these two states being in thermal equilibrium. Indeed, the stabilization of the ^{3}MLCT state resulted in an equivalent increase in the activation energy for population of the LF state.

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Notes

Contribution from the Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

First and Second Ionic Association Constants of Unsymmetrical Metal Chelate Electrolytes from Conductance Measurements: (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Tetraphenylborate, Perchlorate, and Iodide in Nitrobenzene at 25 °C

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Solute–solvent interactions for metal chelate electrolytes with macrocyclic ligands disposed in square-planar fashion about the metal ion have been the subject of considerable investigations: kinetics of axial substitution,[1,2] isomerization,[3,4] and oxidation[5,6] and octahedral–square-planar equilibrium.[7,8]

The effects of the counterion ClO_4^- on the square-planar–octahedral equilibrium for the (1,4,7,10-tetraazacyclotetradecane)nickel(II) cation[9] and on the equilibrium constant for copper(II)–cyclic polythia complexes[10] were observed in aqueous solutions. Bosnich et al.[11] reported that although the conductance of the title complexes, $[Ni([14]aneN_4)]X_2$ (X = halides and perchlorate), in methanol are considerably less than the value expected for a bi-univalent electrolyte and large degree of association is suggested, the spectra are independent of the nature of the anion and not sensitive to the nature of the solvent such as water, methanol, and nitrobenzene, suggesting that the anion is not directly coordinated to the metal ion. However, very little attention has been paid to the quantitative study of ionic association for the unsymmetrically charged metal chelate electrolytes, with the exception of the conductometric study of symmetrically charged (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) sulfate in water–dioxane mixtures.[12]

Table I. Molar Concentrations, C/mol dm^{-3}, and Molar Conductivities, $\Lambda\{^1/_2[Ni([14]aneN_4)]X_2\}$/S cm^2 mol^{-1}, of the Metal Chelate Electrolytes in Nitrobenzene at 25 °C

$[Ni([14]aneN_4)]$-$(BPh_4)_2$		$[Ni([14]aneN_4)]$-$(ClO_4)_2$		$[Ni([14]aneN_4)]I_2$	
$C/10^{-4}$	Λ	$C/10^{-4}$	Λ	$C/10^{-4}$	Λ
0.060 45	28.52	0.036 08	37.33	0.03615	18.65
0.121 92	28.64	0.056 34	36.51	0.12230	14.42
0.222 71	28.50	0.087 10	35.33	0.33444	11.24
0.387 69	28.25	0.165 27	32.88	0.47946	10.16
0.579 50	28.01	0.246 87	31.02	1.4051	7.18
1.144 8	27.44	0.335 77	29.44	2.2365	6.08
2.614 7	26.45	0.475 50	27.55	3.3093	5.24
4.153 0	25.72	0.670 20	25.64	5.0905	4.43
		0.924 95	23.78	7.5715	3.79

In this study conductances for (1,4,8,11-tetraazacyclotetradecane)nickel(II) salts ($[Ni([14]aneN_4)]X_2$; X = BPh_4^-, ClO_4^-, and I^-) were measured in nitrobenzene, which has a moderately high dielectric constant and poor basicity,[13] and analyzed by using the extended Jenkins–Monk method to estimate the second association constant for the bi-univalent electrolytes that we previously proposed.[14] The large association constants for the perchlorate are explained by a hydrogen-bonding interaction of the anion with the N–H protons in the ligand, and those for the iodide are explained by a hydrogen-bonding interaction or a charge-transfer complex.

Experimental Section

Materials. $[Ni([14]aneN_4)](ClO_4)_2$ was synthesized by the published procedure,[15] and the orange crystal was recrystallized from water. Anal. Calcd for $NiC_{10}H_{24}N_4Cl_2O_8$: C, 26.22; H, 5.28; N, 12.24. Found: C, 26.11; H, 5.21; N, 12.29.

$\mathbf{[Ni([14]aneN_4)](BPh_4)_2}$ was prepared by mixing equimolar quantities of aqueous solutions of $[Ni([14]aneN_4)](ClO_4)_2$ and aqueous solutions of sodium tetraphenylborate. The yellow precipitate was recrystallized from acetone–water mixtures. Anal. Calcd for $NiC_{58}H_{64}N_4B_2$: C, 77.62; H, 7.19; N, 6.24. Found: C, 77.48; H, 7.16; N, 6.25.

$\mathbf{[Ni([14]aneN_4)]I_2}$ was prepared by mixing acetone solutions of lithium iodide and $[Ni([14]aneN_4)](ClO_4)_2$. The pale brown precipitate was recrystallized from methanol–ether mixtures. Anal. Calcd for $NiC_{10}H_{24}N_4I_2$: C, 23.42; H, 4.72; N, 10.93. Found: C, 23.22; H, 4.67; N, 10.88. The perchlorate and tetraphenylborate are easily soluble in nitrobenzene, whereas the iodide is much less soluble. The stock solution (ca. 8 × 10^{-4} mol dm^{-3}) of the iodide was prepared by mixing the crystal with nitrobenzene for 2 h under nitrogen atmosphere.

Nitrobenzene of reagent grade was purified as described previously.[14] The specific conductance (in S cm^{-1}) was less than 2 × 10^{-10}, and water content was 0.0026%. Parameters of the solvent used: density 1.198 25 g cm^{-3} at 25 °C; dielectric constant 34.82; viscosity 0.018 39 Pa s.

Apparatus. The instrumentation and the procedure used for the conductance measurements were described previously.[14,16]

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Table II. Conductance Results in Nitrobenzene at 25 °C

electrolyte	K_{a1}/mol^{-1} dm^3	K_{a2}/mol^{-1} dm^3	Λ_0/S cm^2 mol^{-1}	λ_0 $(1/nM^{n+})^a$/S cm^2 mol^{-1}	r_s/ 10^{-1} nm	ref
$[Ni([14]aneN_4)](BPh_4)_2$	0	0	29.1	18.5	4.8	this work
$[Ni([14]aneN_4)](ClO_4)_2$	11 000 ± 160	620 ± 10	39.5	18.4	4.8	this work
$[[Ni([14]aneN_4)]I]I$	*b*	13 600 ± 800	27.9 ± 0.8	7.5	5.9	this work
$[Fe(phen)_3](ClO_4)_2$	39	0	36.48	15.39	5.8	13
$[Co(acac)_2(en)]ClO_4$		56	31.77	10.68	4.2	28
$[Co(acac)_2(en)]I$		149	31.7	11.3	3.9	28
$(i\text{-Pen})_3BuNClO_4$		0	31.72	10.63	4.2	13
Bu_4NClO_4		40	32.72	11.63	3.8	28
Bu_3HNClO_4		257	35.1	14.0	3.2	27
Bu_3HNI		2570	33.4	13.0	3.4	27

[a] The values were calculated by using $\lambda_0(BPh_4^-) = 10.63$ S cm^2 mol^{-1} of ref 14, $\lambda_0(ClO_4^-) = 21.09$ of ref 14, and $\lambda_0(I^-) = 20.4$ of ref 32. [b] Completely associated.

Table III. Derived Parameters Resulting from Changes in the Assumptions for $[Ni([14]aneN_4)](ClO_4)_2$ in Nitrobenzene[a]

R_{λ_0} [b]	Λ_0/S cm^2 mol^{-1}	$d^c/10^{-1}$ nm	$K_{JM}{}^d$/ mol^{-1} dm^3	K_{a1}/ mol^{-1} dm^3	K_{a2}/ mol^{-1} dm^3	å/10^{-1} nm
0.348[e]	39.4	0	11 400 ± 700	10 600 ± 190	820 ± 10	6.3
0.348	39.5	0	11 600 ± 550	11 000 ± 160	620 ± 10	5.6
0.348	39.6	0	11 900 ± 400	11 500 ± 210	430 ± 10	4.9
0.348	39.5	5	11 600 ± 500	11 000 ± 160	590 ± 10	5.5
0.4	39.5	0	12 100 ± 700	11 300 ± 170	740 ± 10	5.9
0.5	39.5	0	12 900 ± 1100	11 700 ± 180	1020 ± 20	6.6
0.5	39.5	5	12 900 ± 1000	11 700 ± 180	990 ± 20	6.5

[a] Parameters obtained at a minimum value of $\pm K_{a1}$. [b] Ratio of $\lambda_0(MX^+)$ to $\lambda_0(^1/_2M^{2+})$. [c] Ionic distance parameter in the Debye–Hückel equation, $f_i = \exp[-Az_i^2I^{1/2}/(1 + BdI^{1/2})]$. [d] First association constant on the basis of $K_{a2} = 0$. [e] Values from eq 3.

Results

The ionic equilibria for a bi-univalent electrolyte (MX_2) are written as

$$M^{2+} + X^- \rightleftharpoons MX^+$$

$$MX^+ + X^- \rightleftharpoons MX_2$$

with the corresponding association constants

$$K_{a1} = \alpha/(1 - \alpha - \beta)(2 - \alpha - 2\beta)Cf_2$$

$$K_{a2} = \beta/\alpha(2 - \alpha - 2\beta)Cf_1^2$$

where C is the molar concentration in mol dm^{-3}, α and β are degrees of first and second associations, and f_1 and f_2 are the activity coefficients of monovalent and divalent ions, respectively.

The measured molar conductances Λ are given Table I. Quite different behaviors are seen for the concentration dependence of conductances among the three electrolytes: Λ for the tetraphenylborate least depends on the concentration, and the one for iodide is considerably less than the value expected for a bi-univalent electrolyte. The perchlorate is situated between them.

Although the more advanced theory of conductance for unsymmetrical electrolytes was developed by Lee and Wheaton[17] and applied to alkaline-earth metal halides in methanol[18] to estimate K_{a1} assuming $K_{a2} = 0$, the form of the conductance function with some unknown parameters is much more complex and data of highest precision are required.[19] The systems studied here are greatly associative. Accordingly, first the Fuoss–Edelson method[20] was used for the evaluation of the limiting molar conductance Λ_0 and K_{a1}. The results showed that the tetraphenylborate was completely dissociated, and the Fuoss–Edelson plot for the perchlorate became nonlinear with increasing concentration because of the failure of the approximations $\lambda_0(MX^+) = 0.5\lambda_0(^1/_2M^{2+})$ and $K_{a2} = 0$ involved in the Fuoss–Edelson method. The conductance data of the iodide did not apply to the Fuoss–Edelson analysis at all. The latter two electrolytes were further examined for the evaluation of their second association constants.

$[Ni([14]aneN_4)](ClO_4)_2$. The K_{a1} and K_{a2} values were estimated by using the extended Jenkins–Monk method proposed previously.[14] Briefly, the conductance Λ is represented by eq 1. Here, Λ_{21} and Λ_{11} are ascribed to the conductance of

$$\Lambda = (1 - \alpha - \beta)\Lambda_{21} + 0.5\alpha\Lambda_{11} \qquad (1)$$

bi-univalent and uni-univalent electrolytes, respectively, and the α and β values are iteratively calculated for each concentration until the difference between observed and calculated conductances becomes less than 1×10^{-5} S cm^2 mol^{-1}. At that time α is related to β by introducing the ratio $R = K_{a1}/K_{a2}$, which is given as a function of the ion distance parameter å only (eq 2) using the Fuoss equation[21] of ion association, where

$$R = \exp(e^2/\epsilon åkT) \qquad (2)$$

the symbols have their usual meanings. Furthermore, the value of λ_0 for the ion pair MX^+ is calculated by the equation[22] based on Stokes' law

$$\lambda_0(MX^+)/\lambda_0(\tfrac{1}{2}M^{2+}) = \tfrac{1}{2}r_{s(M^{2+})}/(r_{s(M^{2+})} + r_{s(X^-)}) \qquad (3)$$

where r_s is the Stokes radius.

When $\beta = 0$, that is, the conventional Jenkins–Monk method[23] was applied, it was found that K_{a1} at each concentration increases with increasing concentration, showing the failure of the assumption $\beta = 0$. The best α and β or K_{a1} and K_{a2} values were evaluated by minimizing the concentration dependence of K_{a1}.

$[Ni([14]aneN_4)]I_2$. The fact that the treatment for bi-univalent electrolytes cannot be applied to this electrolyte suggests

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the complete association for the first step. The Shedlovsky method[24] for a uni-univalent electrolyte was used to determine K_{a2}.

The conductance results obtained for three electrolytes are summarized in Table II, together with those for some electrolytes for comparison. The Stokes hydrodynamic radii are also given.

Discussion

The extended Jenkins–Monk method used here involves several important assumptions, especially (i) the use of the limiting law for conductivities and activity coefficients and (ii) the estimation of $\lambda_0(\mathrm{MX}^+)$ using Stokes' law. Table III gives the derived parameters resulting from changes in the above assumptions for the perchlorate. Although the association constants in nitrobenzene are hardly influenced by the equations used for activity coefficients, K_{a2} depends on Λ_0 and the ratio of $\lambda_0(\mathrm{MX}^+)$ to $\lambda_0(^1/_2\mathrm{M}^{2+})$.

Consistent values of λ_0 for the tetraphenylborate and perchlorate were obtained (Table II). The estimation of λ_0 of monovalent ion-paired species remains controversial in the conductance analysis of bi-univalent electrolytes.[25] A λ_0 value of 7.5 for the ion pair $[\mathrm{Ni([14]aneN_4)]I}^+$ was estimated from $\lambda_0(\mathrm{I}^-) = 20.4$ S cm^2 mol^{-1} and $\Lambda_0\{[\mathrm{Ni([14]aneN_4)]I}]\mathrm{I}\} = 27.9$, this leading to 0.4 for the ratio of $\lambda_0\{\mathrm{Ni([14]aneN_4)]I}^+\}$ to $\lambda_0\{^1/_2[\mathrm{Ni([14]aneN_4)}]^{2+}\}$. Thus, the use of eq 3 for $\lambda_0\{[\mathrm{Ni([14]aneN_4)]ClO_4}^+\}$ does not seem unreasonable in view of the slightly larger $\mathrm{ClO_4}^-$ compared to I^-.

A square-planar (diamagnetic)–octahedral (paramagnetic) equilibrium is known to exist for Ni(II) chelate cations with macrocyclic ligands in water,[8] but it was reported that the $[\mathrm{Ni([14]aneN_4)}]^{2+}$ salts are diamagnetic in methanol.[11] The basicity of solvent molecules is greatly responsible for the position of the equilibrium. Although the donor number (19.0) of methanol, as a measure of basicity,[13] is comparable with that (18.0) of water, the difference between equilibria in water and in methanol may be due to that in the steric factor. Considering the low donor number (4.4) of nitrobenzene, it appears that the $[\mathrm{Ni([14]aneN_4)}]^{2+}$/nitrobenzene interaction is electrostatic in nature and very weak, and the cation is not functioning as an octahedral form. This view is consistent with the perchorate and iodide behavior discussed below.

The association constants in Table II drastically change from the tetraphenylborate to the iodide. Generally, most salts of tetraphenylborate are completely dissociated in nitrobenzene[14] due to its low density of surface charge with aromatic character of the benzene rings.[26] It is noteworthy that $[\mathrm{Ni([14]aneN_4)](ClO_4)_2}$ is greatly associative, as compared to other uni-univalent electrolytes with active hydrogen atoms such as $\mathrm{Bu_3HNClO_4}$[27] and $[\mathrm{Co(acac)_2(en)]ClO_4}$[28] (acac = 2,4-pentanedione anion; en = ethylenediamine); the K_{a1} value of $[\mathrm{Fe(phen)_3](ClO_4)_2}$[14] (phen = 1,10-phenanthroline) is only 39 for K_{a1} where there is no hydrogen bond possibility. When $\mathring{a}$ is 0.4 nm, which corresponds to the contact distance between Ni(II) and $\mathrm{ClO_4}^-$, the Fuoss equation of electrostatic association predicts only 500 for K_{a1} and 9 for K_{a2}.

The X-ray analysis of the perchlorate of the [(5(*SR*),7-(*RS*),12(*RS*),14(*SR*))-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) complex[29] established that in the orange isomer the two perchlorate ions are disposed in the axial position and hydrogen bonded to the cation through N–H···O–Cl hydrogen bonds (N···O = 0.31 nm) but no perchlorate oxygen is directly bonded to nickel. The large association constants for the perchlorate supports the view that even in nitrobenzene such axial approach of the perchlorate ions to nickel is effectively enhanced through N–H···O–Cl hydrogen bonds since nitrobenzene is of low basicity. The perchlorate ion is not usually regarded as a hydrogen-bond acceptor.[30,31] However, the hydrogen-bond donor properties of the N–H protons of ethylenediamine-like ligands disposed in square-planar fashion are very important even in the association phenomena of the perchlorate ion.

The r_s value of 0.59 nm for $[\mathrm{Ni([14]aneN_4)]I}^+$ is nearly the same as the sum of diameter of I^- and the radius of Ni^{2+}. This suggests that the I^- ion is oriented next to the nickel(II). This selective orientation with the large association constants is not what would be expected an ion pair. Such selective orientation may be obtained by either a hydrogen-bonding interaction or a charge-transfer complex. The iodide is light orange in nitrobenzene, although very weak because of its low solubility, but this color does not necessarily support the latter because unfortunately the iodide ion itself also gives a charge-transfer-to-solvent spectrum with a light orange color in nitrobenzene.[33]

Registry No. $[\mathrm{Ni([14]aneN_4)](BPh_4)_2}$, 88730-77-2; $[\mathrm{Ni([14]aneN_4)](ClO_4)_2}$, 15220-72-1; $[\mathrm{Ni([14]aneN_4)]I_2}$, 88730-78-3.

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Preparation and Characterization of Rhodium(III) Polyphosphate Complexes

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ATP, ADP, PP, and other di- and triphosphates exist in the living cell as Mg(II) complexes, and it is in this form that they participate in biochemical processes. Mg(II) complexes undergo rapid ligand exchange, and thus the various stereoisomers and/or structural isomers of a given Mg(II) polyphosphate complex exist in solution in rapid equilibrium.

Independently, Mildvan and Cleland introduced the concept of using exchange-inert metal ions in place of Mg(II) for the preparation of stable metal–polyphosphate complexes for use in kinetic, spectroscopic, and stereochemical studies.[1,2] α,β,γ-Tridentate metal complexes of ATP and PPP have been prepared as well as β,γ-bidentate M(ATP), α,β-bidentate M(ADP) and M(PP), γ-monodentate M(ATP) and β-monodentate M(ADP) and M(PP).[3] The two exchange-inert metal ions that have been used in this capacity are Cr(III) and Co(III). The Cr(III) complexes are potentially useful as paramagnetic probes and the Co(III) species as diamagnetic

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