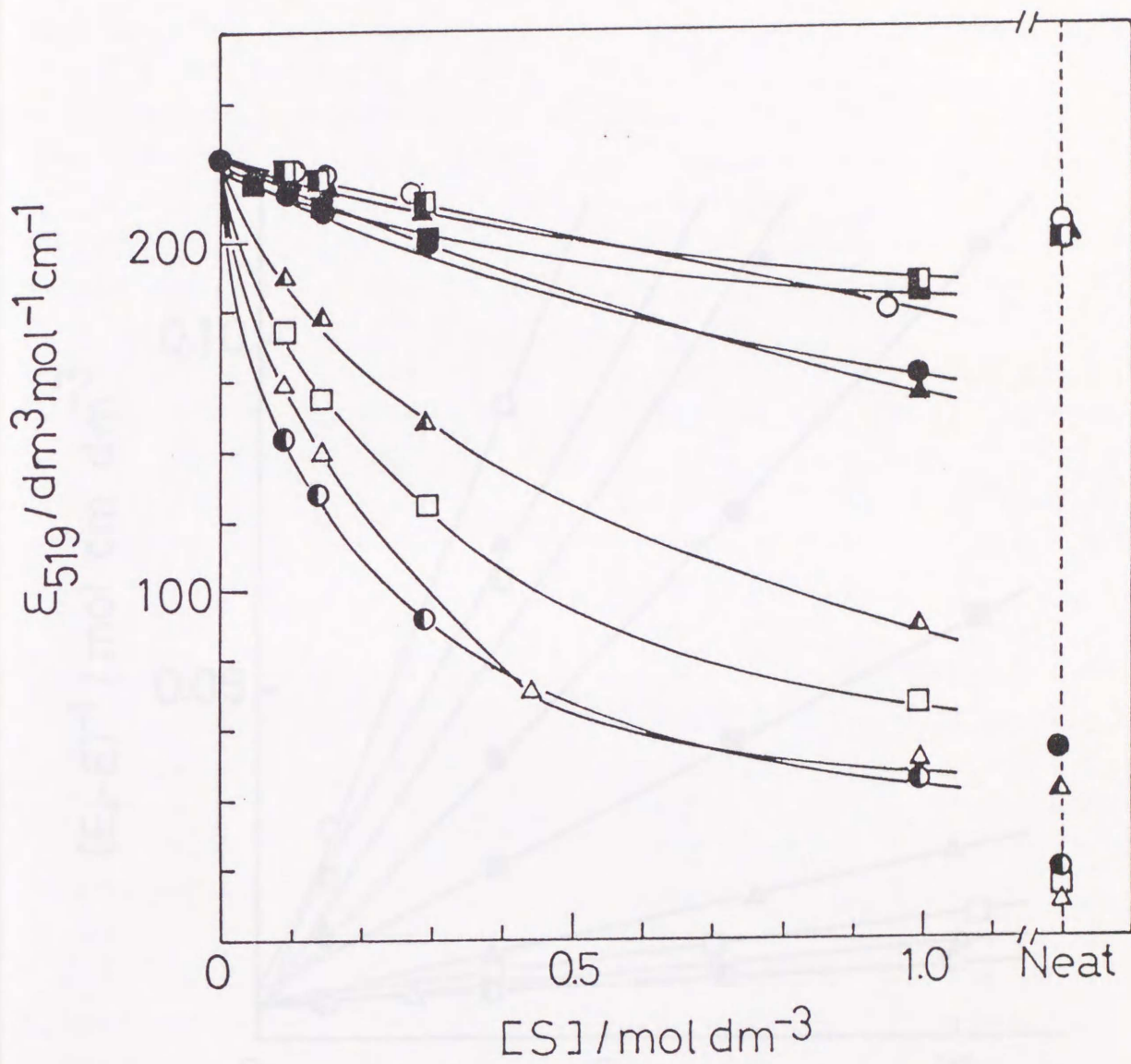


Fig. 4 Variation of molar absorptivity at 519 nm with the donor solvent concentration in NB at 25 °C : (\square) DMA, (\blacksquare) TBP, (\bullet) BzN, (\circ) DMP, (\triangle) n-BuN, (\square) AN, (\triangle) DEF, (\bullet) DMF, and (\blacktriangle) DEA.

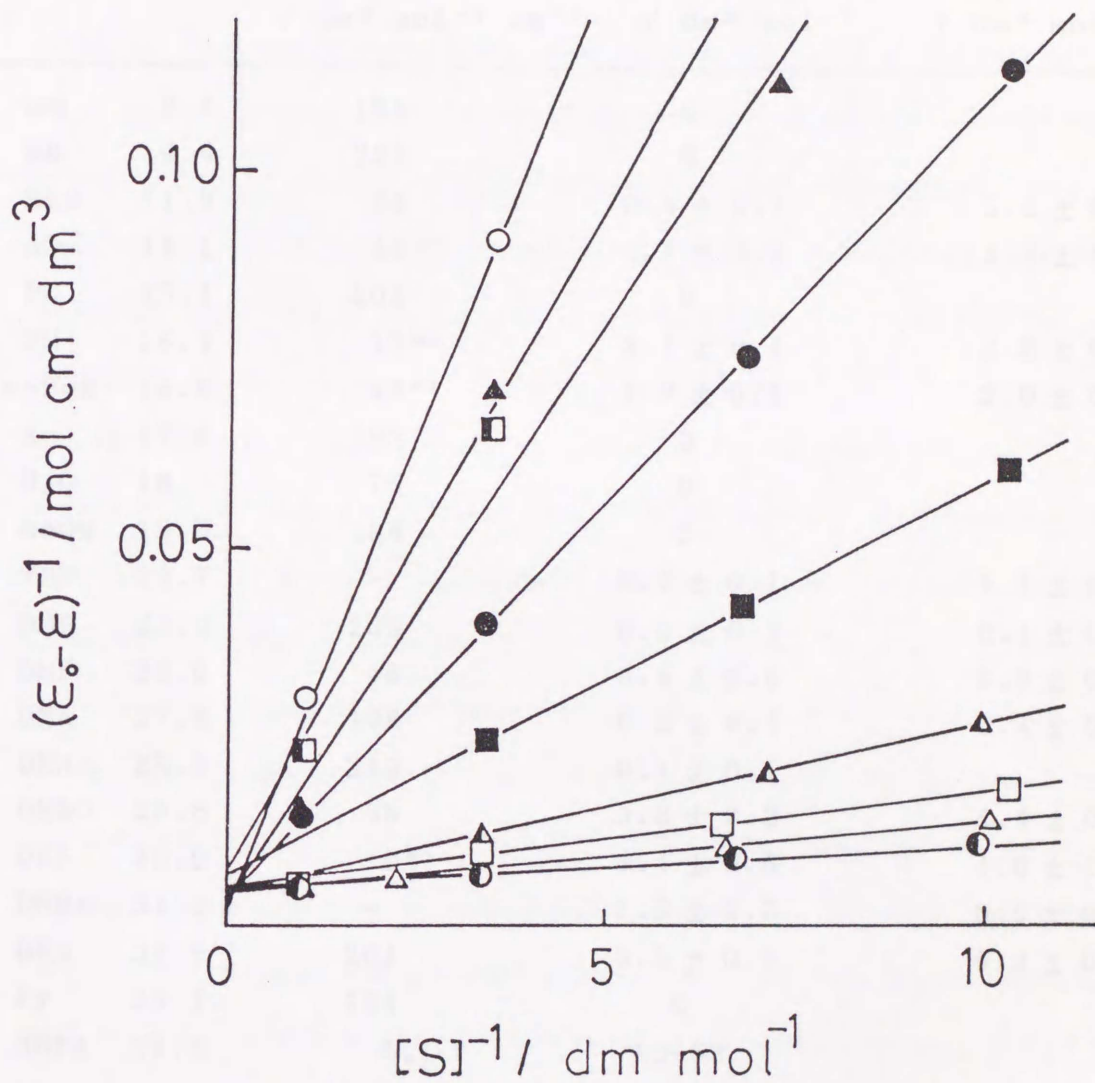


Fig. 5 Benesi-Hildebrand plot [equation (4)] for various donor solvents in NB at 25 °C. Symbols as in Fig. 4.

Table 4 Molar absorptivity (ϵ_{\max}) in pure solvents and coordination constants of various donor solvents with R,S,R,S-[NiL]²⁺ in NB at 25 °C

Solvent	DN ^{a)}	ϵ_{\max} ^{b)} / dm ³ mol ⁻¹ cm ⁻¹	K_{NiS} ^{c)} / dm ³ mol ⁻¹	K_{NiS} ^{d)} / dm ³ mol ⁻¹
NM	2.4	181	0	
NB	4.4	224	0	
BzN	11.9	54	0.4 ± 0.1	0.3 ± 0.1
AN	14.1	16 ^{e)}	3.1 ± 0.1	3.4 ± 0.2
PC	15.1	202	0	
PN	16.1	17 ^{e)}	3.1 ± 0.1	2.8 ± 0.3
n-BuN	16.6	43 ^{e)}	1.9 ± 0.1	2.0 ± 0.1
Ac	17.0	192	0	
H ₂ O	18	75	0	
MeOH	19.0	184	0	
TBP	23.7	-	0.7 ± 0.1	1.1 ± 0.2
DMP	24.0	205	0.2 ± 0.1	0.1 ± 0.1
DMF	26.6	16	5.4 ± 0.6	6.3 ± 0.6
DMA	27.8	198	0.2 ± 0.1	0.4 ± 0.6
DMAc	28.9	210	0.1 ± 0.1	
DMSO	29.8	56	3.8 ± 0.2	4.4 ± 0.2
DEF	30.9	10 ^{e)}	4.4 ± 0.6	4.0 ± 0.4
DMBz	31.2	-	1.3 ± 0.3	0.9 ± 0.4
DEA	32.2	201	0.3 ± 0.2	0.3 ± 0.6
Py	33.1	184	0	
HMPA	38.8	5 ^{e)}	13-53	

a) DN from ref. 32, except for DMP, DMAc, and DMBz of which DN was determined from a correlation of the ¹H chemical shift of MeOH with DN. b) Assigned to four-coordinate species. c) From equation (5). (d) From equation (4). e) No peak four-coordinate species is found and so the values are at 519 nm.

correlation of K_{NiS} with DN of the solvents; (b) oxygen-donor solvents for which DN is less than 20 are not coordinated; (c) the nitrogen atom of nitriles tends to be coordinated in spite of their lower DN.

Trend (a) arises partly from steric factors involving the four N-methyl groups. The coordinated axial site of $R,S,R,S-[NiL]^{2+}$ is surrounded by the four methyl groups and the axial ligation is sterically hindered to some extent. This is clearly illustrated by the fact that highly basic Py is not coordinated at all and the K_{NiS} values for DMA and DEA are much less than those for DMF and DEF. However, it seems that the steric hindrance is not the only reason for trend (a) since the DMA and DEA molecules are slightly coordinated in their dilute solutions in NB and DMP with the ethyl substituent is also coordinated to a similar extent. It should be noted that neat DMA, DMP, and DEA are hardly coordinated as evidenced by their large molar absorptivity (Table 4).

A similar trend is also seen for DMSO: it is easily bonded to the nickel in NB but not always so in neat DMSO, in view of the fact that neat DMSO gives a higher ϵ_{max} of $56 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, which means that ca. 20 % of the complex exists as the square-planar cation. A tentative explanation for these observations is that self-interactions of the donor solvents in the neat solvent are critical and lead to a decrease in the activity of the solvent molecule. Further studies of this are now being undertaken.

The non-coordination of water in trend (b) is not due to steric hindrance because water molecules hydrogen-bonded to $DMA^{15)}$ are coordinated with an equilibrium constant of 6.7, and the water dimers²³⁾ in NM, PC, and Ac are coordinated with equilibrium constants of 1.0, 1.8, and 5.0, respectively.

The fact that the basicity of the oxygen atom of water increases with the DN of the bulk solvents, $NM < PC < Ac < DMA$, was reasonably explained by polarization of O-H bonds through hydrogen-bonding. Popov and co-workers³⁹ suggested a DN of 33 for water, rather than 18 from a correlation of ^{23}Na chemical shifts with DN for pure solvents; Mayer and Gutmann⁴⁰ introduced the concept of 'bulk donicity' to characterize the higher donicity of liquid water resulting from hydrogen-bonding. MeOH hydrogen-bonded to DMA was found not to be coordinated. It is likely that the coordination of the oxygen atom attached to the methyl group is sterically hindered.

It has been pointed out that AN is a much stronger Lewis base than water toward nickel(II) tetramine complexes.⁴¹ The rod-like shape of the nitrile group is favorable for coordination^{4, 41} and this may be responsible partly for trend (c), that is, large K_{NiS} values for the homologous solvents in spite of their relatively smaller DN.

For $[Ni(cyclam)](ClO_4)_2$ with NH protons, the relative stability order for adduct formation was found to be $DMF > AN > DMSO > water$ in each neat solvent,¹⁷ unlike the correlation expected from the DN concept. The unexpected stronger ligation ability of AN was suggested to be due to its relatively weak base character toward interaction with the NH protons, in addition to its rod geometry.¹⁷ In the present system without NH protons, however, a similar trend was obtained, and therefore another factor must be involved. The specific influence of nitriles appears to be related to the π back donation.

Lever et al.⁴² analyzed the diffuse reflectance spectra of

six-coordinate nickel(II) complexes of microsymmetry NiN_2X_2 (N = amine or AN, X = Cl or Br) and reported that AN had the greatest ratio of the effective crystal-field splitting energy, $10Dq'(\text{bromide})/10Dq'(\text{chloride})$, which was correlated with the relative degree of back donation from metal to amines such as Py and ammonia. They concluded that AN was a good π acceptor. A π -acceptor nature of the $\text{C}\equiv\text{N}$ bond of AN has also been suggested from the weakening observed for the C-H bonds and the slight increase in $\text{C}\equiv\text{N}$ frequency upon coordination of AN to copper(I) halides,⁴³⁾ and a greater stabilization of the AN solvate of bis[2,2'-furyl dioximato(1-)]nickel(II).⁴⁴⁾ The possible π -back donation would explain the stronger ligation of AN in the present system.

Further, X-ray studies on $\text{R,S,R,S}[\text{NiL}(\text{AN})](\text{ClO}_4)_2$ ⁴⁵⁾ and $\text{R,S,R,S}[\text{NiL}(\text{DMF})](\text{SO}_3\text{CF}_3)_2$ ¹¹⁾ indicated that although the average Ni-N(ring) bond length (214.3 pm) for the AN adduct is larger than that (210.5 pm) for the DMF adduct, the displacement (34 pm) of the nickel atom from the N_4 plane in the former is still larger than that (29 pm) in the latter. The average Ni-N(ring) bond length for the unsolvated planar chelate is 196.0 pm for $\text{R,S,R,S}[\text{NiL}](\text{ClO}_4)_2$ ⁴⁵⁾ and 198.2 pm for $\text{R,S,R,S}[\text{NiL}](\text{SO}_3\text{CF}_3)_2 \cdot \text{Ac} \cdot \text{H}_2\text{O}$.⁴⁷⁾ Thus, it seems that the greater deformation for the AN adduct on going from the four- to five-coordinate species, compared to the DMF adduct, is consistent with the π bonding contribution to the Ni-AN bond.

The enthalpy and entropy changes for equilibrium (1) for AN and DMF in NB and NM were obtained using the temperature dependence of K_{NiS} corrected for changes in solution volume with temperature (Fig. 6). The values are

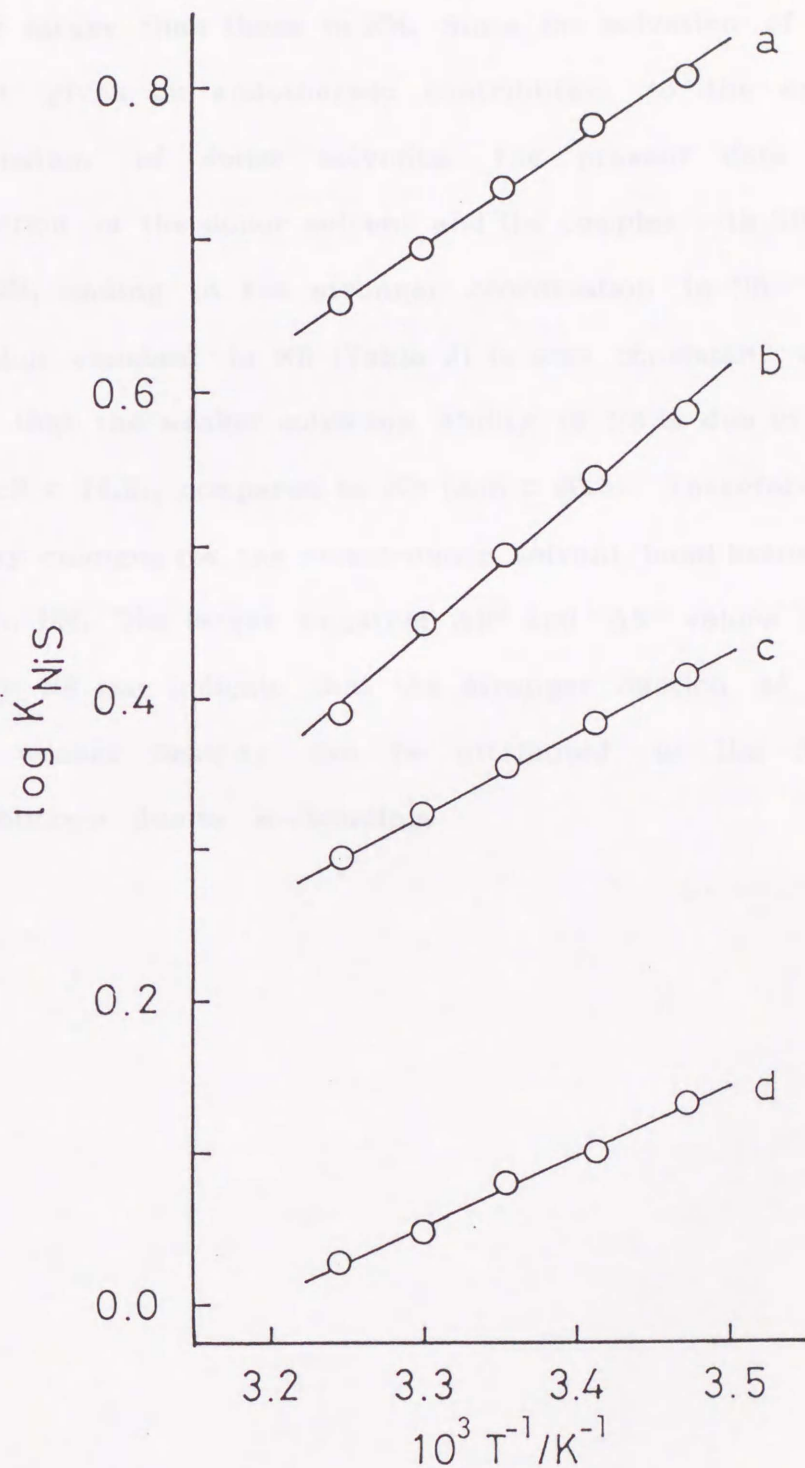


Fig. 6 Temperature dependence of the equilibrium constant K_{NiS} . In NB: (a) DMF, 0.131; (b) AN, 0.378 mol dm⁻³. In NM; (c) DMF, 0.519; (d) AN, 0.759 mol dm⁻³.

given in Table 5. The negative ΔH^\square and ΔS^\square values for both AN and DMF in NB are larger than those in NM. Since the solvation of the solutes by the diluent gives an endothermic contribution to the enthalpy change for coordination of donor solvents, the present data indicate that the interaction of the donor solvent and the complex with NB is weaker than that with NM, leading to the stronger coordination in NB. The larger ion-pair formation constant in NB (Table 2) is also consistent with this view; it is likely that the weaker solvating ability of NB is due to the weak acidity of NB ($\text{AcN} = 14.8$), compared to NM ($\text{AcN} = 20.5$). Therefore, the enthalpy and entropy changes for the nickel-donor solvent bond become more marked in NB than in NM. The larger negative ΔH^\square and ΔS^\square values for AN, compared to DMF, in NB may indicate that the stronger ligation of nitriles in spite of their weaker basicity can be attributed to the favorable enthalpic contributions due to π -bonding.

Table 5. Thermodynamic quantities for formation of the five-coordinate chelate in NB and NM at 25 °C

Donor solvent	ΔH^\square / kJ mol ⁻¹	ΔS^\square / J K ⁻¹ mol ⁻¹	Conditions
AN	-16.4 ± 0.8	-45 ± 3	[AN] = 0.378 mol dm ⁻³ in NB
	-8.8 ± 0.3	-28 ± 1	[AN] = 0.759 mol dm ⁻³ in NM
	-16.8 ± 0.8 ^{a)}	-32 ± 2 ^{a)}	In neat AN and AN-NM (1:1)
DMF	-12.8 ± 0.4	-29 ± 2	[DMF] = 0.131 mol dm ⁻³ in NB
	-10.2 ± 0.1	-28 ± 1	[DMF] = 0.519 mol dm ⁻³ in NM
	-12.8 ± 2.7 ^{b)}	-24.1 ± 9.0	In neat DMF

a) Ref. 9. b) Ref. 11.

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Chapter 2

Ion-pair Formation for R,S,R,S-[NiL](ClO₄)₂

2. Experimental

LiClO₄ and NiCl₂ were purified as described in Chapter 1. All reagents, except NiCl₂ (Vulco Pure Chemicals, industrial grade) were purified by standard methods. Unpurified products through a 0.2 μm filter and NiCl₂ was removed by 10% NaOH.

R,S,R,S-[NiL](ClO₄)₂, R,S,R,S-[NiL](NO₃)₂, R,S,R,S-[NiL](PF₆)₂, and R,S,R,S-[NiL](ClO₄)₂ were prepared by the published method.¹⁰ The purity of all the complexes was confirmed by elemental analysis.

The synthesis and the procedure used for measurements of conductivity, viscosity, relative permittivity, and optical density are described in Chapter 1. The relative permittivities (ε_r) (dielectric constant)

1. Introduction

In Chapter 1, it was found that although DMF, DEF, FA, and NMF were coordinated to $R,S,R,S-[NiL]^{2+}$, DMA, DMP, DMAc, DMBz, and DEA were not coordinated to the square complex, in spite of these solvents having nearly the same basicity. This was explained by steric hindrance between $-CO-Me$ of the DMA, and four $-N-Me$ and methylene groups of L. This led us to inquire as to whether solvation effects of non-coordinating DMA molecules on ionic association of $R,S,R,S-[NiL]^{2+}$ is different from that of coordinating DMF. DCE of a low relative permittivity (10.36) and NB which has nearly the same relative permittivity (34.82) as the amides were used as diluents. The ionic association between $R,S,R,S-[NiL]^{2+}$ and the perchlorate ion is discussed from the viewpoint of steric hindrance and ion-dipole interactions.

2. Experimental

NB, DMF, and DMA were purified as described in Chapter 1. DCE (reagent grade, Wako Pure Chemical Industries Ltd.) was purified by fractional distillation under reduced pressure through a 1.2-m column and left into molecular sieves 4A for a week.

$R,S,R,S-[NiL](ClO_4)_2$, $R,S,R,S-[NiL(N_3)]ClO_4$, $(i-Pent)_3BuNBPh_4$, and $(i-Pent)_3BuNClO_4$ were prepared by the published method.¹⁻³ The purities of all the complexes were confirmed by the elemental analysis.

The instrumentation and the procedure used for measurements of conductances, viscosities, relative permittivities, and spectra were described in Chapter 1. The relative permittivities (D), viscosities (η),

and densities (d) of the solvent mixtures used for analyses were given in Tables 1 to 3. The specific conductances ($S \text{ cm}^{-1}$) of the solvents are $2.2 \times 10^{-8} - 2.9 \times 10^{-7}$ for NB-DMA mixtures, $2.1 \times 10^{-8} - 3.4 \times 10^{-7}$ for NB-DMF, $1.8 \times 10^{-7} - 9.3 \times 10^{-7}$ for DCE-DMA, $2.0 \times 10^{-7} - 9.2 \times 10^{-7}$ for DCE-DMF, and $1.2 \times 10^{-7} - 4.0 \times 10^{-7}$ for DMF-DMA. All solutions were prepared by weight. Densities were measured by using an Anton Paar model DMA 02D digital density meter at $25 \pm 0.002^\circ\text{C}$.

3. Results and Discussion

Conductances for $R,S,R,S\text{-}[\text{NiL}](\text{ClO}_4)_2$ and $R,S,R,S\text{-}[\text{NiL}(\text{N}_3)]\text{ClO}_4$ were measured at seven to ten concentrations ranging from 1×10^{-4} to 4×10^{-3} mol dm^{-3} in each system. Typical molar conductances measured in the DMA-NB system which of nearly the same relative permittivity are shown in Fig. 1. To analyze conductance data for the 2-1 type of electrolyte the limiting molar conductance for ClO_4^- must be evaluated. In this work, $(i\text{-Pent})_3\text{BuNBPh}_4$ was used as a reference electrolyte (i.e. assuming $\lambda_0[(i\text{-Pent})_3\text{BuN}^+] = \lambda_0(\text{BPh}_4^-)$).⁽³⁾ The conductances for $(i\text{-Pent})_3\text{BuNBPh}_4$ and $(i\text{-Pent})_3\text{BuNClO}_4$ in each mixture were measured at 25°C and analyzed by the Fuoss-Hsia conductance equation for symmetrical electrolytes in the form (1)^(4, 5)

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma + J_2(C\gamma)^{3/2} - K_a C\gamma f^2 \quad (1)$$

for associated electrolytes, where the coefficients S , E , J , and J_2 have the usual meaning⁽⁵⁾ and the relative permittivity and viscosity of

Table 1. Solvent properties of mixed solvents of DMA and DMF with DCE at 25°C

X_{DMA}	D	η /cp	d /g cm ⁻³	X_{DMF}	D	η /cp	d /g cm ⁻³
0.000	10.36	0.787	1.2458	0.000	10.36	0.787	1.2458
0.228	17.8	0.858	1.1642				
0.368	22.0	0.900	1.1184				
0.431	23.7	0.914	1.0981	0.443	24.4	0.854	1.1122
0.526	27.0	0.932	1.0696	0.576	28.3	0.858	1.0722
0.630	29.5	0.944	1.0380				
0.728	32.6	0.949	1.0098	0.759	32.6	0.845	1.0170
1.000	37.78	0.919	0.9366	1.000	36.71	0.802	0.9433

Table 2. Solvent properties of mixed solvents of DMA and DMF with NB at 25°C

X_{DMA}	D	η /cp	d /g cm ⁻³	X_{DMF}	D	η /cp	d /g cm ⁻³
0.000	34.82	1.8415	1.1986	0.000	34.82	1.8415	1.1986
0.139	35.7	1.722	1.1651	0.158	35.5	1.675	1.1669
0.319	36.2	1.562	1.1206	0.360	36.0	1.462	1.1231
0.586	36.7	1.312	1.0516	0.627	36.8	1.175	1.0567
0.809	37.3	1.093	0.9900	0.837	37.1	0.959	0.9968
0.926	37.7	0.993	0.9574	0.938	37.1	0.908	0.9644
1.000	37.78	0.919	0.9366	1.000	36.71	0.802	0.9433

Table 3. Solvents properties of mixed solvents of DMA with DMF at 25°C

X_{DMF}	D	η /cp	d /g cm ⁻³
0.000	37.78	0.919	0.9365
0.340	36.6	0.890	0.9387
0.544	36.6	0.864	0.9403
0.735	36.6	0.838	0.9418
0.873	36.6	0.817	0.9428
0.955	36.6	0.807	0.9435
1.000	36.71	0.802	0.9439

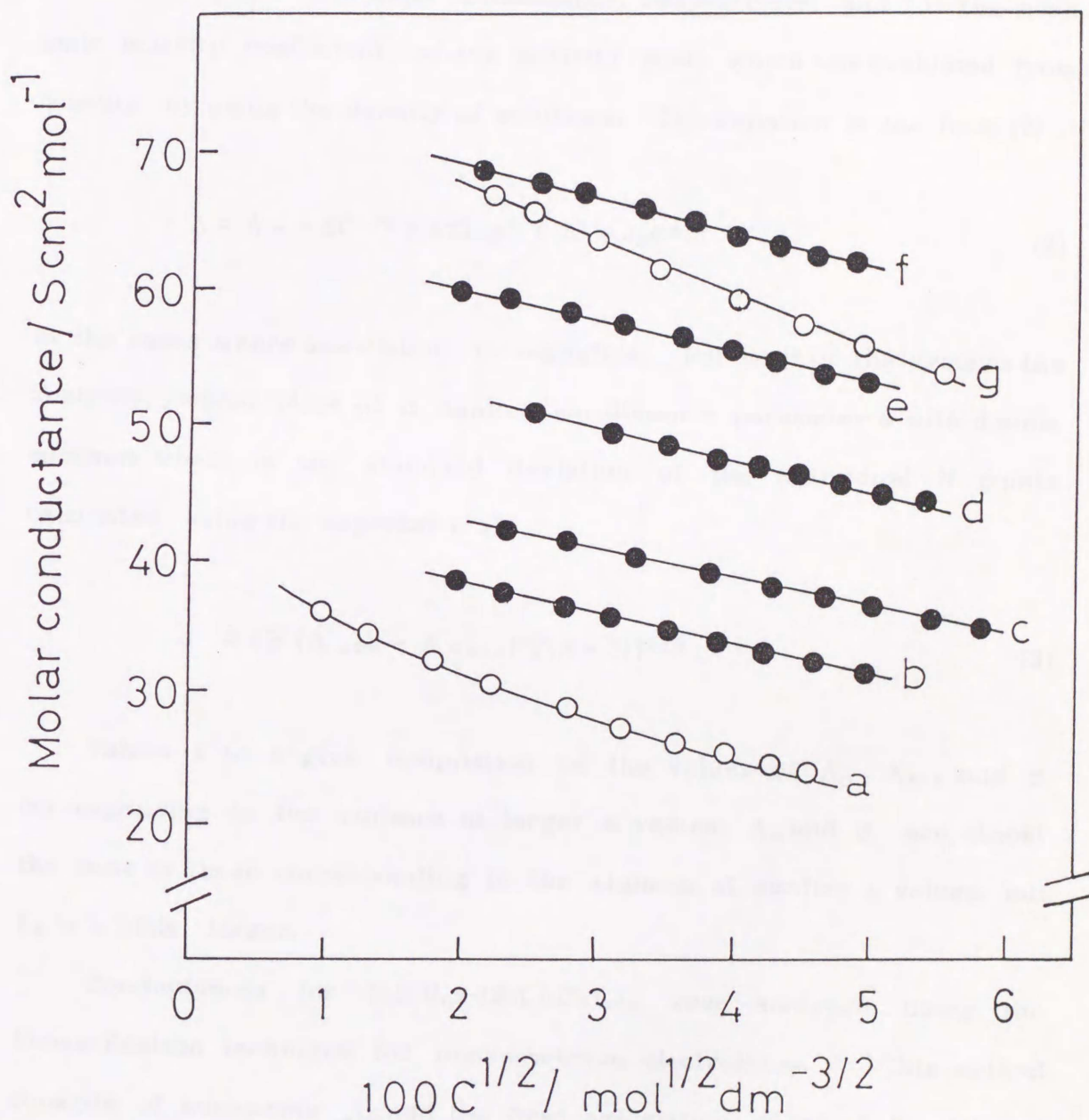


Fig. 1. Plots of molar conductivities of $1/2$ R,S,R,S-[NiL](ClO₄)₂ against the square root of the concentration in DMA-NB mixtures at 25°C. DMA fraction: a, 0.00; b, 0.14; c, 0.32; d, 0.59; e, 0.81; f, 0.93; g, 1.00.

solvents were used to calculate these coefficients. The symbol γ is the fraction of solute present as unpaired ions, Λ_0 and Λ are the limiting molar conductance and molar conductance, respectively, and f is the mean ionic activity coefficient on the molarity scale which was evaluated from molality by using the density of solutions. The equation is the form (2)

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + JC + J_2C^{3/2} \quad (2)$$

in the cases where association is negligible. For most of the systems the analyses yielded plots of σ against ion distance parameter a with double minimum where σ is the standard deviation of the individual N points calculated using the expression (3)

$$\sigma = [\sum (\Lambda_{obs} - \Lambda_{calc})^2 / (N - 3)]^{1/2} \quad (3)$$

Tables 4 to 6 give compilation of the values of Λ_0 , K_{a1} , and σ corresponding to the minimum at larger a values: Λ_0 and σ are almost the same as those corresponding to the minimum at smaller a values, but K_a is a little larger.

Conductances for R,S,R,S-[NiL](ClO₄)₂ were analyzed using the Fuoss-Edelson technique for unsymmetrical electrolytes.⁷ This method consists of evaluating Λ_0 and the first association constant K_{a1} for 2-1 electrolytes with some approximations, such as $\lambda_0(MX^+) = 0.5 \lambda_0(1/2M^{2+})$ and the second association constant $K_{a2} = 0$. Typical Fuoss-Edelson plots of Λ^* against X for DMA-NB solution are shown in Fig. 2, where

Table 4. Conductance parameters for (i-Pent)₃BuNClO₄, R,S,R,S-(NiL)(ClO₄)₂ and R,S,R,S-(NiL)(N₃)ClO₄ in mixed solvents of DMA and DMF with DCE at 25°C

(a) DMA - DCE

X _{DMA}	(i-Pent) ₃ BuNRPh ₄			(i-Pent) ₃ BuNClO ₄			R,S,R,S-(NiL)(ClO ₄) ₂			R,S,R,S-(NiL)(N ₃)ClO ₄		
	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	$\lambda_0(\text{ClO}_4^-)$ /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ
0.228	44.00±0.04	151±1	0.012	59.46±0.06	226±1	0.013	37.46	59.19±1.50	1120±300			
0.368	41.99±0.04	68±1	0.017	58.36±0.05	97±1	0.018	37.36	65.58±0.08	392±10			
0.431	41.70±0.03	57±1	0.016	58.31±0.08	73±3	0.039	37.46	68.62±0.11	496±12			0.023
0.526	41.02±0.04	34±1	0.010	58.02±0.13	53±2	0.072	37.51	70.44±0.05	247±4			
0.630	40.64±0.03	29±1	0.016	58.59±0.07	37±1	0.014	38.27	70.31±0.02	52±1			
0.728	40.43±0.04	23±1	0.035	59.65±0.03	28±1	0.007	39.43	71.86±0.03	31±1			0.028
1.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5	74.79±0.53	0			0.10

(b) DMF - DCE

X _{DMF}	(i-Pent) ₃ BuNRPh ₄			(i-Pent) ₃ BuNClO ₄			R,S,R,S-(NiL)(ClO ₄) ₂			R,S,R,S-(NiL)(N ₃)ClO ₄		
	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	$\lambda_0(\text{ClO}_4^-)$ /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ
0.443	45.06±0.10	54±2	0.065	64.11±0.07	70±7	0.035	41.58	74.79±0.07	424±7			0.047
0.576	44.93±0.09	31±2	0.053	66.09±0.25	30±4	0.049	43.62	77.11±0.25	78±18			
0.759	46.42±0.03	22±2	0.014	69.71±0.04	23±2	0.024	46.50	83.87±0.06	30±3			0.032
1.000	49.27±0.12	20±1	0.06	76.34±0.15	23±2	0.14	51.7	93.70±0.03	6±1			0.13

Table 5. Conductance parameters for (i-Pent)₃BuNBPh₄, (i-Pent)₃BuNC10₄ and R,S,R,S- (NiL) (C10₄)₂ in mixed solvents of DMA and DMF with NB at 25°C

(a) DMA-NB

X_{DMA}	(i-Pent) ₃ BuNBPh ₄				(i-Pent) ₃ BuNC10 ₄				R,S,R,S- (NiL) (C10 ₄) ₂			
	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	λ_0 (C10 ₄ ⁻) /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹	λ_0 (C10 ₄ ⁻) /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹
0.000	21.25 ^a	0 ^a	0.014 ^a	31.72 ^a	0 ^a	0.030 ^a	21.1	39.2	1190	21.1	39.2	1190
0.139	22.73±0.03	13±2	0.014	33.91±0.03	31±1	0.014	22.54	42.35±0.04	216±4	22.54	42.35±0.04	216±4
0.319	25.21±0.04	17±1	0.028	37.56±0.04	28±2	0.028	24.95	46.59±0.06	99±4	24.95	46.59±0.06	99±4
0.586	29.89±0.03	23±1	0.007	44.87±0.02	20±3	0.007	29.92	55.76±0.01	48±1	29.92	55.76±0.01	48±1
0.809	35.34±0.06	17±1	0.029	53.79±0.05	22±1	0.020	36.12	66.91±0.04	30±2	36.12	66.91±0.04	30±2
0.926	38.68±0.12	15±2	0.065	59.81±0.06	18±9	0.028	40.48	74.19±0.04	17±1	40.48	74.19±0.04	17±1
1.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5 ^a	74.79±0.53	0	43.5 ^a	74.79±0.53	0

(b) DMF-NB

X_{DMF}	(i-Pent) ₃ BuNBPh ₄				(i-Pent) ₃ BuNC10 ₄				R,S,R,S- (NiL) (C10 ₄) ₂			
	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	λ_0 (C10 ₄ ⁻) /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹	λ_0 (C10 ₄ ⁻) /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹
0.000	21.25 ^a	0 ^a	0.014 ^a	31.72 ^a	0 ^a	0.030 ^a	21.1	39.2	1190	21.1	39.2	1190
0.158	23.82±0.05	21±1	0.025	35.65±0.09	32±5	0.044	23.75	44.26±0.06	218±6	23.75	44.26±0.06	218±6
0.360	27.16±0.13	11±7	0.066	41.87±0.02	27±1	0.011	27.80	51.24±0.05	109±3	27.80	51.24±0.05	109±3
0.627	34.04±0.03	19±1	0.007	51.92±0.03	24±2	0.013	34.90	64.28±0.02	51±1	34.90	64.28±0.02	51±1
0.837	41.91±0.03	18±1	0.014	63.60±0.14	15±5	0.060	42.65	78.37±0.21	28±7	42.65	78.37±0.21	28±7
0.938	45.84±0.10	20±1	0.052	71.01±0.09	24±1	0.034	48.09	84.26±0.03	13±1	48.09	84.26±0.03	13±1
1.000	49.27±0.12	20±1	0.065	76.34±0.15	23±2	0.14	51.7	93.70±0.03	6±1	51.7	93.70±0.03	6±1

a) Reference 8.

Table 6. Conductance parameters for (i-Pent)₃BuNBPh₄, (i-Pent)₃BuNC10₄, R,S,R,S-(NiL)(C10₄)₂ and R,S,R,S-(NiL(N₃))C10₄ in mixed solvents of DMA with DMF at 25°C

DMF-DMA

X _{DMF}	(i-Pent) ₃ BuNBPh ₄			(i-Pent) ₃ BuNC10 ₄			R,S,R,S-(NiL)(C10 ₄) ₂			R,S,R,S-(NiL(N ₃))C10 ₄		
	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ	λ_0 (C10 ₄ ⁻) /Scm ² mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka ₁ /dm ³ mol ⁻¹	Λ_0 /Scm ² mol ⁻¹	Ka /dm ³ mol ⁻¹	σ
0.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5	74.79±0.53	0	64.68±0.17	20±2	0.10
0.340	43.52±0.01	19±1	0.0049	66.85±0.04	21±1	0.014	45.08	82.52±0.06	0±1	67.34±0.10	24±1	0.033
0.544	44.91±0.10	16±2	0.048	68.83±0.06	19±1	0.025	46.38	85.24±0.08	1±3			
0.735	46.93±0.31	12±6	0.066	71.85±0.10	11±2	0.016	48.38	88.98±0.04	10±1	72.13±0.13	25±1	0.024
0.873	48.11±0.05	18±3	0.025	73.91±0.10	21±1	0.035	49.86	91.72±0.03	15±2			
0.955	48.56±0.03	16±1	0.011	75.05±0.16	19±3	0.059	50.77	93.21±0.03	13±1			
1.000	49.27±0.12	20±1	0.065	76.34±0.15	23±2	0.14	51.7	93.70±0.03	6±1	76.64±0.25	26±3	0.13

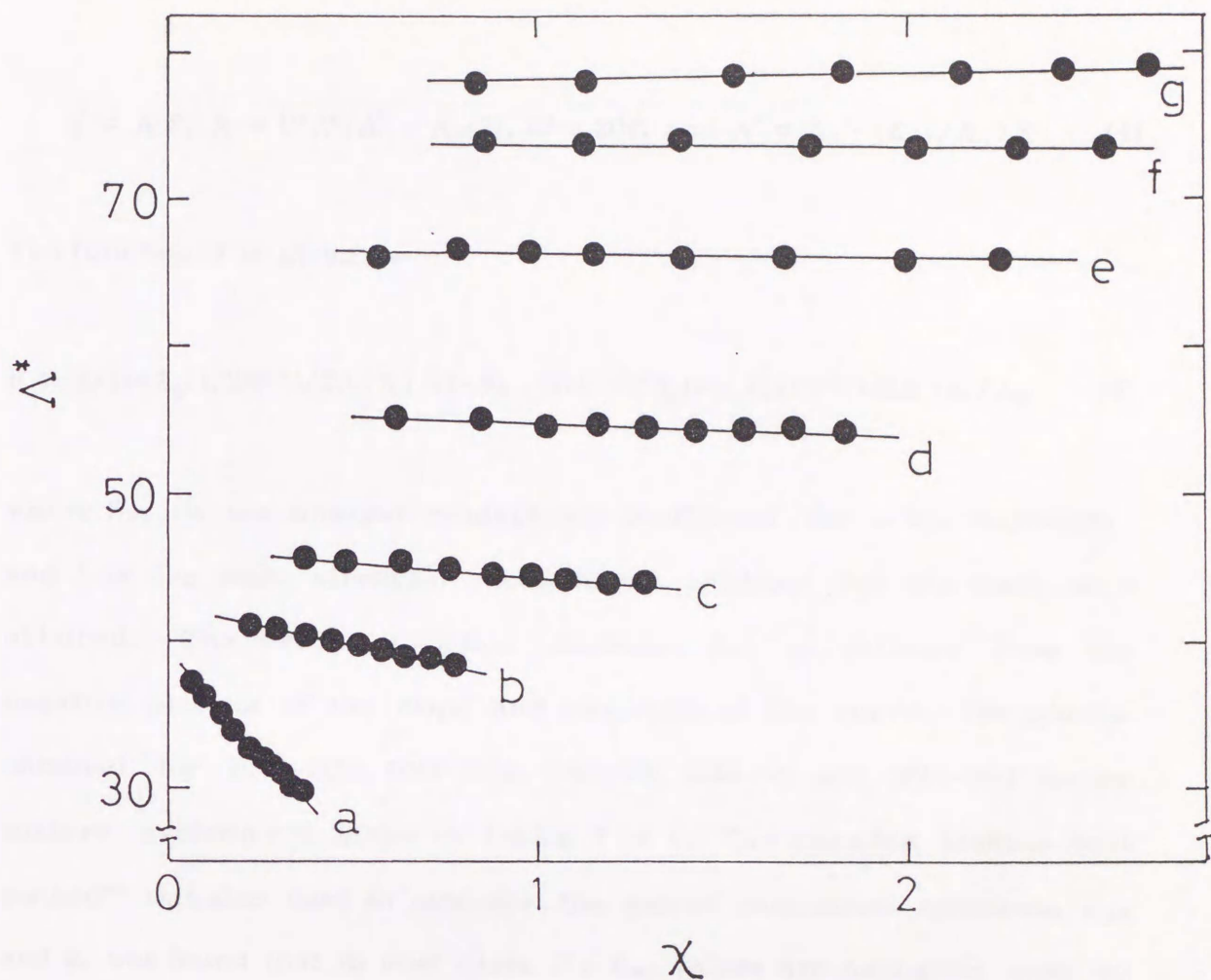


Fig. 2. Fuoss-Edelson plots for R,S,R,S-[NiL](ClO₄)₂ in DMA-NB mixtures at 25°C. DMA fraction: a, 0.00; b, 0.14; c, 0.32; d, 0.59; e, 0.81; f, 0.93; g, 1.00.

$$\Lambda^* = \Lambda F, X = C' \Lambda^* (\Lambda^* - \Lambda_0/2), C' = 2Cf, \text{ and } \Lambda^* = \Lambda_0 - (K_{a1}/\Lambda_0) X \quad (4)$$

The function F is given as

$$F = [1/(1 + \lambda_0(1/2M^{2+})/2\Lambda_0)] [1/\{1 - S_{2:1}(2I)^{1/2}/\Lambda_0\} + \lambda_0(1/2M^{2+})/2\Lambda] \Lambda / \Lambda_0 \quad (5)$$

where $S_{2:1}$ is the Onsager conductance coefficient for a 2-1 electrolyte and I is the ionic strength. Good linear relations for the plots were obtained. The first association constant K_{a1} is obtained from the negative product of the slope and intercept of the curve. The results obtained for DMA-DCE, DMF-DCE, DMA-NB, DMF-NB and DMA-DMF binary mixture systems are given in Tables 4 to 6. The extended Jenkins-Monk method²³ was also used to evaluate the second association constants K_{a2} and it was found that in most cases the K_{a2} values are negligibly small so that neglecting K_{a2} is not serious for evaluating K_{a1} . For example, in NB, where the salts used are most associative, the extended Jenkins-Monk method gave the values of $K_{a1} = 1190$ and $K_{a2} = 12$ and the analysis of conductances on neglecting the K_{a2} value gave the value of $K_{a1} = 1200$.

The visible spectra of R,S,R,S-[NiL]²⁺ in NB, DMF, and DMA are shown in Fig. 3. The absorption peaks at 519 nm in DMA and NB, and 503 nm in DMF are assigned to the square species and those at 660 and 400 nm in DMF are assigned to the square pyramidal species. There is no change in spectra of R,S,R,S-[NiL]²⁺ in those solvents over 40 h at 25°C. Therefore, the isomerization of R,S,R,S-[NiL]²⁺ can be neglected. These spectra

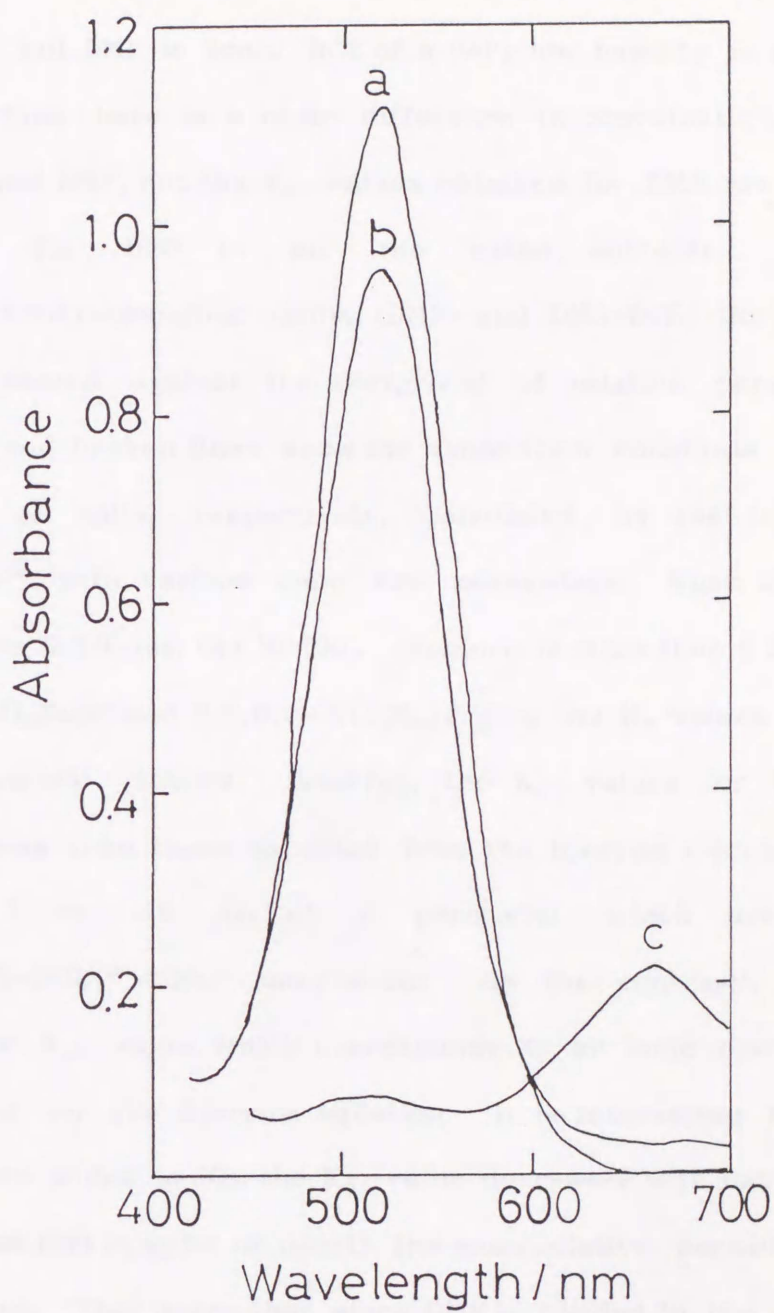


Fig. 3. Visible absorption spectra for R,S,R,S-[NiL](ClO₄)₂ (1.0×10^{-3} mol dm⁻³) in (a) NB, (b) DMA and (c) DMF at 25°C.

clearly show that NB and DMA are not coordinated to the R,S,R,S-[NiL]²⁺ cation but DMF is done. DCE of a very low basicity is not coordinated.

Thus, there is a clear difference in coordination behavior between DMA and DMF, but the K_{a1} values obtained for DMA are almost the same as those for DMF in all the mixed solvents. In the relative permittivity-changing media (DMF- and DMA-DCE) the logarithms of K_{a1} were plotted against the reciprocal of relative permittivity in Fig. 4. Solid and broken lines show the association constants for the 1-1 and 2-1 types of salts, respectively, calculated by the Bjerrum association theory²⁹⁾ with various ionic size parameters. When the ionic radius of ClO_4^- is 0.236 nm, the Ni- ClO_4^- distance is more than 0.31 nm. The salts of (i-Pent)₃BuN⁺ and R,S,R,S-[NiL(N₃)]⁺ give the K_a values expected from the electrostatic theory. However, the K_{a1} values for R,S,R,S-[NiL]²⁺ are much less than those expected from the Bjerrum calculation with a range of 0.3 to 1.0 nm of a parameter which are reasonable for R,S,R,S-[NiL]²⁺- ClO_4^- association. On the contrary, NB gives a much greater K_{a1} value which corresponds to an ionic distance parameter of 0.32 nm for the Bjerrum equation. It is interesting that when DMF and DMA are added to NB, the K_{a1} value decreases with increasing fraction of DMF and DMA in spite of nearly the same relative permittivity of the mixed solvents. This means that since DMF is bonded to the nickel on the same side as the four methyl groups, the site of ion pairing is mainly the axial pocket in the second coordination sphere surrounded by the four nitrogen substituents, and the axially associated perchlorate ions are easily displaced by the basic solvent. Furthermore, a similar

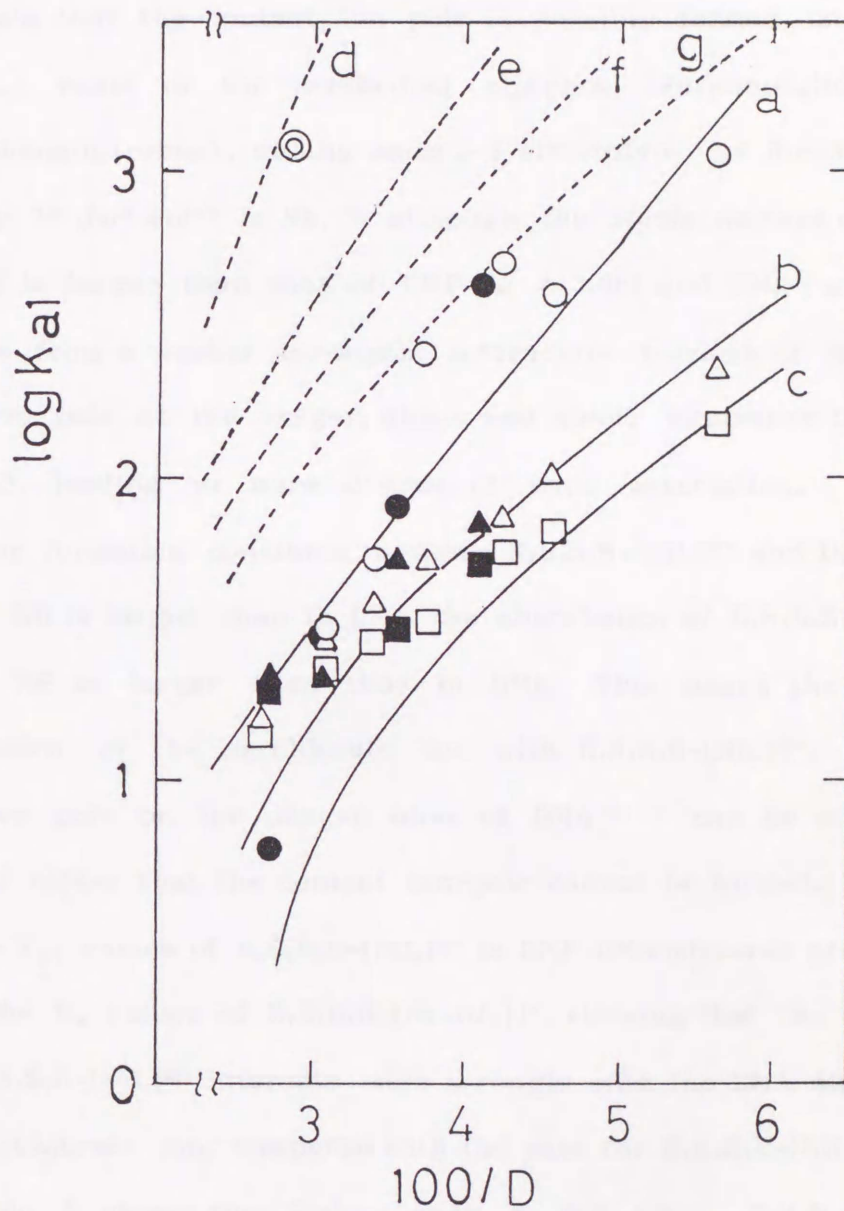


Fig. 4. The dependence of K_{a1} and K_a on the relative permittivity. ●, DMF-DCE; ○, DMA-DCE; ⊙, NB for $R,S,R,S-[NiL](ClO_4)_2$; ▲, DMF-DCE; △, DMA-DCE for $(i-Pent)_3BuNClO_4$; ■, DMF-DCE; □, DMA-DCE for $(i-Pent)_3BuNBPh_4$. Solid and broken lines show the values calculated for 1-1 and 2-1 types of electrolytes, respectively, at 25 °C. Ionic size parameter in nm: a, 0.3; b, 0.5; c, 0.7; d, 0.3; e, 0.5; f, 0.7; g, 1.0.

K_{a1} -decreasing effect of non-coordinating DMA indicates that the perchlorate ion associated is easily displaced by DMA through ion-dipole interactions between R,S,R,S-[NiL]²⁺ and DMA. The large K_{a1} values in NB suggests that the contact ion pair is possibly formed, considering that the K_{a1} value of the octahedral complex, [Fe(phen)₃](ClO₄)₂ (phen = 1,10-phenanthroline), of the same 2-1 electrolyte as R,S,R,S-[NiL](ClO₄)₂ is only 39 dm³ mol⁻¹ in NB,¹⁴⁾ although the dipole moment of NB ($\mu = 4.2$ Debye) is larger than that of DMF ($\mu = 3.86$) and DMA ($\mu = 3.81$). This results from a weaker ion-dipole interaction because of the delocalized negative pole on the oxygen atoms and steric hindrance of nitro group for NB, leading to more degree of ionic association. Although the ion-pair formation constants between R,S,R,S-[NiL]²⁺ and the perchlorate ion in NB is larger than in DMA, the absorbance of R,S,R,S-[NiL]²⁺ at 520 nm in NB is larger than that in DMA. This means the outer-sphere interaction of the perchlorate ion with R,S,R,S-[NiL]²⁺. The localized negative pole on the oxygen atom of DMA^{10,11)} can be so close to the central nickel that the contact ion-pair cannot be formed.

The K_{a1} values of R,S,R,S-[NiL]²⁺ in DMF-DMA mixtures are a little less than the K_a values of R,S,R,S-[NiL(N₃)]⁺, showing that the double charge for R,S,R,S-[NiL]²⁺ interacts more strongly with the DMA dipole than with the perchlorate ion, compared with the case for R,S,R,S-[NiL(N₃)]⁺.

Table 7 shows the Stokes radii r_s for ClO₄⁻, R,S,R,S-[NiL]²⁺, and R,S,R,S-[NiL(N₃)]⁺ ions in all the media used, where

$$r_s = 0.82 |z| / \lambda \eta \quad (6)$$

Table 7. Stokes radii r_s /nm for ClO_4^- , $\text{R,S,R,S}-(\text{NiL})_2^{2+}$ and $\text{R,S,R,S}-(\text{NiL}(\text{N}_3))_2^{2+}$ in various binary mixed solvents at 25°C

(a) with DCE

X_{DMF}	$r_s(\text{ClO}_4^-)$ / nm	$r_s(\text{NiL})_2^{2+}$ / nm	$r_s(\text{NiL}(\text{N}_3))_2^{2+}$ / nm	X_{DMA}	$r_s(\text{ClO}_4^-)$ / nm	$r_s(\text{NiL})_2^{2+}$ / nm	$r_s(\text{NiL}(\text{N}_3))_2^{2+}$ / nm
				0.228	0.26	0.88	
0.443	0.23	0.58	0.44	0.368	0.24	0.65	
0.576	0.22	0.57		0.431	0.24	0.58	0.43
				0.526	0.24	0.53	
0.759	0.21	0.52	0.42	0.630	0.23	0.54	
1.000	0.20	0.49	0.41	0.728	0.22	0.53	0.43
				1.000	0.21	0.57	0.42

(b) with NR

X_{DMF}	$r_s(\text{ClO}_4^-)$ / nm	$r_s(\text{NiL})_2^{2+}$ / nm	X_{DMA}	$r_s(\text{ClO}_4^-)$ / nm	$r_s(\text{NiL})_2^{2+}$ / nm
0.000	0.21	0.49	0.000	0.21	0.49
0.158	0.21	0.48	0.139	0.21	0.48
0.360	0.20	0.48	0.319	0.21	0.49
0.627	0.20	0.48	0.586	0.21	0.48
0.837	0.20	0.48	0.809	0.21	0.49
0.938	0.19	0.50	0.926	0.20	0.49
1.000	0.20	0.49	1.000	0.21	0.57

(c) with DMA

X_{DMF}	$r_s(\text{ClO}_4^-)$ / nm	$r_s(\text{NiL})_2^{2+}$ / nm	$r_s(\text{NiL}(\text{N}_3))_2^{2+}$ / nm
0.000	0.21	0.57	0.42
0.340	0.20	0.49	0.41
0.544	0.21	0.49	
0.735	0.20	0.48	0.41
0.873	0.20	0.48	
0.955	0.20	0.48	
1.000	0.20	0.49	0.41

and z is the charge of ions. The r_s values in each medium are almost constant except for the DCE systems of a lower relative permittivity, and the r_s values of $R,S,R,S-[NiL]^{2+}$ are larger than those of $R,S,R,S-[NiL(N_2)]^+$ in all the mixed solvents. This is compatible with strong solvation by DMA as well as DMF.

In conclusion, the main site of ion pairing for $R,S,R,S-[NiL]^{2+}$ is the axial pocket surrounded by the four N-methyl groups. DMA preferentially solvates the axial pocket by an ion-dipole interaction without a chemical bond between the central nickel and the oxygen atom of DMA, although DMF solvates by the chemical bond. The solvent-separated ion pair is formed in both DMA and DMF, but the contact ion pair is formed in NB.

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Chapter 3

Dimerization of Dimethyl Sulphoxide in Various Polar Solvents

1. Introduction

It is well known that DMSO is a highly associated liquid. Evidence has been obtained from a variety of experimental information.¹⁻⁷ Measurements of the chemical shift of ^{23}Na in DMSO-Py mixtures gave the iso-solvation point at the 0.1 DMSO mole fraction, indicating a strong preference of Na^+ for DMSO molecules.⁸ This was explained by breaking up the polymeric structure of DMSO by the relatively unstructured polar liquid Py, leading to enhancement of the solvating ability comparing with pure DMSO. Thus, the effects of self-association of DMSO on solute-solvent interactions have been often observed in mixed solvent systems. However, only a few reports for estimation of the degree of self-association by an i.r. technique^{3, 9} have been presented. This is partly because the dipole-dipole interaction between DMSO molecules is difficult to be characterized and to be treated quantitatively.

In Chapter 1, the coordination of about twenty donor solvents to the planar $\text{R,S,R,S}[\text{NiL}]^{2+}$ cation in NB as a diluent has been examined spectrophotometrically and it was found that although in DMF the planar chelate is almost changed into a five coordinate, square pyramidal species, in DMSO ca. 20% of the chelate exists as the square-planar cation, in spite of larger $\text{DN}^{(1)}$ of DMSO (29.8) compared with that of DMF (26.6). But this suggests a self-association of DMSO.

In this work, the axial coordination of DMSO to the planar chelate cation was studied in DMSO-NB, -PC, -DMA and -Py mixtures where the four diluents are not coordinated to the cation because of the lower basicity for NB and PC, and of steric hindrance for Py and DMA in spite of

their higher basicity. The self-association constant of DMSO was evaluated from dependence of the apparent coordination constant on the DMSO concentration.

2. Experimental

NB, DMSO, DMF, Py, PC, DMA, and AN were purified as described in Chapter 1. BzN (reagent grade, Wako Pure Chemical Industries Ltd.) was purified by twice fractional distillation under reduced pressure through a 1.2-m column.

The R,S,R,S-isomer of $[\text{NiL}](\text{ClO}_4)_2$ was prepared by the published method.^{11, 12)} I.r. spectra for this salts showed that no NH absorption was present. Elemental analysis was as follows; found C, 32.62; H, 6.40; N, 10.84 %, calculated C, 32.71; H, 6.27; N, 10.90 %. The instrumentation and the procedure used for measurement of spectra and water contents were described in Chapter 1.

$\text{VO}(\text{acac})_2$ was prepared by the published method.¹³⁾ Elemental analysis was as follows; found C, 45.57; H, 5.59 %, calculated C, 45.30; H, 5.32 %.

Optically active tris(1,10-phenanthroline)nickel(II) perchlorate $[\text{Ni}(\text{phen})_3](\text{ClO}_4)_2$ was prepared by the method described previously.¹⁴⁾

3. Results and Discussion

Figure 1 shows a typical example of the variation of the visible spectrum with the DMSO concentration for a 1.0×10^{-3} mol dm^{-3} solution of R,S,R,S- $[\text{NiL}](\text{ClO}_4)_2$ in DMA at 25°C, together with the spectrum in pure DMF. The absorption peak at 519 nm is referred to the four-coordinate

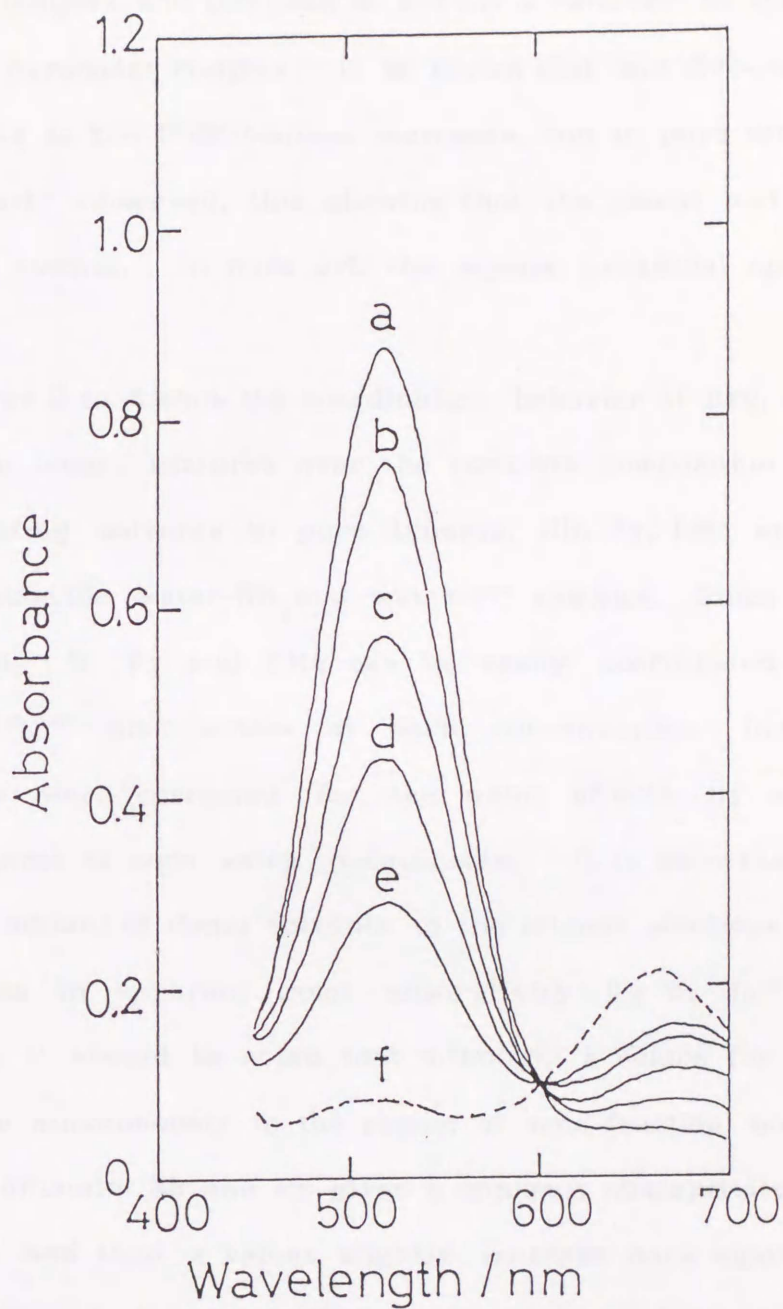


Fig. 1 Variation of visible absorption spectra for R,S,R,S-[NiL](ClO₄)₂ (about 1.0×10^{-3} mol dm⁻³) in DMA-DMSO mixtures and in DMF at 25°C. Mole fraction of DMSO: a, 0.00; b, 0.0340; c, 0.0993; d, 0.2472; e, 1.0; f, DMF.

planar complex and the peak at 673 nm is referred to the five-coordinate square pyramidal complex. It is shown that the five-coordinate species increases as the DMSO content increases, but in pure DMSO the two peaks are clearly observed, this showing that the planar and square pyramidal species coexist. In pure DMF the square pyramidal species exclusively exists.

Figures 2 to 5 show the coordination behavior of BzN, DMSO, DMF, AN and water in binary mixtures over the complete composition range from pure coordinating solvents to pure diluents, NB, Py, DMA and PC, except for the immiscible water-NB and water-PC systems. Since water dissolved especially in Py and DMA can be easily coordinated to the chelate cation,^{15, 16} absorbances at each concentration for organic donor solvents were corrected for the water effects by extrapolating the absorbances to zero water concentration. It is seen that the addition of a small amount of donor solvents to the diluent solutions results in sharp decreases in apparent molar absorptivity (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and further, it should be noted that although ϵ values for BzN, DMF and AN decrease monotonously in the region of mole fraction more than 0.1, DMSO in the diluents NB and Py gives a minimum absorptivity at ca. 0.5 mole fraction and then ϵ values slightly increase once again with increasing the DMSO mole fraction. This means a decreased coordinating ability of DMSO with increasing its mole fraction.

Such curves of a minimum ϵ value are also observed for coordination of water in the Py (Fig. 3) and DMA (Fig. 4) diluents.¹⁷ Although the monomer of water dissolved in DCE and NB of a low basicity is hardly

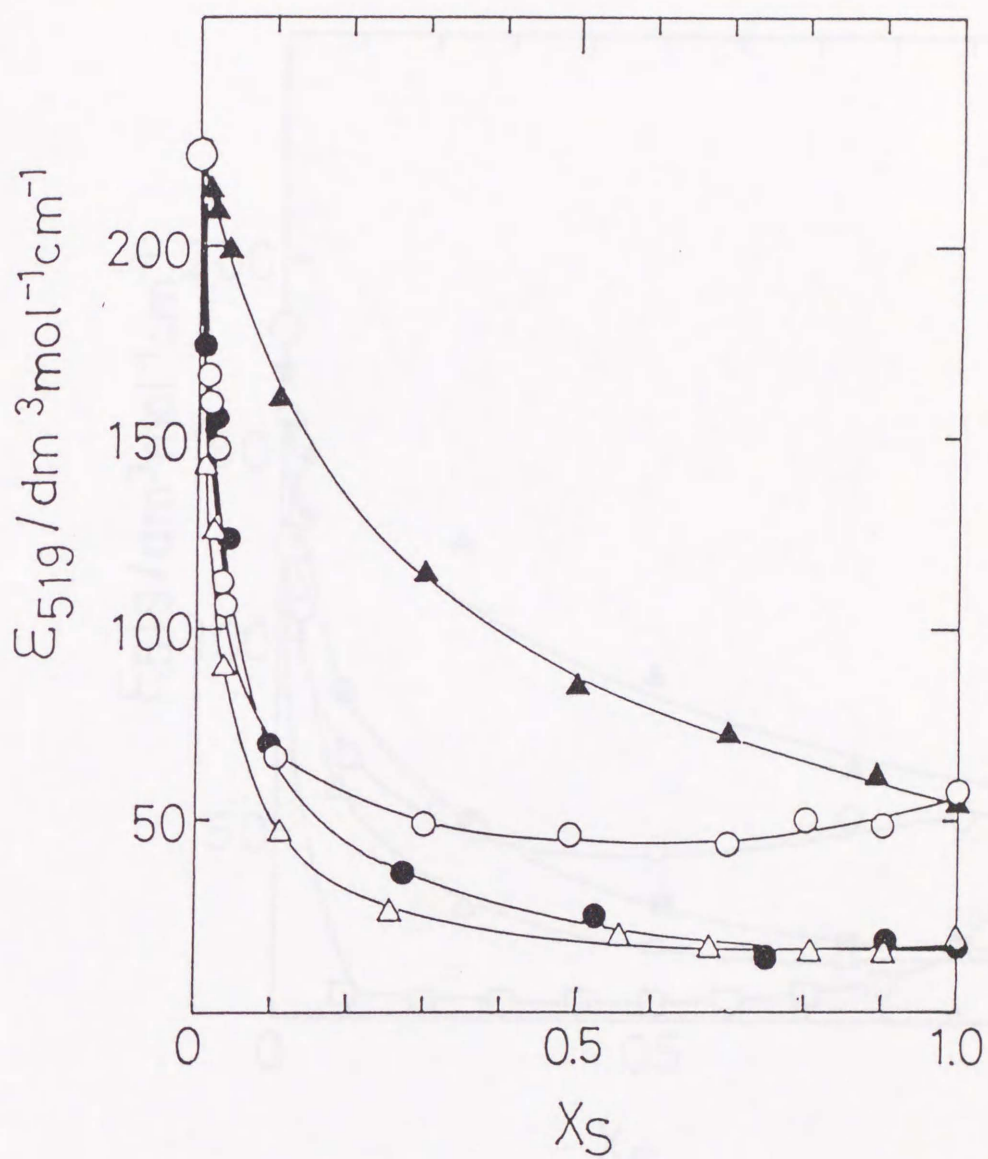


Fig. 2 Variation of molar absorptivity (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) at 519 nm of R,S,R,S-[NiL](ClO₄)₂ with the mole fraction of donor solvent in NB at 25°C. \circ , DMSO; \bullet , AN; \triangle , DMF; \blacktriangle , BzN.

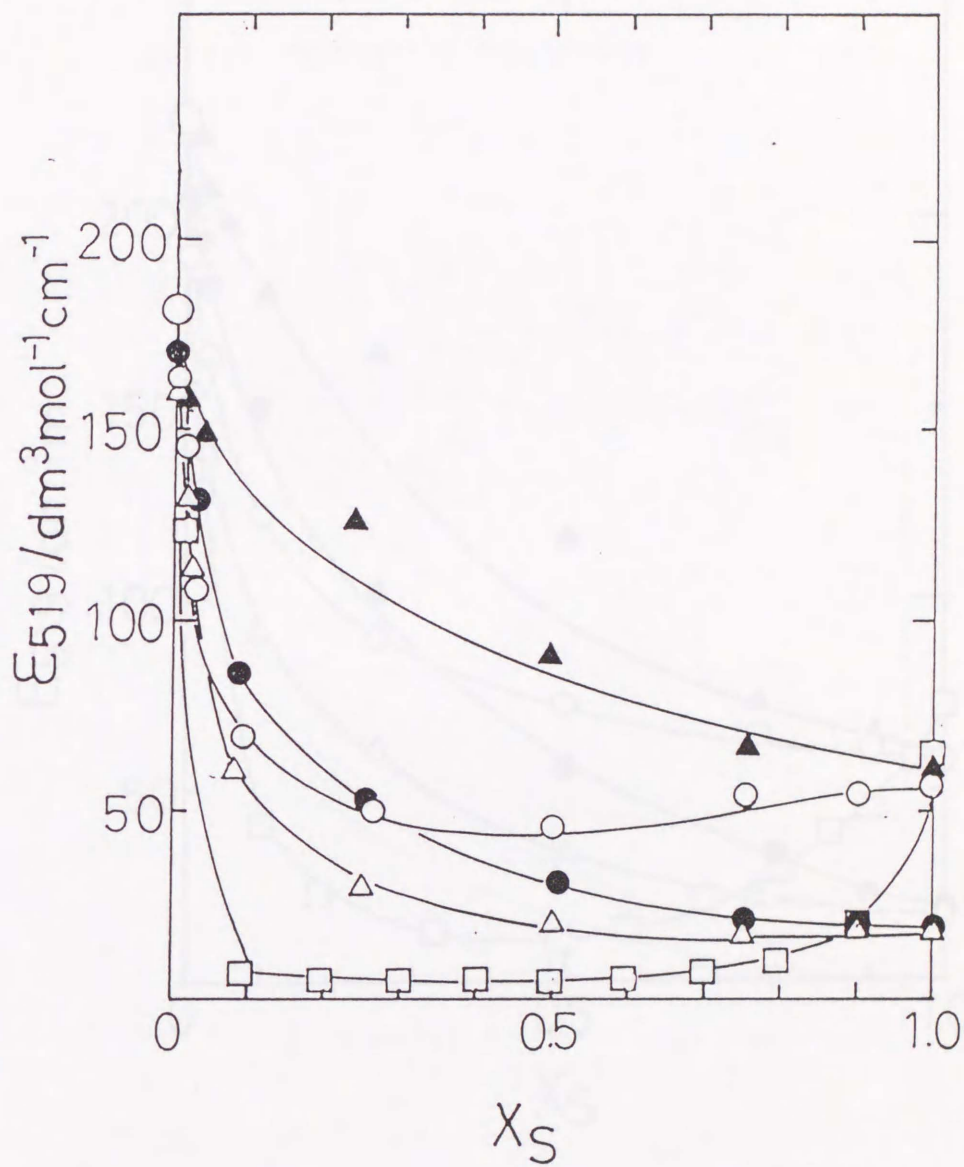


Fig. 3 Variation of molar absorptivity (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) at 519 nm of R,S,R,S-[NiL](ClO₄)₂ with the mole fraction of donor solvent in Py at 25°C. O, DMSO; ●, AN; △, DMF; ▲, BzN; □, H₂O.

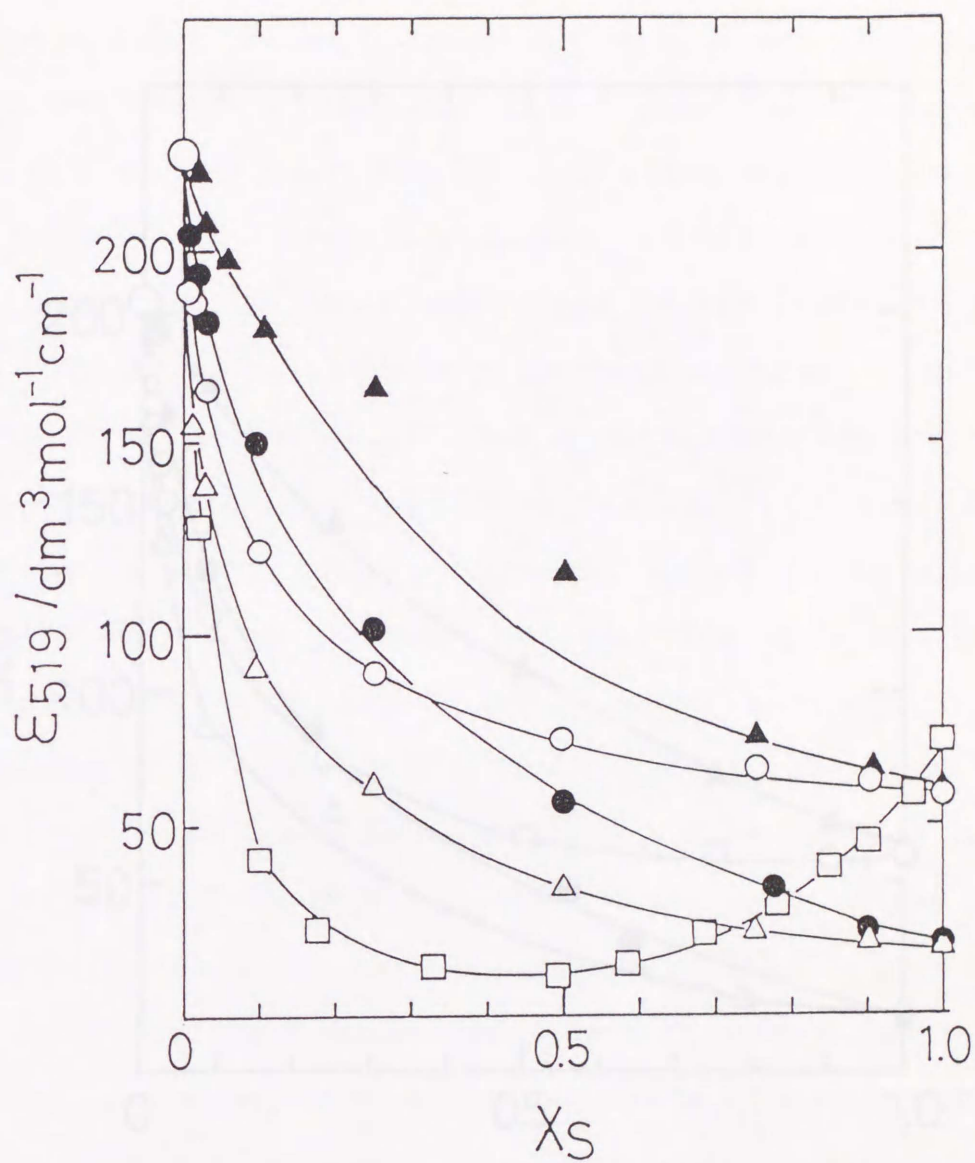


Fig. 4 Variation of molar absorptivity (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) at 519 nm of R,S,R,S-[NiL](ClO₄)₂ with the mole fraction of donor solvent in DMA at 25°C. ○, DMSO; ●, AN; △, DMF; ▲, BzN; □, H₂O.

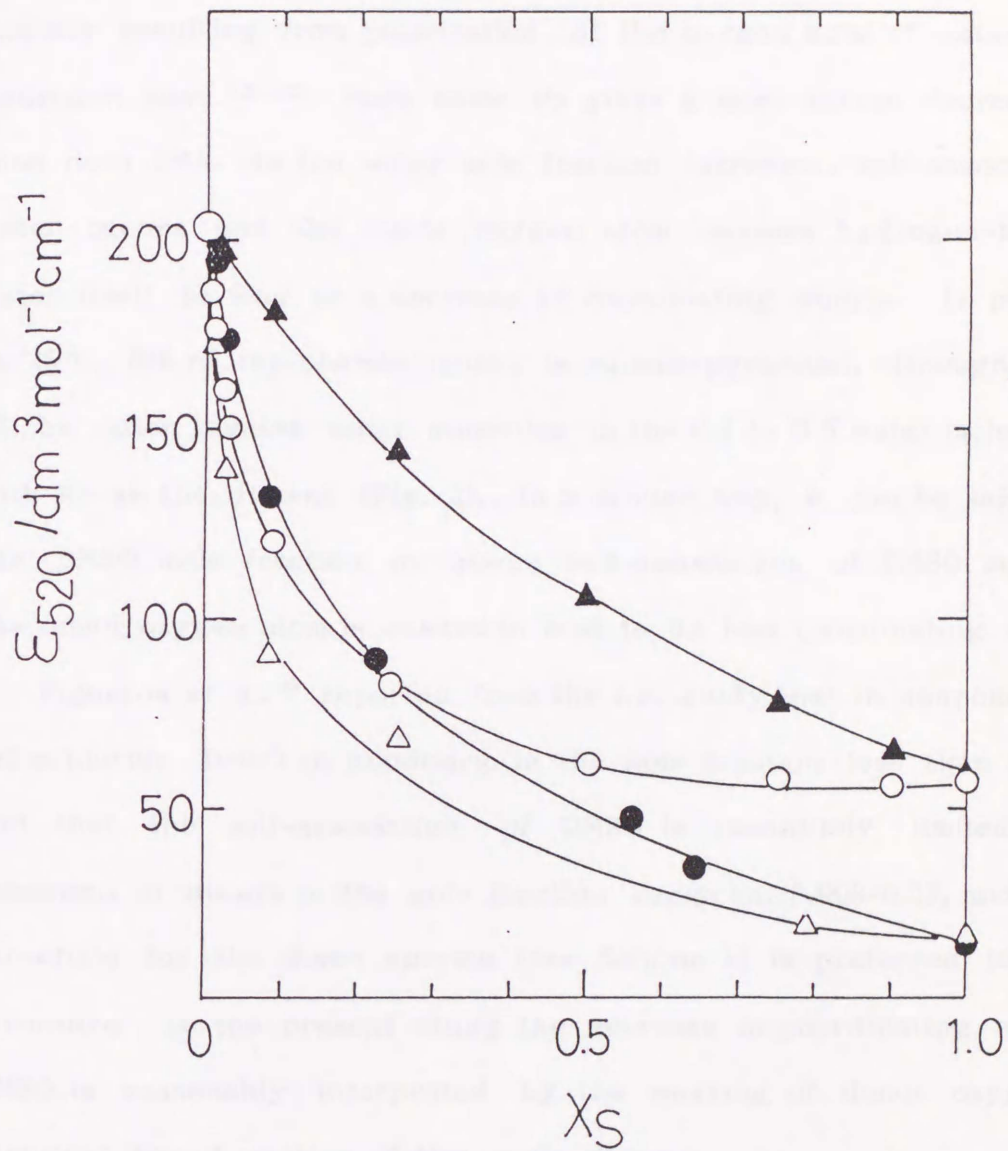
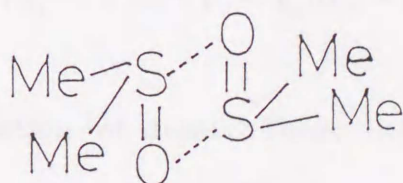


Fig. 5 Variation of molar absorptivity (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) at 519 nm of R,S,R,S-[NiL](ClO₄)₂ with the mole fraction of donor solvent in PC at 25°C. \circ , DMSO; \bullet , AN; \triangle , DMF; \blacktriangle , BzN.

coordinated to the cation, hetero-dimeric water hydrogen bonded with Py and DMA of a high basicity is easily coordinated because of the increased basicity resulting from polarization of the oxygen atom of water through hydrogen bond.^{15, 16)} More basic Py gives a more abrupt decrease in ϵ than does DMA. As the water mole fraction increases, self-association of water occurs and the donor oxygen atom becomes hydrogen-bonded to water itself to lead to a decrease in coordinating ability. In pure water at 25°C, 70% of the chelate cation is square-pyramidal, although ca. 100% of the cation ligates water molecules in the 0.1 to 0.5 water mole fraction with Py as the diluent (Fig. 3). In a similar way, it can be said that as the DMSO mole fraction increases, self-association of DMSO occurs and the donor oxygen atom is masked to lead to its less coordinating ability.

Figueroa et al.²⁰ reported from the i.r. study that in nonpolar carbon tetrachloride DMSO is monomeric in the mole fraction less than ca. 0.008, and that the self-association of DMSO is essentially limited to the formation of dimers in the mole fraction range ca. 0.008-0.03, and a cyclic structure for the dimer species (see Scheme 1) is preferred to a chain structure. In the present study the decrease in coordinating ability of DMSO is reasonably interpreted by the masking of donor oxygen atom resulting from formation of the cyclic dimer.



(Scheme 1)

The above discussion suggests a possibility for estimation of the degree of dimerization of DMSO. Now, we assume that only a monomer-dimer equilibrium exists. The apparent coordination constant $K_{\text{NiS},a}$ in mol fraction⁻¹ is

$$K_{\text{NiS},a} = (\epsilon_0 - \epsilon) / (\epsilon - \epsilon_s) C_S \quad (1)$$

where C_S is the mole fraction of the donor solvent, ϵ_0 is the molar absorptivity at 519 nm in the diluents, ϵ is the apparent molar absorptivity and ϵ_s is the molar absorptivity of the five-coordinate species ($10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Equation (1) is rewritten using the coordination constant K_{NiS} and the dimerization constant K_{dim}

$$K_{\text{NiS},a} = K_{\text{NiS}} / (1 + 2K_{\text{dim}}[S]) \quad (2)$$

where $[S]$ is the mole fraction of the monomeric donor solvent. In the diluted region of the donor solvent ($1 \gg 2K_{\text{dim}}[S]$), $K_{\text{NiS},a}$ equals to K_{NiS} . Once the K_{NiS} values are determined, $[S]$ ($= C_S - 2[S_2]$) is calculated by equation (3)

$$K_{\text{NiS}} = (\epsilon_0 - \epsilon) / (\epsilon - \epsilon_s)(C_S - 2[S_2]) \quad (3)$$

where $[S_2]$ is the concentration of dimer. Thus, the apparent dimerization constant $K_{\text{dim},a}$ is given by the equation (4)

$$K_{d_{im}, a} = [S_2] / (C_S - 2[S_2])^2 \quad (4)$$

The $K_{N_{iS}, a}$ values for DMSO were calculated in its full composition range of mixed solvents and are tabulated in Table 1. It should be noted that the $K_{N_{iS}, a}$ values are almost constant in a small fraction range of the DMSO poor region, for example less than the 0.016 DMSO mole fraction in NB, and then it decreases with increasing the DMSO mole fraction. It is concluded, therefore, that the solution of DMSO consists essentially of monomeric species in the concentration range of the constant $K_{N_{iS}, a}$ values and the decreased coordinating ability or activity is mainly attributed to self-association of DMSO. As shown in Table 2, the upper mole fraction for the identifiable region where constant $K_{N_{iS}}$ values occur decreases in the order, PC (0.15) > DMA (0.07) > NB (0.02) > Py (0.006). PC of the largest dipole moment gives the largest monomer range and Py of the smallest dipole moment gives the smallest. The stronger interaction between DMSO and the diluent would be more liable to disrupt dimerization of DMSO, leading to a larger monomer range.

The $K_{d_{im}, a}$ values obtained by equation (4) at each concentration are given in Table 1. It is seen that the $K_{d_{im}, a}$ values in each diluent are constant in a small range of the DMSO mole fraction and then increase with increasing the DMSO mole fraction except for Py. The increase in $K_{d_{im}, a}$ means that at higher mole fractions of DMSO more highly associated species occurs. It is reasonably assumed that the activity coefficients of the monomeric and dimeric DMSO species are unity, at least, in the DMSO-poor region where the $K_{d_{im}, a}$ values are constant. The $K_{d_{im}}$ value

Table 1. $K_{NiS,a}$ and $K_{dim,a}$ in various binary mixtures

NB			Py		
X_{DMSO}	$K_{NiS,a}$	$K_{dim,a}$	X_{DMSO}	$K_{NiS,a}$	$K_{dim,a}$
0.0038	40	-	0.0037	28	-
0.0053	38	-	0.0041	29	-
0.0071	40	-	0.0054	26	-
0.0090	40	-	0.013	22	13
0.0099	37	-	0.033	17	17
0.011	38	-	0.042	17	13
0.015	38	-	0.057	17	10
0.033	34	2.8	0.077	16	9.4
0.051	31	3.0	0.11	15	7.3
0.072	31	2.4	0.20	14	5.5
0.10	28	2.6	0.26	13	5.4
0.11	27	3.0	0.50	7.7	9.6
0.14	26	2.7	0.75	3.8	31
0.30	15	7.0	0.90	3.3	35
0.49	10	12			
0.70	7.5	16			
0.81	5.4	28			
0.90	5.0	30			

Table 1. (continued)

DMA			PC		
X_{DMSO}	$K_{\text{NiS,a}}$	$K_{\text{dim,a}}$	X_{DMSO}	$K_{\text{NiS,a}}$	$K_{\text{dim,a}}$
0.016	12	-	0.0084	10	-
0.017	13	-	0.011	8.5	-
0.029	12	-	0.026	9.8	-
0.034	12	-	0.028	9.0	-
0.048	11	-	0.084	8.7	-
0.065	11	-	0.12	8.7	-
0.076	9.6	2.1	0.15	8.4	-
0.084	9.8	1.6	0.21	7.8	0.49
0.099	9.1	2.2	0.24	7.4	0.56
0.13	8.9	1.7	0.27	7.5	0.46
0.20	7.4	2.6	0.32	7.0	0.62
0.25	6.7	2.8	0.35	6.8	0.66
0.50	4.9	3.5	0.40	7.0	0.50
0.75	3.9	4.3	0.50	5.3	1.2
0.90	3.6	4.3	0.75	4.1	1.9
			0.90	3.5	2.3

obtained increases in the order, Py (14) > NB (2.8) > DMA (1.9) > PC (0.6). Reported K_{dim} values in mol fraction⁻¹ at 25 °C are 5.5 in carbon tetrachloride²³ and 6.2 in carbon disulfide.²⁴ Since the diluents used in this work are polar solvents and DMSO molecules are strongly solvated by the diluents, they are more liable to break up the DMSO structure than carbon tetrachloride and carbon disulfide, leading to less K_{dim} values except for Py. It is not clear why the K_{dim} value in Py is larger than that in carbon tetrachloride although the data show some scatter.

The K_{NIS} values for another donors in diluents which were obtained in the mole fraction range less than 0.1 are tabulated in Table 2 together with donor and acceptor numbers and dipole moments (μ). These aprotic diluents can be taken as those of weak acidity. It is seen that the K_{NIS} values in all of the diluents increase in the order BzN<AN<DMSO<DMF, unlike the order of donor number, BzN<AN<DMF<DMSO: DMSO coordinates more weakly than does DMF. It has also been reported that the stability order for the five coordinate chelate in pure solvents is DMSO < DMF < AN at 25 °C.¹⁸ Although the dipole of the DMF molecule is deeply embedded, the DMSO molecule has a trigonal pyramid structure in which the dipole lies almost along the S=O bond and is exposed¹⁹: the C-S-C and C-S-O bond angles are 97.86° and 107.25°,²⁰ respectively. Therefore, it is likely that the less coordinating ability of DMSO compared with DMF is attributed both to steric hindrance imposed by the methyl groups of both DMSO and the L ligand, and to dipole-dipole interactions between DMSO and the diluents. The latter is supported by the fact that the K_{NIS} values in PC of the largest dipole moment is the smallest. The exposed

Table 2. Coordination constants (K_{NiS} in mol fraction⁻¹) in various diluents at 25°C

Donor solvent	Diluent		NB	PC	DMA	Py
	μ	D_N				
BzN	3.9	11.9	4.2	4.98	3.81	2.2
AN	3.96	14.1	4.4	15.1	27.8	33.1
DMF	3.86	26.6	14.8	18.3	13.6	14.2
DMSO	3.90	29.8	14.8	18.3	13.6	14.2
			4.3 ± 0.2	1.0 ± 0.2	4.3 ± 0.3	6.0 ± 0.3
			29 ± 2	8.6 ± 0.4	9.5 ± 1.1	15 ± 1
			56 ± 2	19 ± 1	18 ± 1	35 ± 4
			39 ± 1	9.0 ± 0.6	12 ± 1	28 ± 2

dipole and the property of the sulfur atom as an electron-pair acceptor for DMSO make the dipole-dipole interaction stronger. Of the diluents, Py of the smallest dipole moment and NB of the smallest donor number value give larger K_{NiS} values and PC of the largest dipole moment gives smaller K_{NiS} values, the results showing an important role of both dipole-dipole and electron-pair donor-acceptor interactions.

As stated earlier, the effects of self-association of DMSO on solute-solvent interactions have been often observed in mixed solvent systems. However, little anomaly is observed for solute-solvent interactions in pure DMSO. For example, the ^{23}Na chemical shift of pure DMSO²¹⁾ is the value expected from a linear correlation of the chemical shifts in several unstructured pure solvents with their donor numbers which correspond to each diluted solvent in DCE, while the chemical shift in pure water greatly deviates. The coordination of a donor solvent at the sixth site to $VO(acac)_2$ alters the positions of two absorption bands: the first band is red-shifted and the second band is blue-shifted. The difference between the first and second bands $D_{11,1}$ for pure solvents involving DMSO also gave a good linear correlation with donor numbers.^{22,23)} The octahedral $[Ni(phen)_3](ClO_4)_2$ which racemizes through an intermolecular process gave a linear relationship between the logarithms of the racemization rate constant, k_{rac} and DN,²⁴⁾ and the k_{rac} value in DMSO was larger than that in DMF as expected. $D_{11,1}$ for $VO(acac)_2$ and the racemization rate of $[Ni(phen)_3]^{2+}$ in DMSO-NB mixtures are shown in Figs. 6 and 7. The effect of DMSO's self-association is not seen: the $D_{11,1}$ and k_{rac} values for more basic DMSO are larger than those

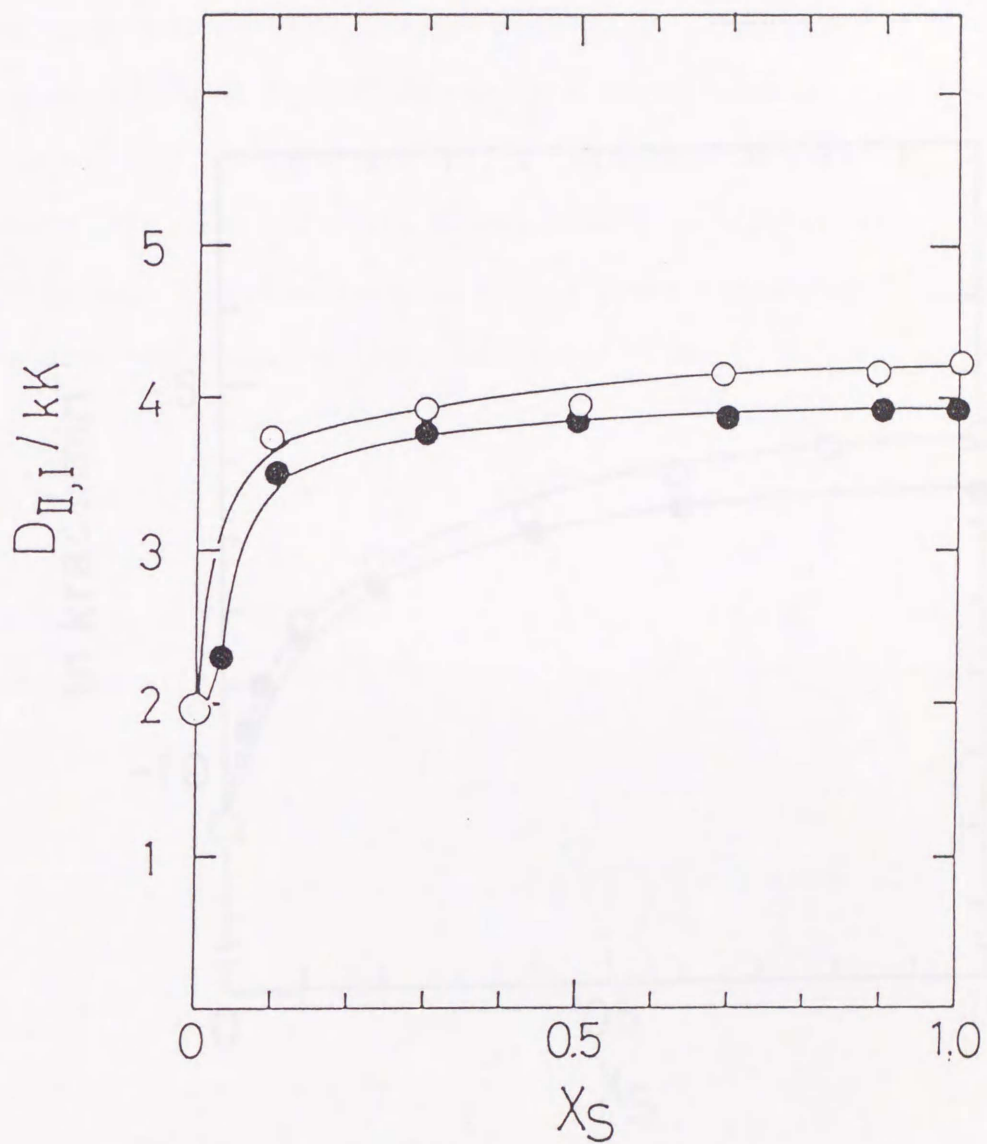


Fig. 6 Variation of the difference in kK between two absorption bands of $VO(acac)_2$ with the mole fraction of DMSO and DMF in NB. ○, DMSO; ●, DMF

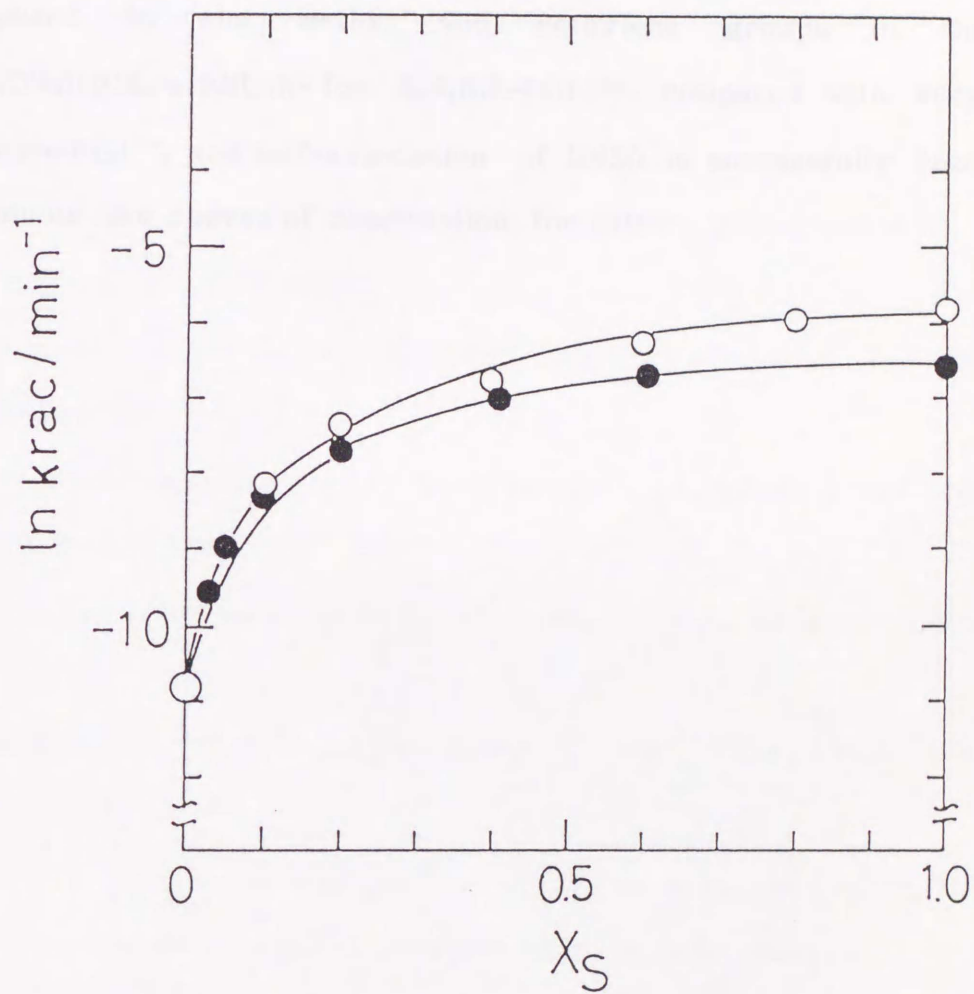


Fig. 7 Variation of the rate constants of racemization with the mole fraction of DMSO and DMF in NB. ○, DMSO; ●, DMF

for DMF over the full composition range.

It can be said that coordination of a donor solvent to the square-planar cation $R,S,R,S-[NiL]^{2+}$ is sensitively affected by the geometric conditions of the donor molecule because of steric hindrance imposed by the methyl and methylene groups in the skewed $-N(CH_3)[(CH_2)_2](CH_3)N-$ for $R,S,R,S-[NiL]^{2+}$, compared with $VO(acac)_2$ and $[Ni(phen)_3]^{2+}$, and self-association of DMSO is successfully recognized to evaluate the degree of dimerization for DMSO.

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Chapter 4

π -Back Donation of Nitriles in Nitrobenzene

1. Introduction

$[\text{NiL}]^{2+}$ has two stable isomers of R,R,S,S-nitrogen and R,S,R,S-nitrogen configurations.¹⁻⁹⁾ R,R,S,S- $[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ form the six-coordinated complexes where two solvent molecules are attached to the central nickel.^{9, 10)} However, R,S,R,S- $[\text{NiL}]^{2+}$ forms the five-coordinated complex where only one solvent molecule is attached to the nickel.⁷⁾ The rate constants for exchange reaction of the coordinated solvent have been reported in H_2O , AN and DMF.¹¹⁻¹⁴⁾ Accordingly, the observed values of enthalpy of activation for R,R,S,S- $[\text{NiL}]^{2+}$ were about twice as large as those for R,S,R,S- $[\text{NiL}]^{2+}$. It was also found that the coordination of the AN molecule to both isomers of $[\text{NiL}]^{2+}$ is stronger than that of other basic solvents.

The axial coordination constants for R,S,R,S- $[\text{NiL}]^{2+}$ in various binary mixed solvents using NB as a diluent were reported in Chapter 1, and the values obtained were decreased in the order DMF ($5.4 \text{ mol}^{-1} \text{ dm}^3$) > DMSO (3.8) > AN (3.1) > BzN (0.4), while in pure solvents, the order was AN (13.4) > DMF (10.8) > DMSO (3.5) > BzN (2.4) > H_2O (1.8).¹⁵⁾ In these cases, the coordination constant of AN molecules is larger than that expected from DN, because DN of the solvents is decreased in the order DMSO > DMF > H_2O > AN > BzN, thus suggesting π -back donation. The first and second coordination constants (K_{NiS1} and K_{NiS2}) for R,R,S,S- $[\text{NiL}]^{2+}$ have not been reported yet. An investigation of K_{NiS1} and K_{NiS2} might help in understanding the strong coordination of AN. Therefore, the stepwise coordination constants for R,R,S,S- $[\text{NiL}]^{2+}$ and a comparison with the results for R,S,R,S- $[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ in NB mixtures are reported.

2. Experimental

NB, DMF, DMSO, AN and BzN were purified as described in Chapters 1 and 3. $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$, $[\text{Ni}(\text{cyclam})](\text{BPh}_4)_2$ and $\text{R,R,S,S-}[\text{NiL}](\text{ClO}_4)_2$ were prepared according to the published methods.^{7-9, 15} The purities were confirmed by the elemental analyses of the respective complexes. The instrumentation and procedure used for measurements of conductances and spectra are as reported previously.^{16, 17}

3. Results and Discussion

NB was selected as the diluent for the donor solvents because polar NB dissolves $\text{R,R,S,S-}[\text{NiL}](\text{ClO}_4)_2$ enough to permit measurements of the molar absorptivities spectrophotometrically. As NB has a weak basicity, NB is not coordinated to both $\text{R,R,S,S-}[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$, and furthermore larger coordination constants of donor solvents were obtained in NB rather than in NM and PC in Chapters 1 and 3. Figures 1 and 2 show variations of the visible spectra for $\text{R,R,S,S-}[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ with AN concentration in NB. The wavelength of absorption maximum is 500 nm and 450 nm for the square-planar species $\text{R,R,S,S-}[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$, respectively. In both Figs. 1 and 2 the absorbance decreases with increasing donor solvent concentration.

Figures 3 and 4 show variations of the molar absorptivities for $\text{R,R,S,S-}[\text{NiL}]^{2+}$ and $[\text{Ni}(\text{cyclam})]^{2+}$ with the concentration of the donor solvents, respectively. The molar absorptivities for both complexes decreased with increasing donor solvent concentration. It should be noted that the decreasing ratio of AN is larger than those of DMF and DMSO for

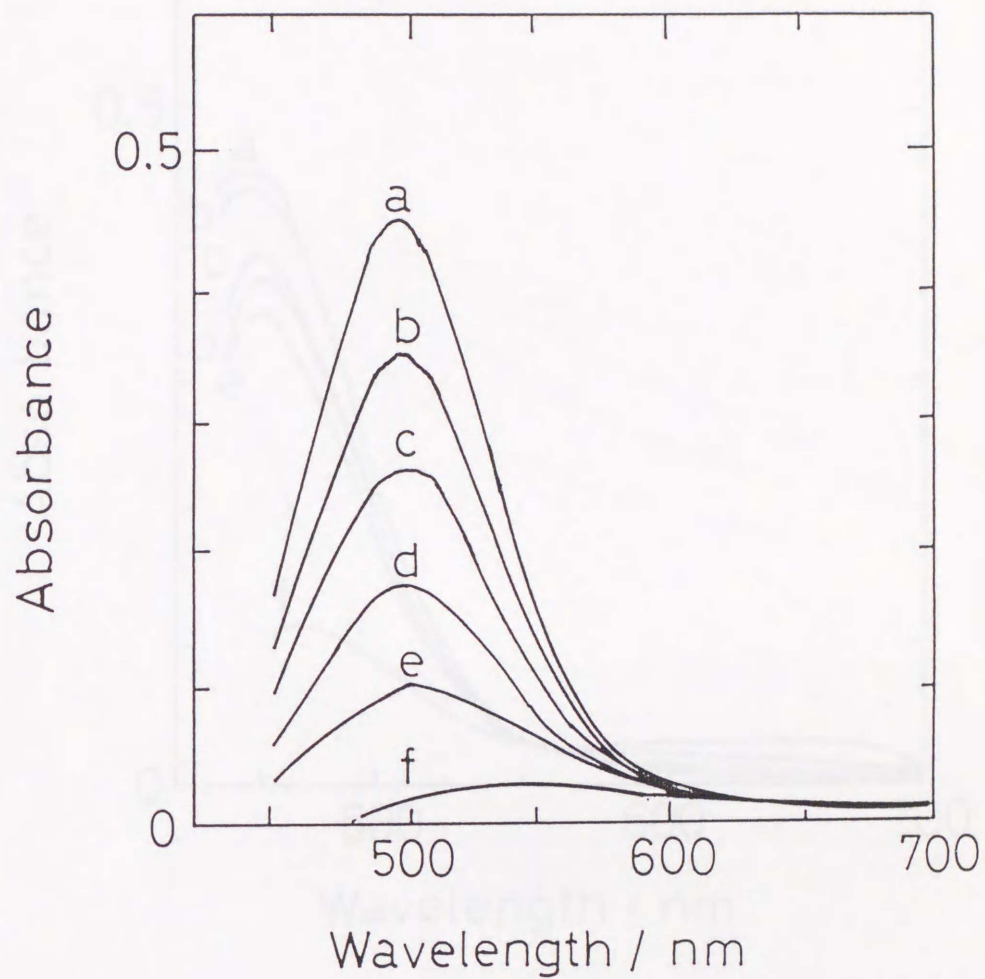


Fig. 1. Variation of the visible spectrum with AN concentration for a solution of R,R,S,S-[NiL](ClO₄)₂ (1×10^{-3} mol dm⁻³) in NB at 25 °C. AN concentration (mol dm⁻³): (a) 0.0, (b) 0.067, (c) 0.13, (d) 0.19, (e) 0.33, (f) neat.

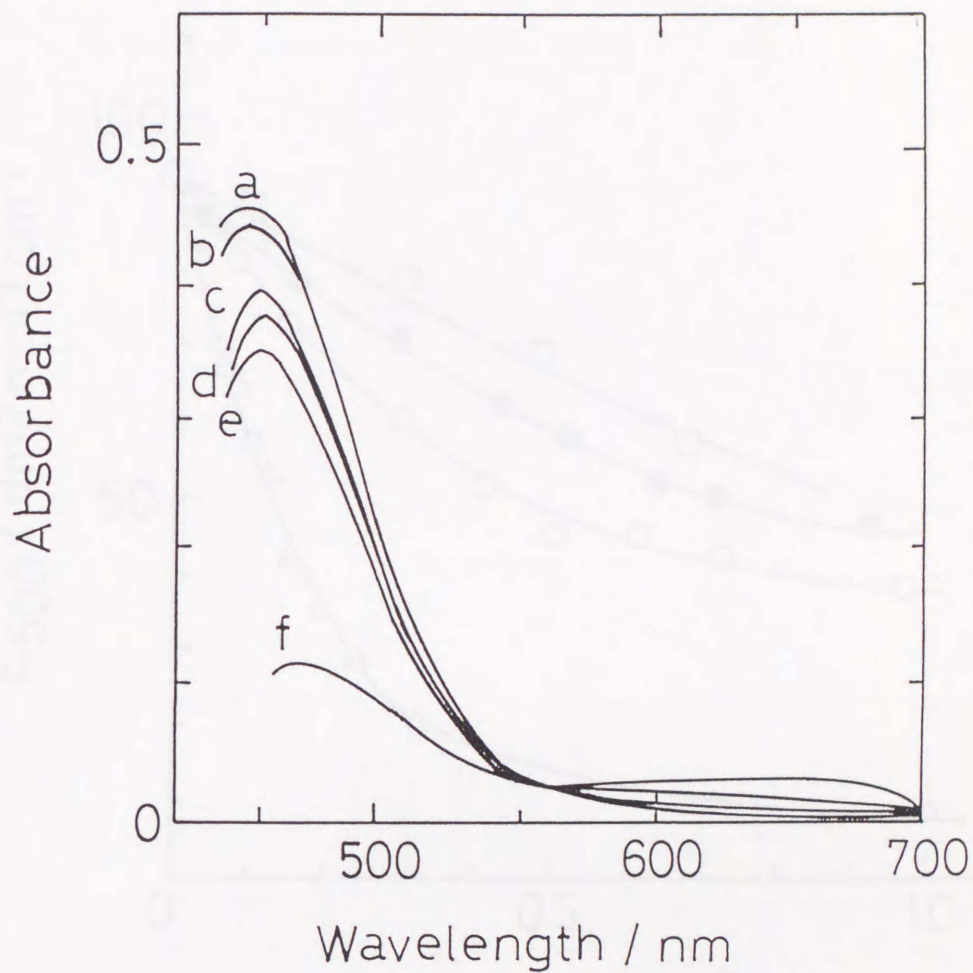


Fig. 2 Variation of the visible spectrum with AN concentration for a solution of $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ ($1 \times 10^{-3} \text{ mol dm}^{-3}$) in NB at 25 °C. AN concentration (mol dm^{-3}): (a) 0.0, (b) 0.32, (c) 0.54, (d) 0.71, (e) 1.0, (f) neat.

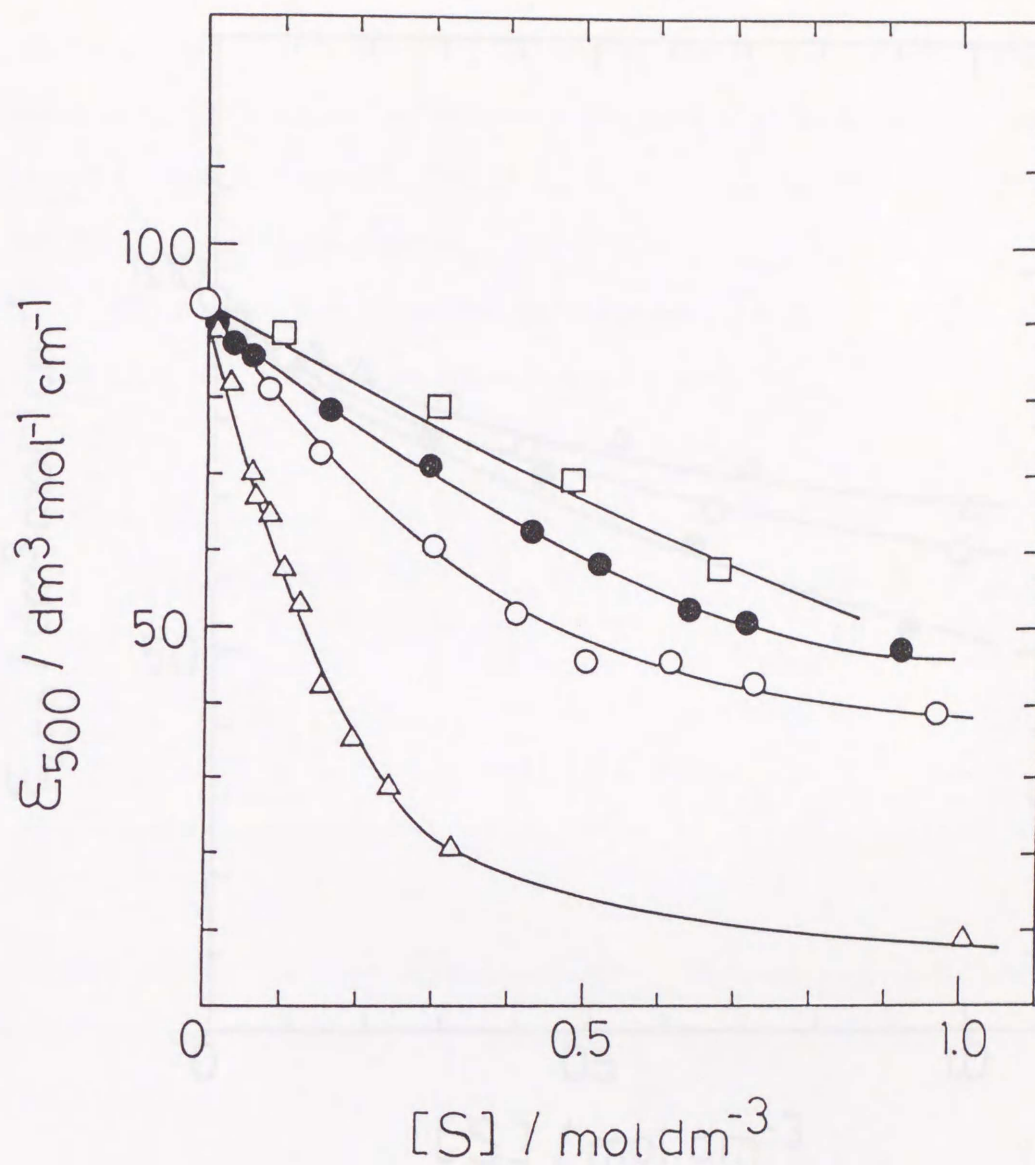


Fig. 3. Variation of molar absorptivities for R,R,S,S-[NiL]²⁺ with the donor solvent concentration in NB at 25°C. ○, DMSO; ●, DMF; △, AN; □, BzN.

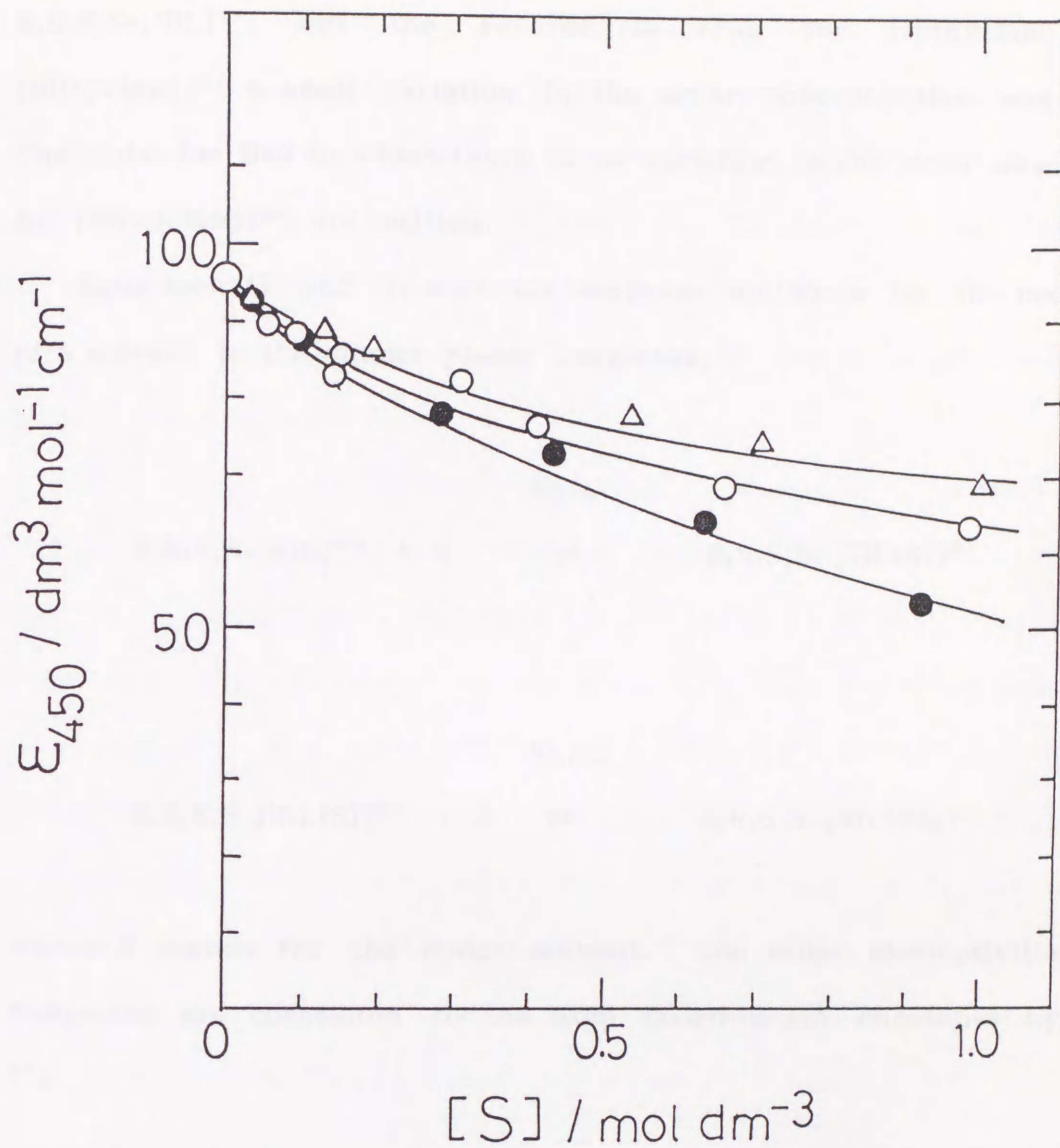
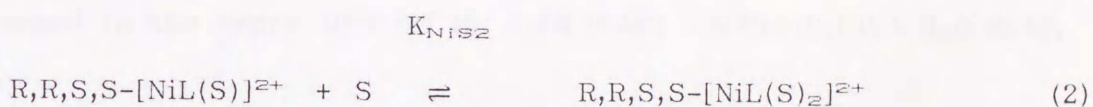
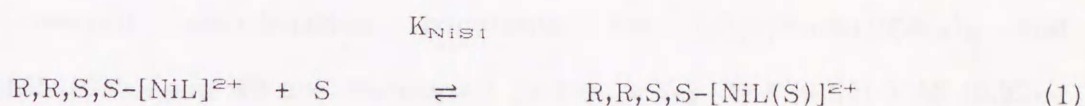


Fig. 4. Variation of molar absorptivities for $[\text{Ni}(\text{cyclam})]^{2+}$ with the donor solvent concentration in NB at 25°C. ○, DMSO; ●, DMF; △, AN.

R,R,S,S-[NiL]²⁺, but the reverse is true for [Ni(cyclam)]²⁺. For [Ni(cyclam)]²⁺ a small variation in the molar absorptivities was observed. The plots for BzN in which there is no variation in the molar absorptivities for [Ni(cyclam)]²⁺, are omitted.

Equations (1) and (2) show the stepwise equilibria for the coordination of a solvent to the square-planar complexes,



where S stands for the donor solvent. The molar absorptivities of the complexes are correlated to the axial coordination constants by equation (3).

$$(\epsilon_0 - \epsilon) / (\epsilon - \epsilon_s) [S] = K_{\text{NiS1}} + K_{\text{NiS1}} K_{\text{NiS2}} [S] \quad (3)$$

The molar absorptivity, ϵ_0 of square-planar species for R,R,S,S-[NiL]²⁺ and for [Ni(cyclam)]²⁺ is 92.2 dm³ mol⁻¹ cm⁻¹ at 500 nm and 94.9 at 450 nm, respectively. The symbol ϵ is the apparent molar absorptivity, and ϵ_s is the combined molar absorptivity for five- and six-coordinated species and is 1.0 dm³ mol⁻¹ cm⁻¹ at 500 nm for R,R,S,S-[NiL]²⁺ and 14.2 at 450 nm for

$[\text{Ni}(\text{cyclam})]^{2+}$. A typical plot of equation (3) for $\text{R,R,S,S-}[\text{NiL}]^{2+}$ is shown in Fig. 5 where a good linear relationship is obtained for all solvents used. In all the plots of Fig. 5, the concentration of S bonded to the cation is negligible compared with that of unbonded S, since the complex cation concentration used for measurements is $1 \times 10^{-3} \text{ mol dm}^{-3}$. The K_{NiS1} and K_{NiS2} values can be obtained from the intercept and slope, and the results obtained are summarized in Table 1.

The overall coordination constants for $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ and $\text{R,R,S,S-}[\text{NiL}](\text{ClO}_4)_2$ in NB are decreased in the order $\text{DMF} (0.24) > \text{AN} (0.22) > \text{DMSO} (0.021)$ and $\text{AN} (23) > \text{DMSO} (0.80) > \text{BzN} (0.76) > \text{DMF} (0.11)$, respectively. In pure solvents the overall coordination constants for $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ are decreased in the order $\text{DMF} (27.15) > \text{AN} (8.85) > \text{DMSO} (2.13) > \text{H}_2\text{O} (0.43, 0.38)$.^{18, 19}

Coordination ability of DMSO and H_2O as pure solvents is less than that expected from their basicity. This is attributed to the self-association which masks the donor oxygen atom: DMSO forms a cyclic dimer and water forms a three dimensional polymer in Chapter 3.

From Table 1, it is obvious that the coordination constants for $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ are smaller than those for $\text{R,R,S,S-}[\text{NiL}](\text{ClO}_4)_2$. This can be explained, first, through the phenomenon of hydrogen-bonding of the four N-H protons of $[\text{Ni}(\text{cyclam})]^{2+}$. Effects of hydrogen-bonding of N-H protons on ionic association in NB were studied. The ionic association constants K_a obtained by the Fuoss-Edelson method,²⁰ were 0, 1190, and 11000 $\text{mol}^{-1} \text{ dm}^3$ for $[\text{Ni}(\text{cyclam})](\text{BPh}_4)_2$, $\text{R,S,R,S-}[\text{NiL}](\text{ClO}_4)_2$, and $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$, respectively, indicating that $[\text{Ni}(\text{cyclam})](\text{ClO}_4)_2$ is

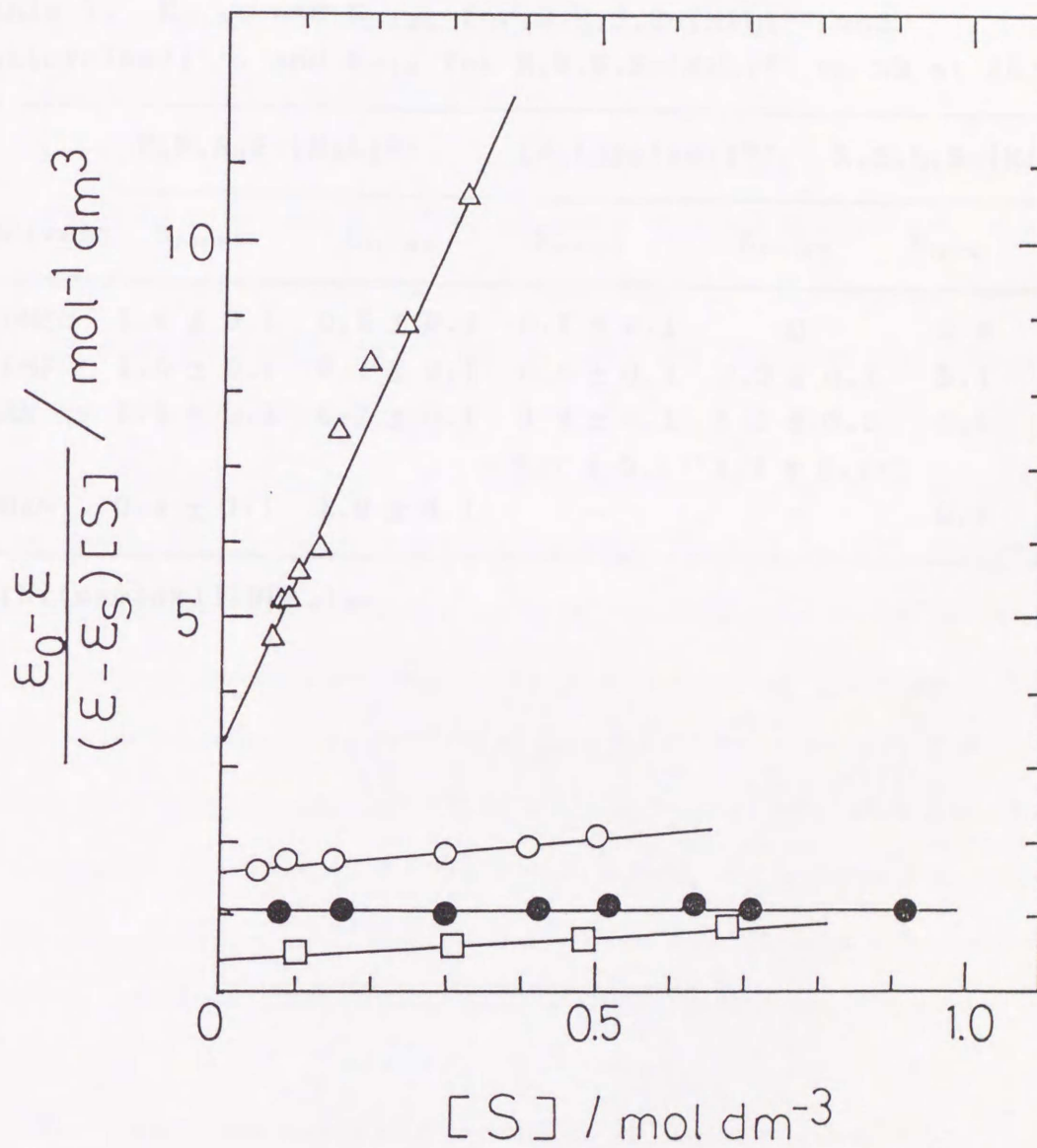


Fig. 5. Plots of $(\epsilon_0 - \epsilon) / (\epsilon - \epsilon_s)[S]$ for R,R,S,S-[NiL]²⁺. O, DMSO; ●, DMF; △, AN; □, BzN.

Table 1. K_{NiS1} and K_{NiS2} for R,R,S,S-[NiL]²⁺ and [Ni(cyclam)]²⁺, and K_{NiS} for R,S,R,S-[NiL]²⁺ in NB at 25 °C

Solvent	R,R,S,S-[NiL] ²⁺		[Ni(cyclam)] ²⁺		R,S,R,S-[NiL] ²⁺
	K_{NiS1}	K_{NiS2}	K_{NiS1}	K_{NiS2}	K_{NiS}
DMSO	1.6 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	0	3.8
DMF	1.0 ± 0.1	0.1 ± 0.1	0.8 ± 0.1	0.3 ± 0.1	5.4
AN	3.4 ± 0.3	6.7 ± 0.1	0.2 ± 0.1	1.1 ± 0.2	3.1
BzN	0.4 ± 0.1	1.9 ± 0.1	-	-	0.4

a) [Ni(cyclam)](BPh₄)₂.

greatly associative.¹⁶⁾ The difference in K_a between BPh_4^- and ClO_4^- for $[Ni(cyclam)]^{2+}$ is slightly reflected on the K_{NiS1} values: the ClO_4^- complex gives a little smaller K_{NiS1} value compared with BPh_4^- . The basic donor solvents can be also hydrogen-bonded to the N-H protons, and their attack on the central nickel is hampered.

Secondly, the stability of square-planar configuration for $[Ni(cyclam)]^{2+}$ is considered. The logarithm of the stability constant is 8.6 for $R,S,R,S-[NiL]^{2+}$ and 20.1 for $[Ni(cyclam)]^{2+}$.²¹⁾ The absorption wavelength of the d-d transition observed is 450 nm, 500 nm and 520 nm for $[Ni(cyclam)]^{2+}$, for $R,R,S,S-[NiL]^{2+}$ and for $R,S,R,S-[NiL]^{2+}$, respectively, indicating that the stability for the square-planar configuration decreases in the order $[Ni(cyclam)]^{2+} > R,R,S,S-[NiL]^{2+} > R,S,R,S-[NiL]^{2+}$. Cyclam is the secondary amines while L is the tertiary ones. As the coordination of the tertiary amine is stronger than the secondary one,²¹⁾ the stability for $[NiL]^{2+}$ must be larger than that for $[Ni(cyclam)]^{2+}$. However, the repulsion between the methyl groups of $[NiL]^{2+}$ leads to less stability for the square-planar configuration. In other words, it is easy for $[NiL]^{2+}$ to change its configuration from the square-planar into the square-pyramidal or the octahedral. Therefore, $[NiL]^{2+}$ easily receives the attack of the solvent.

Table 1 also compiles the coordination constants obtained together with K_{NiS} for $R,S,R,S-[NiL]^{2+}$. The K_{NiS1} values of DMF and DMSO are less than K_{NiS} , but those of AN and BzN are the same as K_{NiS} . The calculation of the strain energy showed that each coordination site for $R,R,S,S-[NiL]^{2+}$ is more sterically crowded than the coordination site for $R,S,R,S-[NiL]^{2+}$.^{3, 4)} It is

likely that coordination of DMF and DMSO molecules with $-N(CH_3)_2$ and two $-CH_3$, respectively, is sterically hindered, and the rod like cyano group receives little steric hindrance.

Cyano groups show a striking and different trend from other solvents. K_{NiS_2} for AN is twice as large as K_{NiS_1} , although K_{NiS_2} for DMF is only one tenth of K_{NiS_1} . This anomalous behavior of AN may refer to π -back donation. Evidence has been reported for the π -back bonding of AN: the increase of the CN stretching frequency for copper halide adducts with AN,²² the large stability constant of bis(α -furyl dioximato) diiodo-cobaltate(III) in AN,²³ the large ratio of $10Dq'$ (nickel bromide AN complex) / $10Dq'$ (nickel chloride AN complex),²⁴ the dependence of the coordination power value (the relative Gibbs free energy change for solvation of the nickel ion) on other parameters,²⁵ and the deviation of ν_{max} for the copper complexes in AN from a correlation of ν_{max} with solvent donor number.²⁶ In all these cases, AN is strongly bonded to the complex than expected from its basicity. The coordination of one AN molecule via π -back donation makes another axial trans-coordination site active (a trans-effect). On receiving the electron-pair of AN, the nickel atom loses the positive charge slightly, but when the electrons of the nickel atom flow in the AN molecule via π -back donation, the density of positive charge on nickel increases. Therefore, the larger the π -back donation becomes, the stronger the second coordination, resulting in $K_{NiS_2} > K_{NiS_1}$ for nitriles. The activation enthalpy for the loss of a single solvent molecule from $R,R,S,S-[NiL(AN)_2]^{2+}$ and $R,R,S,S-[NiL(DMF)_2]^{2+}$ are 41.5 kJ mol^{-1} and 38.3 , respectively.¹⁴ This indicates that the coordination of AN to $R,R,S,S-[NiL]^{2+}$ is stronger than

that of DMF, thus supporting π -back donation. In addition, the wavelength of the absorption maximum is 349 nm and 373 nm for the octahedral species R,R,S,S-[NiL(S)₂]²⁺ in AN and in DMF, respectively, and indicates blue-shifts in AN compared with DMF in Chapter 1.

X-ray crystallographic data showed that the deformation in the square-planar configuration of R,S,R,S-[NiL]²⁺ is larger for one AN molecule coordination than that of DMF,^{5,27,28)} hence supporting the above view. The Ni-N (ring) bond lengths for the non-coordinated, DMF-coordinated, and AN-coordinated species are 0.1960 nm, 0.2105 nm, and 0.2143 nm, respectively. For DMF-coordinated species the distance of nickel atom displaced from the N₄ plane is 0.029 nm, while for the AN-coordinated it is 0.034 nm. The trans non-coordinating axial site of R,S,R,S-[NiL(AN)]²⁺ is also activated, but the solvent cannot be coordinated because of the steric hindrance of methylene groups.

Influence of the ligand trans to O₂ on the O₂ adduct formation for the square-planar complex has already been reported.²⁹⁻³¹⁾ The coordination constants of O₂ (K_{O₂}) increases in the order H₂O < Py < imidazole (Im) < NH₃ < CN⁻ for [Co(cyclam)]²⁺, Cl⁻ < ClO₄⁻ < Br⁻ < Py < Im for [Co(Me₆(14)4,11-dien N₄)]²⁺, and ClO₄⁻ < Cl⁻ < SCN⁻ for [Co(C-meso-Me₆[14]aneN₄)]²⁺. As a matter of fact, when the axial ligand trans to O₂ is coordinated to the cobalt atom by π -back donation (e.g. CN⁻), the K_{O₂} is large. A correlation between axial ligand basicity and oxygen affinity is stronger for a fully saturated macrocycle than that for unsaturated ones.²⁹⁾ It is likely that the π -electrons of the macrocycle interrupt the approaching ligand through repulsion, resulting in a large K_{NiS₂} for R,R,S,S-[NiL]²⁺ which has a

saturated macrocyclic ligand.

In conclusion, the introduction of AN into the coordination sphere of R,R,S,S-[NiL]²⁺ is supported by π -back donation and hence AN is strongly bonded to the nickel atom. Coordination of nitriles by π -back donation activates the opposite axial trans-site of the square-planar complexes, contrary to DMF and DMSO, where no influence on its trans position is observed. The fact that K_{NiS2} is larger than K_{NiS1} for AN in AN-NB mixture, provides conclusive evidence for π -back donation to the nickel atom.

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Summary

The square-root method is a powerful tool for solving systems of linear equations. It is particularly useful for symmetric positive definite matrices. The method involves decomposing the matrix into a product of a lower triangular matrix and its transpose. This decomposition is unique and can be used to solve the system efficiently. The algorithm is stable and requires only a few operations per element. The method is widely used in numerical linear algebra and is a key component of many iterative solvers.

In Chapter 1, the mathematical foundations of the square-root method are presented. The method is derived from the Cholesky decomposition, which is a special case of the LU decomposition. The Cholesky decomposition is a factorization of a symmetric positive definite matrix into a product of a lower triangular matrix and its transpose. The square-root method is a more efficient way to compute the Cholesky decomposition. It is based on the fact that the square root of a symmetric positive definite matrix is also symmetric positive definite. This property is used to derive the square-root method, which is a more efficient and stable algorithm for solving systems of linear equations.

In Chapter 2, the square-root method is applied to the solution of systems of linear equations. The method is used to solve the system $Ax = b$, where A is a symmetric positive definite matrix. The square-root method is used to compute the Cholesky decomposition of A , which is then used to solve the system. The method is efficient and stable, and it is widely used in numerical linear algebra. The square-root method is also used in many other applications, such as in the solution of least squares problems and in the computation of the inverse of a matrix. The square-root method is a key component of many iterative solvers and is a powerful tool for solving systems of linear equations.

In Chapter 3, the square-root method is applied to the solution of systems of linear equations. The method is used to solve the system $Ax = b$, where A is a symmetric positive definite matrix. The square-root method is used to compute the Cholesky decomposition of A , which is then used to solve the system. The method is efficient and stable, and it is widely used in numerical linear algebra.

The square-planar, macrocyclic tetramine nickel complex ion, R,S,R,S-[NiL]²⁺ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) which has axial sites available for coordination was found to be a useful probe to explore the solvent-solvent and solute-solvent interactions by using the coordination constants of donor solvent, and the characteristic properties of solvents on coordination were investigated.

In Chapter 1, the coordination constants of the donor solvent to the nickel complex in nitrobenzene (NB) were determined spectrophotometrically. These were discussed from the viewpoint of steric hindrance, basicity of the donor solvent, and the solvent-solvent interaction. It was found that R,S,R,S-[NiL]²⁺ has a sterically unique coordination site.

In Chapter 2, the ion-pair formation constant by conductometry was discussed. Although N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) have an almost similar relative permittivity and basicity, DMF was coordinated to R,S,R,S-[NiL]²⁺, but DMA was not. The first ionic association constant of R,S,R,S-[NiL]²⁺ with the perchlorate ion in the mixtures with NB decreased with increasing fraction of both DMF and DMA. DMA as well as DMF in NB selectively solvated the axial coordination site of R,S,R,S-[NiL]²⁺ to change from contact ion-pairs to solvent-separated ion-pairs. Bulky and delocalized negative pole of NB of which the dipole moment is larger than that of DMF and DMA results in a weak ion-dipole interaction, leading to a larger degree of ionic association. The ionic association was discussed from the viewpoint of steric hindrance and ion-dipole interactions.

In Chapter 3, the self-association of dimethyl sulphoxide (DMSO) was

described. The dimerization constants of DMSO which are difficult to determine in dipolar solvents such as NB, DMA, propylene carbonate, and pyridine (Py) were obtained by using the dependence of the coordination constant to $R,S,R,S-[NiL]^{2+}$ on the DMSO concentration. A fraction of coordinated species of DMSO in NB and Py became maximum at ca. 0.5 DMSO mole fraction and decreases with increasing DMSO mole fraction, unlike other coordinating solvents such as acetonitrile and DMF. As the dimerization masks the coordinating oxygen atom of DMSO, the inhibition of coordination of DMSO occurs. The dimerization constants obtained were large, when the dipole moment of diluent solvent is small.

In Chapter 4, the π -back donation of nitriles was described. Coordination of dipolar aprotic solvents to $R,R,S,S-[NiL]^{2+}$ and $[Ni(cyclam)]^{2+}$ which form an octahedral complex by axial ligation of two donor molecules was investigated in NB spectrophotometrically. The second coordination constants of nitriles to $R,R,S,S-[NiL]^{2+}$ were larger than that of other oxygen atom-coordinating solvents, and furthermore, the first coordination constant was smaller than the second coordination constant for the nitriles. This extraordinariness was discussed in terms of the characteristic properties of the square-planar and macrocyclic tetramine nickel complex, and the π -back donation of nitriles.

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