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

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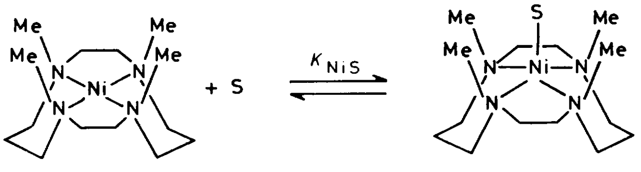
Conductance measurements of the complex *R,S,R,S*-[NiL][ClO$_4$]$_2$ (L = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane), in mixed solvents of *N,N*-dimethylacetamide (dma) and acetonitrile with nitrobenzene, which are of iso-relative permittivity, have shown that the first ion-pair formation constant (1 190 dm^3 mol^{-1}) in nitrobenzene of much lower basicity decreases with increasing fraction of dma and MeCN, although MeCN is axially bonded to the nickel but dma is hardly co-ordinated. The axial co-ordination constant, K_{NiS} = [NiL(S)$^{2+}$]/[NiL^{2+}][S], of twenty donor solvents (S) in nitrobenzene as a non-co-ordinating diluent was also determined spectrometrically. It was found that the oxygen-donor co-ordinating solvents such as acetone and water for which Gutmann's donor number (DN) is less than 20 are not co-ordinated to the nickel, and the nitrogen-donor co-ordinating solvents with a nitrile group such as acetonitrile tend to be strongly co-ordinated in spite of their lower DN. These results show no correlation of K_{NiS} with DN and are discussed in terms of the π-acceptor properties of the C–N bond, steric hindrance due to the four methyl groups, and self-interactions of the donor solvents.

It is well known that 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II), [NiL]$^{2+}$, has two stable isomers, *R,S,R,S* and *R,S,S,R* configurations at nitrogen, depending on the method of synthesis, and in co-ordinating solvents or in the presence of unidentate anions the former and latter isomers readily form five- and six-co-ordinate 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 (1) has been studied in water, dimethylformamide, dimethyl sulphoxide, and acetonitrile 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 we reported[16] that nitrobenzene and *N,N*-dimethylacetamide solutions of *R,S,R,S*-[NiL]$^{2+}$ are red, showing that both these solvents are not co-ordinated; water dissolved in nitrobenzene is not co-ordinated to the complex cation, but when dissolved in *N,N*-dimethylacetamide it is easily co-ordinated to give green solutions. These phenomena suggest that [NiL]$^{2+}$ exhibits unique axial interactions with solvents.



The axial interactions of square-planar complexes have been examined with respect to the co-ordinating and solvating ability of solvents: 1,4,8,11-tetra-azacyclotetradecanenickel(II), [Ni(cyclam)]$^{2+}$,[17,18] *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecanecopper(II),[18] bis(dimethylglyoximato)cobalt(III),[19] and mixed-ligand copper(II) complexes of ethylenediamine and β-diketones.[20,21] The complex [Ni(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 order of adducts formed by the axial co-ordination was dimethylformamide > acetonitrile > dimethyl sulphoxide > water.[17] This order was not predicted by the basicity of the solvents and it was suggested that, compared to water, rod-like acetonitrile molecules would more effectively enter into the first co-ordination sphere due to weak interaction with NH protons on the ligand. Conductance measurements for [Ni(cyclam)][ClO$_4$]$_2$ in nitrobenzene[24] 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 [NiL]$^{2+}$ without NH protons possesses only a single free co-ordination site and so it is interesting to investigate systematically its axial interactions.

In this study the ion-pair formation constants of *R,S,R,S*-[NiL]$^{2+}$ with the perchlorate ion were determined by conductance measurements and are discussed in relation to the axial co-ordination of solvents. The perchlorate salt was selected in order to minimize specific anionic interactions with solvents and the cation. Equilibrium (1) in nitrobenzene as a non-co-ordinating 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 the donor solvents.

Experimental

The salts $[NiL][ClO_4]_2$ with *R,S,R,S* and *R,S,S,R* nitrogen configurations were prepared by the published methods,[1,2,25,26] and were recrystallized from acetone–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*-$[NiL][ClO_4]_2$: C, 32.70; H, 6.25; N, 11.00. Found for *R,S,S,R*-$[NiL][ClO_4]_2$: C, 32.80; H, 6.50; N, 11.10%). The salt *R,S,R,S*-$[NiL(N_3)]ClO_4$ was prepared by adding sodium azide to an aqueous *R,S,R,S*-$[NiL][ClO_4]_2$ solution[26] and recrystallized from methanol–diethyl ether mixtures {Found: C, 36.80; H, 7.35; N, 21.70. Calc. for $[NiL(N_3)]ClO_4$: C, 36.85; H, 7.05; N, 21.45%}.

Nitrobenzene (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. Nitromethane, dimethylformamide (dmf), dimethyl sulphoxide, hexamethylphosphoramide $[P(NMe_2)_3O]$, *N,N*-dimethylacetamide (dma), $CH_3\overline{CHOC(O)OCH_2}$ (pdc), and pyridine (py) (reagent grade, Wako) were purified by fractional distillation under reduced pressure. Acetonitrile, acetone, and methanol were purified by fractional distillation. Benzonitrile, propionitrile, n-butyronitrile, and *N,N*-dimethylpropionamide (dmp) (reagent grade, Tokyo Kasei Kogyo Co., Ltd.), and *N,N*-diethylformamide (def), *N,N*-diethylacetamide (dea), *N,N*-dimethylacrylamide (dmac), and *N,N*-dimethylbenzamide (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 1.6×10^{-9}—3×10^{-7} for $PhNO_2$–MeCN mixtures, 1.6×10^{-9}—3×10^{-7} for $PhNO_2$–dma, 4.5×10^{-8} for pdc, 2.1×10^{-7} for Me_2SO, 3.7×10^{-7} for dmf, 8.3×10^{-8} for Me_2CO, and 6.6×10^{-7} for $MeNO_2$.

The instrumentation and the procedure used for 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 meter equipped with a dielectric constant cell shielded with wire netting in a water-bath thermostatted to 25 ± 0.01 °C. Carbon tetrachloride, $PhNO_2$, MeCN, 1,2-dichloroethane, 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.[16]

Results and Discussion

The *R,S,R,S*, *R,S,S,R*, and *R,S,R,R* isomers of $[NiL]^{2+}$ 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 the *R,S,R,S* and *R,S,S,R* isomers in $PhNO_2$, MeCN, and dmf at 25 °C are shown in Figure 1. The maximum wavelength $\lambda_{max.}$ in nm and the molar absorptivity $\varepsilon_{max.}$ in $dm^3\ mol^{-1}\ cm^{-1}$ of the *R,S,R,S* isomer are 610 (37) and 382 (119) in MeCN, 660 (41) and 400 (131) in dmf, and 519 (224) in $PhNO_2$; literature values are 610 (39.6) and 386 (128),[5] and 610 (34) and 390 (118)[2] in MeCN. The corresponding values for the *R,S,S,R* isomer are 543 (6.0) and 349 (14) in MeCN, 503 (21) and 373 (20) in dmf, and 498 (92) in $PhNO_2$; literature values in MeCN are 540 (5.9) and 340 (14.0).[5] The absorption peaks at 519 and 498 nm in $PhNO_2$ 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 MeCN and dmf indicate complete and almost complete conversion of the low-spin into the high-spin species, respectively, and those in $PhNO_2$ indicate no conversion. A blue shift of the absorption peaks occurs for the MeCN adduct compared to the dmf adduct.

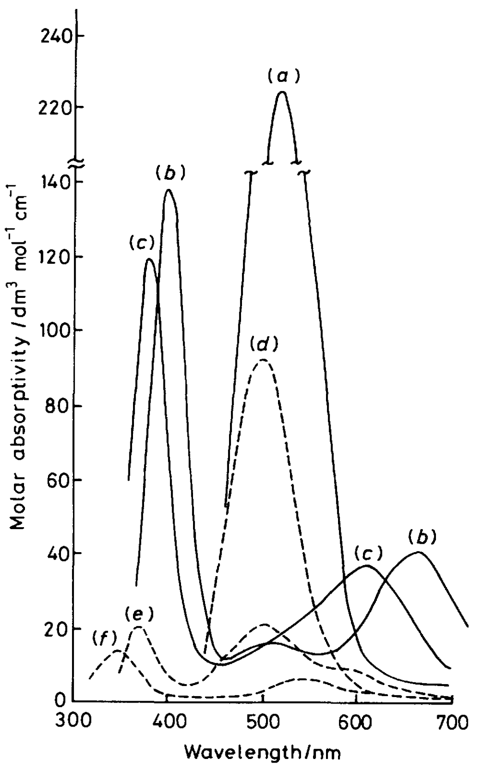


Figure 1. Visible absorption spectra for the *R,S,R,S* and *R,S,S,R* isomers of $[NiL][ClO_4]_2$ in some organic solvents at 25 °C. For the *R,S,R,S* isomer: (*a*) $PhNO_2$; (*b*) dmf; (*c*) MeCN. For the *R,S,S,R* isomer: (*d*) $PhNO_2$; (*e*) dmf; (*f*) MeCN

As the $\varepsilon_{max.}$ values for the *R,S,S,R* 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 nitrobenzene, except for $P(NMe_2)_3O$ 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,S,S,R* isomers is negligible under the present experimental conditions.

Ion-pair Formation.—Conductances for the *R,S,R,S* isomers of $[NiL][ClO_4]_2$ and $[NiL(N_3)]ClO_4$ 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 $PhNO_2$–MeCN mixtures which are of iso-relative permittivity are shown in Figure 2. All the solutions of $[NiL(N_3)]ClO_4$ are green, the complex cation being five co-ordinate.[26] The large conductances in MeCN are due to its low viscosity.

The conductances for the 2:1 electrolyte $[NiL][ClO_4]_2$ were analysed 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

$$[NiL]^{2+} + ClO_4^- \overset{K_{a1}}{\rightleftharpoons} [NiL]ClO_4^+ \quad (2)$$

$$[NiL]ClO_4^+ + ClO_4^- \overset{K_{a2}}{\rightleftharpoons} [NiL][ClO_4]_2 \quad (3)$$

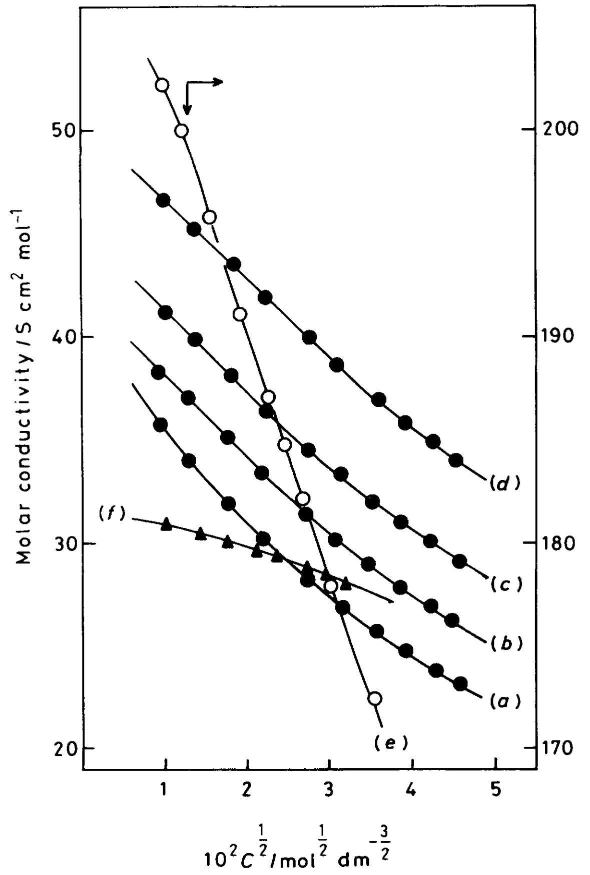


Figure 2. Plots of the molar conductivities of $\frac{1}{2}[NiL][ClO_4]_2$ and $[NiL(N_3)]ClO_4$ against the square root of the concentration in $PhNO_2$–MeCN mixtures at 25 °C. Acetonitrile fraction: for *R,S,R,S*-$[NiL][ClO_4]_2$, (*a*) 0.0, (*b*) 0.038, (*c*) 0.093, (*d*) 0.178, (*e*) 1.0; for *R,S,R,S*-$[NiL(N_3)]ClO_4$, (*f*) 0.0

perchlorate ion outside the square bracket refers to an ion pair formed by long-range electrostatic forces. As shown in Figure 1, the $PhNO_2$ 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 $[NiL(N_3)]ClO_4$, the cation of which is regarded as approximately as $[NiL]ClO_4^+$, were measured. The limiting molar conductance of the perchlorate ion, $\lambda_0(ClO_4^-)$, was estimated using the Fuoss–Coplan split,[29] $\Lambda_0[NBu(CH_2CH_2CHMe_2)_3BPh_4]/2 = \lambda_0[NBu(CH_2CH_2CHMe_2)_3^+]$. The conductance data for 1:1 electrolytes were analysed by the Fuoss–Hsia conductance equation.[30] Results are given for pure solvents in Table 1 and for $PhNO_2$–MeCN and $PhNO_2$–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 $[NiL][ClO_4]_2$ in pyridine were measured in the concentration range 1.4×10^{-4}—4.2×10^{-3} mol dm^{-3}, they could not be reasonably analysed by any method.

The five solvents, *i.e.* dma, dmf, $MeNO_2$, MeCN, and $PhNO_2$, have nearly the same relative permittivity although different basicities. When the distance of closest approach between Ni^{II} and ClO_4^- is 0.5 nm, the Bjerrum equation of electrostatic association[31] predicts $K_{a1} = 20$ and $K_{a2} = 0$ for pdc, 80 and 2 for Me_2SO, 200 and 8 for dmf, 250 and 10 for MeCN, 300 and 12 for $PhNO_2$, and 8 400 and 130 dm^3 mol^{-1} for Me_2CO. The results obtained show that the complex forms ion pairs more readily in $PhNO_2$ and less so in dma and dmf than expected from electrostatic theory. Since K_{a1} and K_{a2} for $[Ni(cyclam)][ClO_4]_2$ in $PhNO_2$ are 11 000 and 620 dm^3 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, MeCN and dma. As shown in Figure 1, since MeCN 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 co-ordination 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 co-ordinated in $PhNO_2$ compared to MeCN as will be shown later, dma has the same effect on ion-pair formation as MeCN; also dma molecules in neat dma are hardly bonded to the nickel but result in complete dissociation of the

Table 1. Solvent parameters and conductances for *R,S,R,S*-$[NiL][ClO_4]_2$ in pure solvents at 25 °C

Solvent	D	$10^2\eta$/Pa s	$\lambda_0(ClO_4^-)$/S cm^2 mol^{-1}	$\Lambda_0(\frac{1}{2}MX_2)$/S cm^2 mol^{-1}	$r_s{}^a$/nm	K_{a1}/dm^3 mol^{-1}	K_{a2}/dm^3 mol^{-1}
pdc	64.4	2.530	18.4	33.98	0.42	0	0
Me_2SO	46.68	1.996	24.4	42.87	0.44	0	0
dma	37.78	0.919	43.5	76.72	0.54	0	0
dmf	36.71	0.802	51.7	92.76	0.50	6 ± 3	0
$MeNO_2$	36.67	0.627	53.8	104.2	0.52	155 ± 5	0
MeCN	36.0	0.344	103.7[b]	212.2	0.44	190 ± 5	0
$PhNO_2$	34.82	1.842	21.1	39.2	0.49	1 190 ± 10	12 ± 1
Me_2CO	20.7	0.304	118.35[c]	217.0	0.55	12 200 ± 20	155 ± 1

[a] Stokes' radii. [b] C. H. Springer, J. F. Coetzee, and R. L. Kay, *J. Phys. Chem.*, 1969, **73**, 471. [c] D. F. Evans, J. Thomas, J. A. Nadas, and S. M. A. Mateshich, *J. Phys. Chem.*, 1971, **75**, 1714.

Table 2. Solvent parameters and conductances for the *R,S,R,S* isomers of $[NiL][ClO_4]_2$ and $[NiL(N_3)]ClO_4$ in mixed solvents of MeCN and dma with $PhNO_2$ at 25 °C

				$[NiL][ClO_4]_2$				$[NiL(N_3)]ClO_4$		
Solvent	D	$10^2\eta$/Pa s	$\lambda_0(ClO_4^-)$/S cm² mol⁻¹	$\Lambda_0(\frac{1}{2}MX_2)$/S cm² mol⁻¹	$r_s{}^a$/nm	K_{a1}/dm³ mol⁻¹	K_{a2}/dm³ mol⁻¹	Λ_0/S cm² mol⁻¹	$r_s{}^a$/nm	K_a/dm³ mol⁻¹
X(MeCN)[b]										
0.0	34.82	1.8415	21.1	39.2	0.49	1 190 ± 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(dma)[b]										
0.0	34.82	1.8415	21.1	39.2	0.49	1 190 ± 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.

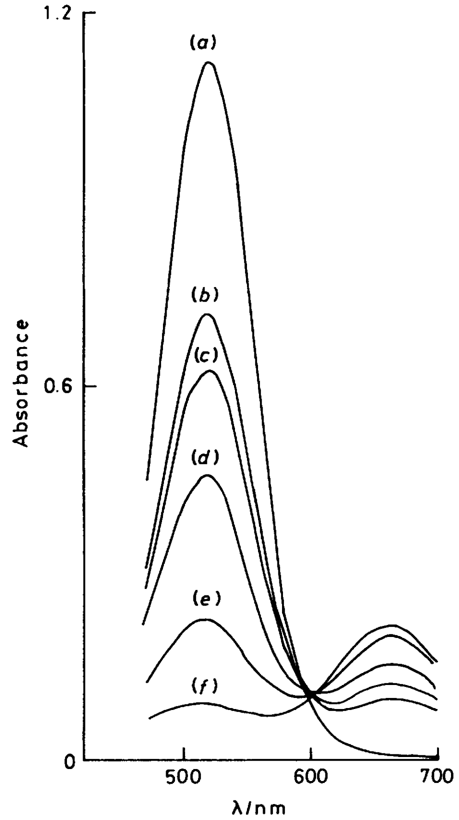


Figure 3. Variation of the visible spectrum with the dmf concentration for a 1.0×10^{-3} mol dm⁻³ solution of $[NiL][ClO_4]_2$ in $PhNO_2$ at 25 °C. Dimethylformamide concentration (mol dm⁻³): (*a*) 0.00, (*b*) 0.102, (*c*) 0.151, (*d*) 0.301, (*e*) 1.01, and (*f*) neat

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 co-ordination plays an important role. A similar effect is observed for $[NiL(N_3)]ClO_4$ for which K_a slightly decreases with increasing MeCN 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 N_3 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 co-ordination sphere is easily displaced by solvating donor solvents. However, such solvation is too weak to be reflected in the Stokes radii.

Co-ordination 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 co-ordinate to the nickel, and to interact as little as possible with donor solvents added. Therefore, dipolar aprotic solvents, *i.e.* $PhNO_2$, $MeNO_2$, and pdc, were examined as diluents. Nitrobenzene (donor number,[32] DN = 4.4) and $MeNO_2$ (DN = 2.7) are of low basicity and do not co-ordinate, although in $PhNO_2$ the complex forms ion pairs; pdc is not co-ordinated 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*-$[NiL][ClO_4]_2$ in $PhNO_2$ with dmf content are shown in Figure 3. The amount of the five-co-ordinate 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 nickel(II).

The equilibrium constant (K_{NiS}) for co-ordination of donor solvents was evaluated using equation (4)[33] where ε_0 is the

$$1/(\varepsilon_0 - \varepsilon) = 1/(\varepsilon_0 - \varepsilon_s) + 1/(\varepsilon_0 - \varepsilon_s)K_{NiS}[S] \quad (4)$$

molar absorptivity at 519 nm in $PhNO_2$ (224 ± 1 dm³ mol⁻¹ cm⁻¹), ε is the apparent molar absorptivity, and ε_s is the molar absorptivity of the five-co-ordinate 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 1×10^{-3} 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 MeCN, dmf, and Me_2SO obtained in the three diluents are given in Table 3. The largest values were obtained in $PhNO_2$ for all the three donor solvents, although *ca.* 50% of the complex forms ion pairs with the perchlorate ion at 1×10^{-3} 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 $MeNO_2$ and pdc may be attributed to their higher acidities ($MeNO_2$, acceptor number,[34] AN = 20.5; pdc, AN = 18.3), while for $PhNO_2$ AN = 14.8. Therefore, $PhNO_2$ was selected as diluent throughout the co-ordination study.

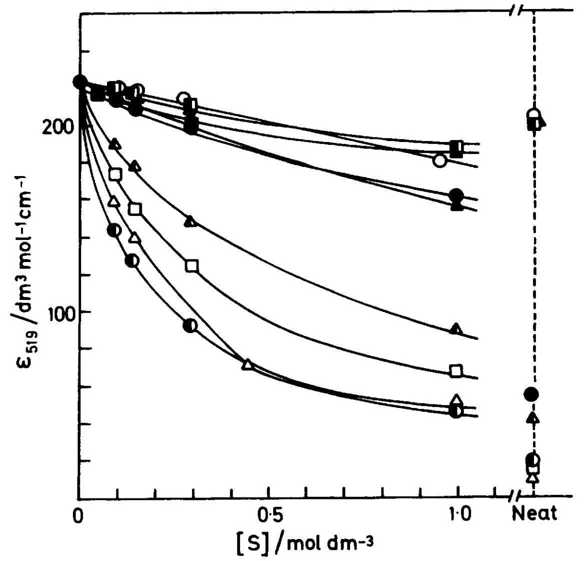


Figure 4. Variation of molar absorptivity at 519 nm with the donor solvent concentration in $PhNO_2$ at 25 °C: (◧) dma, (■) $PO(OBu)_3$, (●) PhCN, (○) dmp, (◭) Pr^{n}CN, (□) MeCN, (△) def, (◐) dmf, and (▲) dea

Table 3. Co-ordination constants K_{NiS} [equation (4)] in $PhNO_2$, $MeNO_2$, and pdc at 25 °C

Donor solvent	$PhNO_2$	$MeNO_2$	pdc
MeCN	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
Me_2SO	4.4 ± 0.2	1.0 ± 0.1	1.0 ± 0.2

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, and 0.03 mol dm^{-3} for $P(NMe_2)_3O$. Figure 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 co-ordinated.

These absorbance data were plotted according to equation (4) (Figure 5). In all cases good linear relationships were

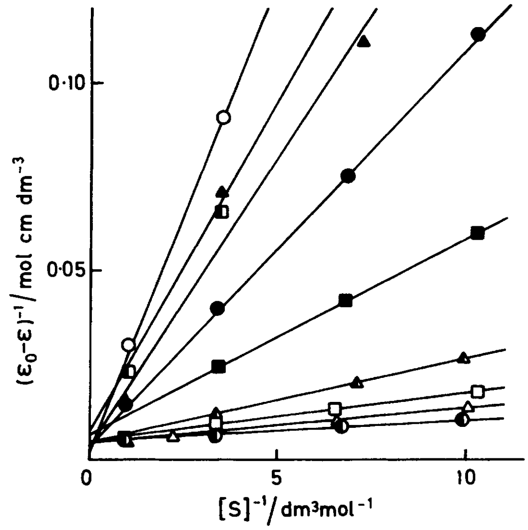


Figure 5. Benesi–Hildebrand plot [equation (4)] for various donor solvents in $PhNO_2$ at 25 °C. Symbols as in Figure 4

Table 4. Molar absorptivity ($\varepsilon_{max.}$) in pure solvents and co-ordination constants of various donor solvents with *R,S,R,S*-$[NiL]^{2+}$ in $PhNO_2$ at 25 °C

Solvent	DN[a]	$\varepsilon_{max.}$[b]/dm^3 mol^{-1} cm^{-1}	K_{NiS}[c]/dm^3 mol^{-1}	K_{NiS}[d]/dm^3 mol^{-1}
$MeNO_2$	2.4	181	0	
$PhNO_2$	4.4	224	0	
PhCN	11.9	54	0.4 ± 0.1	0.3 ± 0.1
MeCN	14.1	16[e]	3.1 ± 0.1	3.4 ± 0.2
pdc	15.1	202	0	
EtCN	16.1	17[e]	3.1 ± 0.1	2.8 ± 0.3
Pr^{n}CN	16.6	43[e]	1.9 ± 0.1	2.0 ± 0.1
Me_2CO	17.0	192	0	
Water	18	75	0	
MeOH	19.0	184	0	
$PO(OBu)_3$	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	
Me_2SO	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	
$P(NMe_2)_3O$	38.8	5[e]	13—53	

[a] Donor number 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-co-ordinate species. [c] From equation (5). [d] From equation (4). [e] No peak for four-co-ordinate species is found and so the values are at 519 nm.

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 dm^3 mol^{-1} cm^{-1} for PhCN. 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 $\varepsilon_s = 10$ dm^3 mol^{-1} cm^{-1} obtained in neat def. In the case of strongly basic $P(NMe_2)_3O$, equation (4) gave a negative intercept and equation (5) increasing K_{NiS} with

$$K_{NiS} = (\varepsilon_0 - \varepsilon)/(\varepsilon - \varepsilon_s)[S] \qquad (5)$$

increasing concentration of $P(NMe_2)_3O$. 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 methanol in various donor solvents with the DN values of the solvents.[37]

The equilibrium constants show three main trends: (*a*) there is no correlation of K_{NiS} with DN of the solvents; (*b*) oxygen-donor solvents for which DN is less than 20 are not co-ordinated; (*c*) the nitrogen atom of nitriles tends to be co-ordinated in spite of their lower DN.

Trend (*a*) arises partly from steric factors involving the four N-methyl groups. The co-ordinated 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 co-ordinated 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 co-ordinated in their dilute solutions in $PhNO_2$ and dmp with the ethyl substituent is also co-ordinated to a similar extent. It should be noted that neat dma, dmp, and dea are hardly co-ordinated as evidenced by their large molar absorptivity (Table 4).

A similar trend is also seen for Me_2SO: it is easily bonded to the nickel in $PhNO_2$ but not always so in neat Me_2SO, in view of the fact that neat Me_2SO gives a higher $\varepsilon_{max.}$ of 56 dm^3 mol^{-1} 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-co-ordination of water in trend (*b*) is not due to steric hindrance because water molecules hydrogen-bonded to dma[16] are co-ordinated with an equilibrium constant of 6.7, and the water dimers[38] in $MeNO_2$, pdc, and Me_2CO are co-ordinated 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, $MeNO_2$ < pdc < Me_2CO < dma, was reasonably explained by polarization of O–H bonds through hydrogen bonding. Popov and co-workers[39] 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 Gutmann[40] introduced the concept of 'bulk donicity' to characterize the higher donicity of liquid water resulting from hydrogen bonding. Methanol hydrogen-bonded to dma was found not to be co-ordinated. It is likely that the co-ordination of the oxygen atom attached to the methyl group is sterically hindered.

It has been pointed out that MeCN is a much stronger Lewis base than water toward nickel(II) tetra-amine complexes.[41] The rod-like shape of the nitrile group is favourable for co-ordination[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.

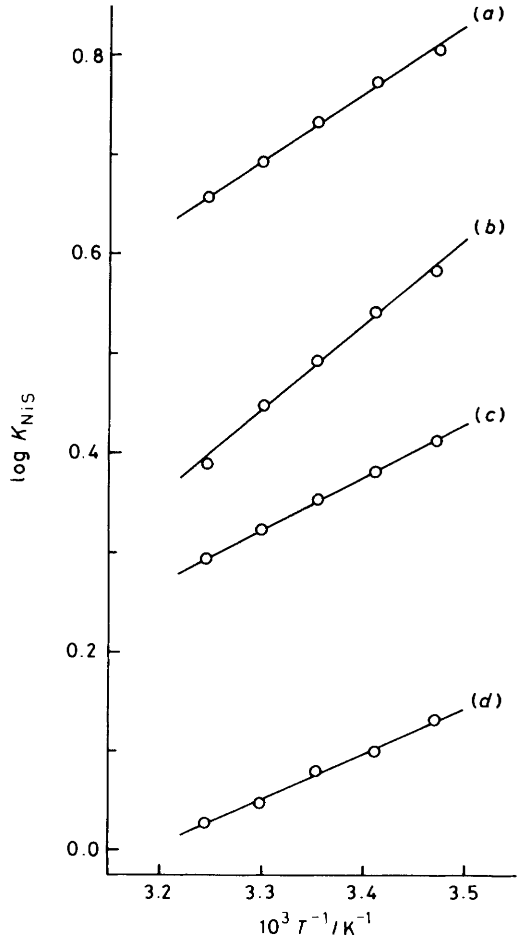


Figure 6. Temperature dependence of the equilibrium constant K_{NiS}. In $PhNO_2$: (*a*) dmf, 0.131; (*b*) MeCN, 0.378 mol dm^{-3}. In $MeNO_2$; (*c*) dmf, 0.519; (*d*) MeCN, 0.759 mol dm^{-3}

For $[Ni(cyclam)][ClO_4]_2$ with NH protons, the relative stability order for adduct formation was found to be dmf > MeCN > Me_2SO > H_2O in each neat solvent,[17] unlike the correlation expected from the DN concept. The unexpected stronger ligation ability of MeCN 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 π back donation.

Lever *et al.*[42] analysed the diffuse reflectance spectra of six-co-ordinate nickel(II) complexes of microsymmetry NiN_2X_2 (N = amine or MeCN, X = Cl or Br) and reported that MeCN had the greatest ratio of the effective crystal-field splitting energy, $10Dq'$(bromide)/$10Dq'$(chloride), which was correlated with the relative degree of back donation from metal to amines such as py and ammonia. They concluded that MeCN was a good π acceptor. A π-acceptor nature of the C≡N bond of MeCN has also been suggested from the weakening observed for the C–H bonds and the slight increase in C≡N frequency upon co-ordination of MeCN to copper(I) halides,[43] and a greater stabilization of the MeCN solvate of bis[2,2′-furil dioximato(1 −)]nickel(II).[44] The possible π back donation would explain the stronger ligation of MeCN in the present system.

Table 5. Thermodynamic quantities for formation of the five-co-ordinate chelate in $PhNO_2$ and $MeNO_2$ at 25 °C

Donor solvent	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}	Conditions
MeCN	-16.4 ± 0.8	-45 ± 3	[MeCN] = 0.378 mol dm^{-3} in $PhNO_2$
	-8.8 ± 0.3	-28 ± 1	[MeCN] = 0.759 mol dm^{-3} in $MeNO_2$
	-16.8 ± 0.8[a]	-32 ± 2[a]	In neat MeCN and MeCN–$MeNO_2$ (1:1)
dmf	-12.8 ± 0.4	-29 ± 2	[dmf] = 0.131 mol dm^{-3} in $PhNO_2$
	-10.2 ± 0.1	-28 ± 1	[dmf] = 0.519 mol dm^{-3} in $MeNO_2$
	-12.8 ± 2.7[b]	-24.1 ± 9.0[b]	In neat dmf

[a] Ref. 9. [b] Ref. 11.

Further, *X*-ray studies on $[NiL(MeCN)][ClO_4]_2$[45] and $[NiL(dmf)][SO_3CF_3]_2$[11] indicated that although the average Ni–N (ring) bond length (214.3 pm) for the MeCN 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 $[NiL][ClO_4]_2$[46] and 198.2 pm for $[NiL][SO_3CF_3]_2\cdot Me_2CO\cdot H_2O$.[47] Thus, it seems that the greater deformation for the MeCN adduct on going from the four- to five-co-ordinate species, compared to the dmf adduct, is consistent with the π-bonding contribution to the Ni–NCMe bond.

The enthalpy and entropy changes for equilibrium (1) for MeCN and dmf in $PhNO_2$ and $MeNO_2$ were obtained using the temperature dependence of K_{NiS} corrected for changes in solution volume with temperature (Figure 6). The values are given in Table 5. The negative $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values for both MeCN and dmf in $PhNO_2$ are larger than those in $MeNO_2$. Since the solvation of the solutes by the diluent gives an endothermic contribution to the enthalpy change for co-ordination of donor solvents, the present data indicate that the interaction of the donor solvent and the complex with $PhNO_2$ is weaker than that with $MeNO_2$, leading to the stronger co-ordination in $PhNO_2$. The larger ion-pair formation constant in $PhNO_2$ (Table 2) is also consistent with this view; it is likely that the weaker solvating ability of $PhNO_2$ is due to the weak acidity of $PhNO_2$ (AN = 14.8), compared to $MeNO_2$ (AN = 20.5). Therefore, the enthalpy and entropy changes for the nickel–donor solvent bond become more marked in $PhNO_2$ than in $MeNO_2$. The larger negative $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values for MeCN, compared to dmf, in $PhNO_2$ may indicate that the stronger ligation of nitriles in spite of their weaker basicity can be attributed to the favourable enthalpic contributions due to π bonding.

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