

## Ionic Association of Mixed Nickel(II) Chelates in Alcohols, Ketones, and Nitrobenzene

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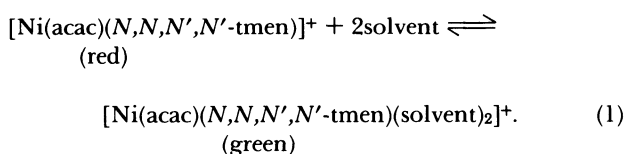
(Received December 26, 1988)

The conductances of mixed nickel(II) chelates,  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{X}$  (where  $\text{acac}$ =2,4-pentanedionato,  $N,N,N',N'\text{-tmen}$ = $N,N,N',N'$ -tetramethylethylenediamine, and  $\text{X}^-=\text{ClO}_4^-$  or  $\text{NO}_3^-$ ), in alcohols {ethanol (EtOH), 1-propanol ( $n$ -PrOH), 2-propanol ( $i$ -PrOH), and 1-butanol ( $n$ -BuOH)}, ketones {acetone ( $\text{Me}_2\text{CO}$ ), methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK)}, and nitrobenzene ( $\text{PhNO}_2$ ) were measured at 25 °C. The obtained ionic association constants ( $K_a$ ) of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$  which were derived by using the extended Fuoss–Hsia function indicated that (1) the perchlorate complex is a normal type of uni-uni-valent electrolyte and (2) it is more dissociated than  $[\text{Co}(\text{acac})_2(N,N,N',N'\text{-tmen})]\text{ClO}_4$  in EtOH,  $n$ -PrOH, and  $n$ -BuOH. Walden products of the cations suggest that the nickel(II) chelate cation in the alcohols is present as an octahedral form with the coordination of two solvent molecules. On the other hand,  $K_a$  of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{NO}_3$  are much larger than those of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$ . This can be ascribed to the coordination of a nitrate ion to the nickel(II) ion. The effect is large and approximately the same in the ketones and  $\text{PhNO}_2$ , though small in EtOH,  $n$ -PrOH, and  $n$ -BuOH due to the coordination of solvent molecules.

Since the central metal ion of a quadratic-planar chelate cation is available to interact with solvents and anions, the complex offers interesting information which helps in understanding solute-solvent interactions different from those of octahedral complexes. However, very little attention have been paid to ionic association,<sup>1)</sup> although there have been a number of studies concerning axial interaction by solvents with coordinating ability.

In this study, in order to obtain information on the ionic association of quadratic-planar complexes, the conductances of nickel(II) chelates,  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{X}$  ( $\text{acac}$ =2,4-pentanedionato,  $N,N,N',N'\text{-tmen}$ = $N,N,N',N'$ -tetramethylethylenediamine, and  $\text{X}^-=\text{ClO}_4^-$  or  $\text{NO}_3^-$ ) were measured in some alcohols and ketones as well as nitrobenzene. The conductance measurement is a useful tool for determining the ionic association constant and size of solvated- and coordinated-chelate cations.

It is well known that the color of the mixed nickel(II) chelate,  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$ , which was prepared successfully by Fukuda and Sone,<sup>2)</sup> changes abruptly from red to green on varying the solvent basicity. This has been ascribed to an equilibrium between two forms, one quadratic-planar (diamagnetic low-spin) and the other octahedral (paramagnetic high-spin),



As for the nitrate complex, on the other hand, the  $\text{NO}_3^-$  ion acts as a bidentate ligand and a counter anion in non-coordinating and strongly coordinating

solvents, respectively.<sup>2)</sup>

Since the alcohols and ketones in this study have similar basicities, but different dielectric constants and steric structures, the equilibrium of ionic association may be different from each other. Nitrobenzene, which is an inert solvent in basicity, was selected for a comparison. The obtained conductance parameters were compared in detail with those of an octahedral complex  $[\text{Co}(\text{acac})_2(N,N,N',N'\text{-tmen})]\text{ClO}_4$  in the solvents,<sup>3–5)</sup> thus elucidating such solvent effects as solvent basicity, steric factor, and dielectric constant on ionic association.

### Experimental

**Material.**  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$  was synthesized and recrystallized according to a published procedure,<sup>2)</sup> followed by vacuum drying at ca. 50 °C. Calcd. for  $\text{NiC}_{11}\text{H}_{23}\text{N}_2\text{ClO}_6$ : C, 35.38; H, 6.21; N, 7.50%. Found: C, 35.10; H, 6.43; N, 7.67%.

$\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})(\text{NO}_3)$  was synthesized according to a published procedure,<sup>2)</sup> recrystallized from 2-propanol, and then vacuum dried at ca. 50 °C. Calcd. for  $\text{NiC}_{11}\text{H}_{23}\text{N}_3\text{O}_5$ : C, 39.32; H, 6.90; N, 12.51%. Found: C, 39.54; H, 7.01; N, 12.50%.

Ethanol (EtOH), 1-propanol ( $n$ -PrOH), 2-propanol ( $i$ -PrOH), acetone ( $\text{Me}_2\text{CO}$ ), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and nitrobenzene ( $\text{PhNO}_2$ ) of reagent grade were purified as described previously.<sup>3–5)</sup> 1-Butanol ( $n$ -BuOH) was refluxed over calcium oxide and fractionally distilled.

**Apparatus.** The instrumentation and procedure used for the conductance measurements were described previously.<sup>3)</sup>

### Results

**(A)  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$ .** The measured molar conductances,  $\Lambda$  ( $\text{S cm}^2 \text{ mol}^{-1}$ ) and the corresponding concentrations,  $C$  ( $\text{mol dm}^{-3}$ ) are given

Table 1. Molar Concentrations ( $C/\text{mol dm}^{-3}$ ) and Molar Conductances ( $\Lambda/\text{S cm}^2 \text{mol}^{-1}$ ) of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$  in Alcohols, Ketones, and Nitrobenzene at 25 °C

EtOH		<i>n</i> -PrOH		<i>i</i> -PrOH		<i>n</i> -BuOH	
$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$
30.918	39.541	42.326	15.818	42.095	11.007	50.466	8.319
23.791	41.027	25.114	17.659	36.196	11.529	32.994	9.292
17.842	42.540	20.547	18.358	28.508	12.366	22.941	10.150
13.524	43.745	16.396	19.120	23.515	13.092	16.488	10.936
10.587	44.768	11.807	20.184	18.959	13.904	12.529	11.529
7.6498	46.005	7.8290	21.405	13.968	15.080	8.0525	12.565
5.8780	46.882	5.5427	22.314	9.6619	16.496	4.4196	13.784
4.9481	47.444	3.5231	23.312	6.6765	17.922	2.0132	15.092
—	—	2.4217	24.055	4.1567	19.616	—	—

Me <sub>2</sub> CO		MEK		MIBK		PhNO <sub>2</sub>	
$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$	$C/10^{-4}$	$\Lambda$
46.640	141.58	36.869	97.267	22.376	40.685	42.344	30.104
29.550	150.66	28.905	101.64	16.698	44.162	35.410	30.570
15.930	161.47	22.970	105.62	12.430	47.850	28.594	31.090
12.212	165.69	17.164	110.51	8.9069	52.267	21.100	31.758
9.5289	169.50	13.074	115.21	5.9929	57.650	15.203	32.387
5.6724	176.12	9.3209	120.69	4.3787	62.032	10.543	33.006
4.3342	179.06	7.1014	124.74	2.9139	67.716	7.8916	33.408
—	—	4.6619	130.38	1.9400	73.186	5.1132	33.908
—	—	2.8327	136.10	0.9179	82.470	3.3470	34.323

Table 2. Solvent Parameters

Solvent	$\epsilon$	$\eta/\text{mPa s}$	DN	AN
EtOH	24.33	1.082	20	37.9
<i>n</i> -PrOH	20.45	1.948	19.6	37.3
<i>i</i> -PrOH	19.41	2.078	—	33.5
<i>n</i> -BuOH	17.45	2.589	—	36.8
Me <sub>2</sub> CO	20.56	0.3052	17	12.5
MEK	18.01	0.3803	—	—
MIBK	12.8	0.5478	—	—
PhNO <sub>2</sub>	34.82	1.847	4.4	14.8

in Table 1. In EtOH, a slight increase in conductivity with time (ca. 0.1%/h) was observed. Therefore, a small correction was made by extrapolating to time zero. The data were analyzed by the Fuoss–Hsia function with Fernández–Prini coefficients and  $E = E_1A_0 - 2E_2$ ,<sup>6)</sup>

$$\Lambda = \gamma(A_0 - SC^{1/2}\gamma^{1/2} + EC\gamma \log C\gamma + J_1(d)C\gamma + J_2(d)C^{3/2}\gamma^{3/2}), \quad (2)$$

where the symbols have their usual meanings. The ionic association constant  $K_a$  can be expressed as

$$K_a = (1 - \gamma)/\gamma^2 C f_{\pm}^2. \quad (3)$$

The mean ionic activity coefficient  $f_{\pm}$  is given by the extended Debye–Hückel equation,

$$-\log f_{\pm} = AC^{1/2}\gamma^{1/2}/(1 + BdC^{1/2}\gamma^{1/2}). \quad (4)$$

The method for fitting in terms of  $A_0$ ,  $K_a$ , and ion-size parameter  $d$  was described previously.<sup>3)</sup> The standard deviation  $\sigma_A$  is defined as

$$\sigma_A = [\sum(\Lambda_{\text{calcd.}} - \Lambda_{\text{obsd.}})^2/(n - 3)]^{1/2}, \quad (5)$$

where  $n$  is the number of experimental points. The dielectric constant ( $\epsilon$ ) and viscosity ( $\eta$  in mPa s) of the solvents<sup>3,5,7–12)</sup> used in this study for analyses are given in Table 2, together with the donor number (DN) and acceptor number (AN) as measures of solvent basicity and acidity, respectively.<sup>13)</sup> The obtained conductance parameters are given in Table 3. The limiting conductances ( $\lambda_0^+/S \text{ cm}^2 \text{ mol}^{-1}$ ) and Walden products ( $\lambda_0^+ \cdot \eta/S \text{ cm}^2 \text{ mol}^{-1} 10^{-1} \text{ Pa s}$ ) of the nickel(II) chelate cation were obtained from the limiting conductances of the perchlorate ion,  $\lambda_0^- (\text{ClO}_4^-)$ : in EtOH, 32.04;<sup>5)</sup> in *n*-PrOH, 16.42;<sup>7)</sup> in *i*-PrOH, 15.24;<sup>8)</sup> in *n*-BuOH, 11.22;<sup>9)</sup> in Me<sub>2</sub>CO, 118.35;<sup>10)</sup> in MEK, 93.0;<sup>5)</sup> in MIBK,  $\lambda_0^- \cdot \eta = 0.34$ ;<sup>5)</sup> in PhNO<sub>2</sub>, 20.9.<sup>12)</sup>

(B)[Ni(acac)(*N,N,N',N'*-tmen)]NO<sub>3</sub>. The molar conductivities of [Ni(acac)(*N,N,N',N'*-tmen)]NO<sub>3</sub> in the alcohols, the ketones, and PhNO<sub>2</sub> are given in Fig. 1. Since the conductivities are extremely small, due to a coordination of the nitrate ion to the nickel(II) ion, it is impossible to obtain  $A_0$  and, consequently,  $K_a$  using the extended Fuoss–Hsia function (Eq. 2).

Thus, only  $K_a$  was estimated from Eq. 3, in which the fraction of electrolyte present as ions  $\gamma$  is simply expressed in the form

$$\gamma = \Lambda/(A_0 - SC^{1/2}\gamma^{1/2}), \quad (6)$$

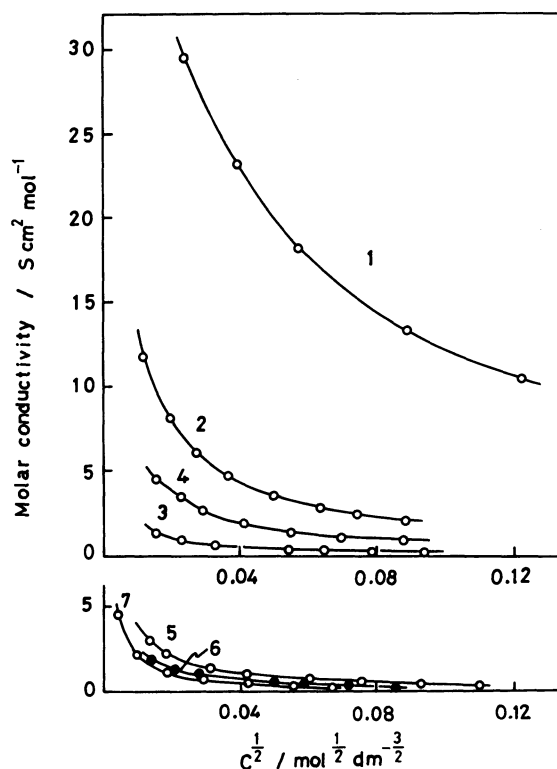
where  $A_0$  of [Ni(acac)(*N,N,N',N'*-tmen)]NO<sub>3</sub> was obtained from  $\lambda_0^+$  ([Ni(acac)(*N,N,N',N'*-tmen)]<sup>+</sup>) in Table 3 and  $\lambda_0^- (\text{NO}_3^-)$  from the literature.<sup>12,14–16)</sup> The activity coefficient  $f_{\pm}$  was estimated by using Eq. 4 and

Table 3. Conductance Results for  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$  in Alcohols, Ketones, and Nitrobenzene at 25 °C

Solvent	$\Lambda_0$ $\text{S cm}^2 \text{mol}^{-1}$	$\lambda_0^+$ $\text{S cm}^2 \text{mol}^{-1}$	$\lambda_0^+ \cdot \eta$ $\text{S cm}^2 \text{mol}^{-1} 10^{-1} \text{Pa s}$	$K_a$ $\text{dm}^3 \text{mol}^{-1}$	$d$ $10^{-1} \text{nm}$	$\sigma_A$
EtOH	52.55±0.08	20.51	0.222	145± 10	13.8	0.05
<i>n</i> -PrOH	26.98±0.02	10.56	0.206	389± 11	14.3	0.02
<i>i</i> -PrOH	26.52±0.14	11.28	0.234	1160± 80	15.4	0.02
<i>n</i> -BuOH	17.58±0.03	6.36	0.165	749± 16	16.0	0.03
Me <sub>2</sub> CO	199.0 ±0.1	80.6	0.246	162± 3	12.9	0.09
MEK	154.7 ±0.2	61.7	0.235	382± 28	13.2	0.11
MIBK	101.2 ±0.4	—	0.21	2900±100	17.5	0.15
PhNO <sub>2</sub>	35.85±0.01	14.95	0.276	34± 5	7.6	0.007

Table 4. Limiting Conductances and Ionic Association Constants for  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{NO}_3$  in Alcohols, Ketones, and Nitrobenzene at 25 °C

Solvent	$\Lambda_0$ $\text{S cm}^2 \text{mol}^{-1}$	$\lambda_0^-(\text{NO}_3^-)$ $\text{S cm}^2 \text{mol}^{-1}$	$K_a$ $\text{dm}^3 \text{mol}^{-1}$
EtOH	46.2	25.65	$(1.26 \pm 0.21) \times 10^3$
<i>n</i> -PrOH	23.8	13.2	$(1.66 \pm 0.07) \times 10^4$
<i>i</i> -PrOH	23.6	12.3	$(1.22 \pm 0.14) \times 10^6$
<i>n</i> -BuOH	15.2	8.8	$(3.53 \pm 0.17) \times 10^4$
Me <sub>2</sub> CO	200.7	120.1	$(2.63 \pm 0.01) \times 10^7$
MEK	147.7	86.0	$(3.48 \pm 0.23) \times 10^7$
PhNO <sub>2</sub>	37.6	22.6	$(3.36 \pm 0.26) \times 10^6$

Fig. 1. Plots of the molar conductivity of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{NO}_3$  against the square root of the concentration in organic solvents at 25 °C. 1, EtOH; 2, *n*-PrOH; 3, *i*-PrOH; 4, *n*-BuOH; 5, Me<sub>2</sub>CO; 6, MEK; 7, PhNO<sub>2</sub>.

Bjerrum's critical distance in each solvent. The mean  $K_a$  values of a series of experimental points are given in Table 4 together with the values of  $\Lambda_0$  and  $\lambda_0^-(\text{NO}_3^-)$ .

### Discussion

(A) $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$ . The following classification becomes feasible toward the color change of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]\text{ClO}_4$  in the solvents, as described in Eq. 1:

Class I (Me<sub>2</sub>CO, MEK, MIBK, PhNO<sub>2</sub>, and *i*-PrOH) Red

Class II (EtOH, *n*-PrOH, and *n*-BuOH) Green

This indicates that the nickel(II) chelate ion is mainly present as a quadratic-planar  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]^+$  for Class I and an octahedral  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})(\text{solvent})_2]^+$  for Class II.<sup>20</sup> This can be confirmed from the mobility data shown in Fig. 2. Walden products ( $\lambda_0^+ \cdot \eta$ ) of  $[\text{Ni}(\text{acac})(N,N,N',N'\text{-tmen})]^+$  should be larger than those of  $[\text{Co}(\text{acac})_2(N,N,N',N'\text{-tmen})]^+$  since the molal volume of the former is smaller than that of the latter due to a difference in the number of the ligand acac. This is the case for Class I, except for *i*-PrOH; the difference in  $\lambda_0^+ \cdot \eta$  is particularly large in PhNO<sub>2</sub>. For Class II, on the other hand, the opposite result is observed. In addition, the difference increases in the order EtOH < *n*-PrOH < *n*-BuOH.<sup>17</sup> This can not be explained in terms of coordination by one molecule, supporting

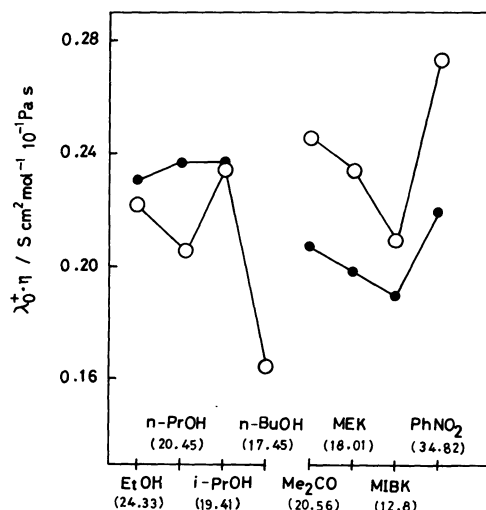


Fig. 2. Walden products of ○,  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  and ●,  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  in organic solvents at 25°C. The values in parentheses are the dielectric constant ( $\epsilon$ ) of each solvent.

coordination by two molecules in Eq. 1.

The transfer of a quadratic-planar  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  to an octahedral  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})\text{-(solvent)}_2]^+$  is influenced by solvent basicity.<sup>2)</sup> The DN value, which is a measure of the basicity of a solvent, is 20 and 19.6 for EtOH and *n*-PrOH, respectively, suggesting that *i*-PrOH and *n*-BuOH have similar DN values (Table 2). Thus, although the configuration of the nickel(II) chelate cation in these solvents should be equal (Class II), the configuration in *i*-PrOH, which is quadratic-planar, is different from the result regarding primary alcohols. This may be due to a steric hindrance by branched methyl groups: The donor number, which was defined by Gutmann, is obtained from the solvation enthalpy of antimony pentachloride by the donor solvent in 1,2-dichloroethane. Therefore, it indicates the "bulk" donicity of the solvent and does not take into account the structural factor. However,  $\lambda_0^+ \cdot \eta$  of the nickel(II) chelate ion in *i*-PrOH is compatible with that of the cobalt(III) chelate ion, suggesting that the solvation of the oxygen atom in acac (the nickel(II) chelate ion) by the OH proton occurs without steric hindrance.

The ketones do not interact with the nickel(II) ion, due to the steric hindrance, in analogy with *i*-PrOH. In addition, they have no solvation site to the nickel(II) chelate ion, resulting in an increase in mobility compared to the cobalt(III) chelate ion. However, the difference in  $\lambda_0^+ \cdot \eta$  ( $\text{Me}_2\text{CO}=0.038$ ,  $\text{MEK}=0.035$ , and  $\text{MIBK}=0.02$ ) is small compared to that (0.054) in  $\text{PhNO}_2$  which is inert in donicity, indicating the presence of a weak interaction between the ketones and the nickel(II) ion.<sup>2)</sup> This is also confirmed from the fact that dimethyl sulfoxide (DN=29.8), which is very strong in donicity, coordi-

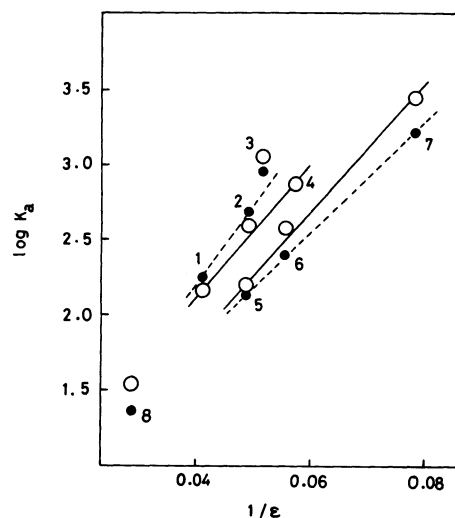


Fig. 3. Plots of  $\log K_a$  with  $1/\epsilon$  for ○,  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  and ●,  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  in organic solvents at 25°C. 1, EtOH; 2, *n*-PrOH; 3, *i*-PrOH; 4, *n*-BuOH; 5,  $\text{Me}_2\text{CO}$ ; 6, MEK; 7, MIBK; 8,  $\text{PhNO}_2$ .

nates directly to the nickel(II) ion, although the geometry of the solvent is similar to the ketones.

Figure 3 shows that  $\log K_a$  of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$ , in analogy with those of octahedral complex  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$ , increases with a decrease in the dielectric constant of the solvents (increase in  $1/\epsilon$ ). This is expected from the coulombic theory of ionic association,<sup>18)</sup>

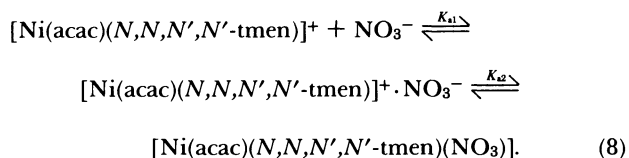
$$\log K_a = e^2/akT \cdot 1/\epsilon + \log K_a^\circ, \quad (7)$$

where  $a$  is the contact distance between the cation and the anion and other symbols ( $e$ ,  $k$ , and  $T$ ) have their usual meanings.  $K_a^\circ$  contains the contribution to  $K_a$  for all factors, except for the long-range coulombic interaction.  $K_a$  is larger in the alcohols than in the ketones at the same dielectric constant. This larger  $K_a$  in the alcohols could be explained in terms of (1) diminution in the dielectric constant due to a breaking of the hydrogen-bonding structure in the vicinity of an ion pair and (2) a multiple-step association process occurring from the solvation of  $\text{ClO}_4^-$  by the alcohol molecules. This pattern is set up for other uni-univalent electrolytes such as  $[\text{Co}(\text{acac})_2(\text{en})]\text{ClO}_4$  ( $\text{en}$ =ethylenediamine),<sup>3-5)</sup> and  $\text{R}_4\text{NClO}_4$  ( $\text{R}$ : alkyl group ( $\text{C}=2-4$ )).<sup>7-9)</sup> Moreover, the  $K_a$  values of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  are not so much different from those of  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$ . Thus, it is considered that  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  in the solvents behaves as a normal-type of uni-univalent electrolyte and that the nickel(II) ion does not interact with the  $\text{ClO}_4^-$  ion.

However, the  $K_a$  values of the nickel(II) chelate complex can be classified into two groups as described previously: (1) The  $K_a$  values of the nickel(II) complex

are larger than those of the cobalt(III) complex in the ketones,  $\text{PhNO}_2$ , and  $i\text{-PrOH}$  (Class I). (2) The reverse trend is obtained in  $\text{EtOH}$ ,  $n\text{-PrOH}$ , and  $n\text{-BuOH}$  (Class II). Since the nickel(II) ion does not directly interact with the  $\text{ClO}_4^-$  ion, it seems that the classification can not be only attributed to the difference in the central metal ion {Ni(II) or Co(III)} and the number of the acac. Thus, it may be explained as follows: For Class I, since the nickel(II) chelate ion is present as a quadratic-planar ion, the entity is small compared to  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$ . This suggests that  $K_a$  of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  should be larger than that of  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$ . For Class II, on the other hand, the reverse trend may be obtained due to the large volume of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})(\text{alcohol})_2]^+$  compared with  $[\text{Co}(\text{acac})_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  (Fig. 2).

**(B)[Ni(acac)(N,N,N',N'-tmen)]NO<sub>3</sub>.** The nitrate ion, as a bidentate ligand, can coordinate directly to  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  in organic solvents.<sup>2)</sup> This behaviour is accounted for by two association processes, outer-sphere ionic association and the formation of an inner-sphere octahedral complex,



The observed association constant ( $K_a$ ) can be shown to be equal to

$$K_a = K_{a1} \cdot K_{a2}. \quad (9)$$

Table 4 shows that (1) the  $K_a$  values of the nitrate complex are larger than those of the perchlorate complex and (2) may be conveniently classified into two groups; the  $K_a$  values in the ketones,  $\text{PhNO}_2$ , and  $i\text{-PrOH}$  are remarkably larger than those in  $\text{EtOH}$ ,  $n\text{-PrOH}$ , and  $n\text{-BuOH}$ . This classification is in good agreement with the classification by the color change of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+$  in each solvent, Classes I and II. For Class I, the nickel(II) chelate ion in Eq. 8 is present as a quadratic-planar chelate ion, resulting in an octahedral complex  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})(\text{NO}_3)]$ . On the other hand, for Class II the nickel(II) chelate ion is present as an octahedral chelate ion  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})(\text{alcohol})_2]$ , resulting in an octahedral complex  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})(\text{NO}_3)]$  accompanied by a decoordination of two alcohol molecules from the nickel(II) ion. The coordination of anions is obtained for the copper complex in nitromethane:<sup>2)</sup>  $[\text{Cu}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]^+ + \text{X}^- \rightleftharpoons [\text{Cu}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})(\text{X})]$  (where  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{SCN}^-$ ). The formation constants are large compared to that from the coulombic theory of ionic association.

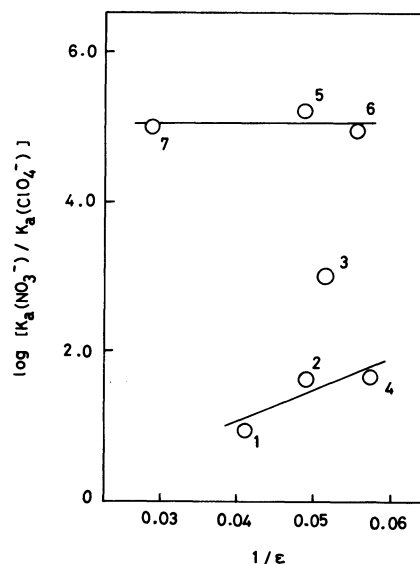


Fig. 4. The ratio of  $\log K_a$  of  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{NO}_3$  to  $[\text{Ni}(\text{acac})(\text{N},\text{N},\text{N}',\text{N}'\text{-tmen})]\text{ClO}_4$  as a function of  $1/\epsilon$  in organic solvents at  $25^\circ\text{C}$ . 1,  $\text{EtOH}$ ; 2,  $n\text{-PrOH}$ ; 3,  $i\text{-PrOH}$ ; 4,  $n\text{-BuOH}$ ; 5,  $\text{Me}_2\text{CO}$ ; 6,  $\text{MEK}$ ; 7,  $\text{PhNO}_2$ .

The  $K_{a1}$  value in Eq. 8 seems to be roughly equal to that of the perchlorate complex, since  $K_a$  for  $\text{R}_4\text{NNO}_3$  is similar to that for  $\text{R}_4\text{NClO}_4$  (from the coulombic theory of ionic association) and the  $\text{ClO}_4^-$  ion does not interact with the nickel(II) ion. Thus,  $K_{a2}$  can be reasonably estimated from Eq. 9. Figure 4 shows plots of  $\log K_a(\text{NO}_3^-)/K_a(\text{ClO}_4^-)$ , ( $\approx K_{a2}$ ) vs.  $1/\epsilon$ . Similar  $K_{a2}$  values are obtained for Class I, indicating that coordination by solvent molecules is very weak for Class I, as discussed in a preceding section. The difference between Classes I and II is ascribed to the energy of decoordination of two alcohol molecules and the desolvation of  $\text{NO}_3^-$  by the alcohol molecules with high acidities (AN, Table 2). It is considered that the data for  $i\text{-PrOH}$  support the solvation of the acac by 2-propanol molecules, as shown in Fig. 2.

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- 16) Since a sequence of  $\lambda_0^-$  in the methanol and EtOH is  $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{ClO}_4^-$  (Ref. 14),  $\lambda_0^-(\text{NO}_3^-)$  in *n*-PrOH, *i*-PrOH, and *n*-BuOH were estimated from  $\lambda_0^-$  of other anions (Refs. 7–9). Similarly,  $\lambda_0^-(\text{NO}_3^-)$  in MEK was estimated from  $\lambda_0^-(\text{NO}_3^-)$  in  $\text{Me}_2\text{CO}$  (Ref. 15) and  $\text{PhNO}_2$  (Ref. 12), and  $\lambda_0^-$  of other anions in  $\text{Me}_2\text{CO}$ , MEK, and  $\text{PhNO}_2$  (Refs. 10–12).
- 17) The  $\lambda_0^+ \cdot \eta$  value of  $[\text{Co}(\text{acac})_2(\text{N}, \text{N}, \text{N}', \text{N}'\text{-tmen})]^+$  in *n*-BuOH, which is not available due to limited solubility may be similar to the values in EtOH, *n*-PrOH, *i*-PrOH, since the chelate ion have no specific site for solvation by the alcohols. This agrees well with the data of the bulky tetraalkylammonium ions such as  $\text{Bu}_4\text{N}^+$  and  $(i\text{-C}_5\text{H}_{11})_3\text{-BuN}^+$  which indicate similar  $\lambda_0^+ \cdot \eta$  values (Refs. 7–9).
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