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Solvation and Ionic Association of Bis(β-diketonato)(diamine)-cobalt(III) Perchlorates in Alcohols and Ketones

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The conductances of bis(2,4-pentanedionato)(diamine)cobalt(III) perchlorates, $[Co(acac)_2(diamine)]ClO_4$ (where acac: 2,4-pentanedionato; diamine: en (ethylenediamine) and *N,N,N′,N′*-tmen (*N,N,N′,N′*-tetramethylethylenediamine)) in methanol (MeOH), ethanol (EtOH), 2-propanol (*i*-PrOH), methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) and of bis(β-diketonato)(ethylenediamine)cobalt(III) perchlorates, $[Co(\beta\text{-dik})_2(en)]ClO_4$ (where β-dik: acacBr (3-bromo-2,4-pentanedionato) and $acacNO_2$ (3-nitro-2,4-pentanedionato)) in EtOH, acetone (Me_2CO), and MEK were measured at 25 °C. $[Co(acac)_2(en)]ClO_4$ in the alcohols was found to be more dissociated than $[Co(acac)_2(N,N,N'N'\text{-tmen})]ClO_4$. This behavior was explained as being due to the strong solvation of $[Co(acac)_2(en)]^+$ by the alcohols. $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ seems to be solvated in ketones rather than alcohols. The sequence of the ionic association constant for $[Co(\beta\text{-dik})_2(en)]ClO_4$, acac<acacBr<$acacNO_2$, could be interpreted in terms of an enhanced polarity of the cations with the electron-withdrawing groups.

In order to understand the solute–solvent interactions characteristic of metal-chelate ions, we have measured the conductances of 17 metal-chelate electrolytes, bis(β-diketonato)(diamine)cobalt(III) complexes, $[Co(\beta\text{-dik})_2(diamine)]X$ ($X^-=ClO_4^-$, I^-, and Br^-) in organic solvents at 25 °C.[1–5] From the obtained conductance parameters (the limiting conductance, Λ_0, the Walden product of the cations, $\lambda_0^+\cdot\eta$, and the ionic association constant, K_a), we have clarified the effects of the following factors on the mobility of the chelate cations and ionic association: (a) interactions between NH protons of diamine in the cations and solvent dipole;[1,2] (b) solvation of the ligands in the cations through hydrogen bonding;[3] (c) *N*-methylation of the ligand ethylenediamine in the cations[1–3] and the relative acidity of the residual NH protons;[4] and (d) polar substituents such as the nitro group in the ligand β-diketonato.[5]

However, factors (b) and (d) have been examined only in 1-propanol (*n*-PrOH) and acetone (Me_2CO), and nitrobenzene ($PhNO_2$), respectively. In this study, in order to obtain more information on their factors, the conductances of $[Co(\beta\text{-dik})_2(diamine)]ClO_4$ were measured in several alcohols and ketones. The obtained results are discussed in detail regarding the difference in solvation of the chelate cations by alcohols and ketones as well as the polarity of the chelate cations.

Experimental

(a) $[Co(\beta\text{-dik})_2(diamine)]ClO_4$ was prepared and purified as described previously.[1,5] Tetraethylammonium perchlorate (Et_4NClO_4, commercial product) was purified by two recrystallizations. The purity of all products was checked by chemical analyses of C, H, and N. Methanol (MeOH) and ethanol (EtOH) were refluxed for 3 days over magnesium methoxide and magnesium ethoxide, respectively, and fractionally distilled. 1-Propanol (*n*-PrOH) and 2-propanol (*i*-PrOH) were refluxed over calcium oxide for 2 days and fractionally distilled. Acetone (Me_2CO), methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) were refluxed over Drierite after dehydration and fractionally distilled. The distillation was performed under a flow of N_2 gas.

(b) The procedure for the conductance measurements and other measurements (viscosity and density) were described previously.[1] The dielectric constant (ε) and viscosity (η in mPa s) of the solvents for an analysis were as follows: for MeOH $\varepsilon=32.62$,[6] $\eta=0.5460$; for EtOH $\varepsilon=24.33$,[7] $\eta=1.082$; for *n*-PrOH $\varepsilon=20.45$,[7] $\eta=1.948$; for *i*-PrOH $\varepsilon=19.41$,[8] $\eta=2.078$; for Me_2CO $\varepsilon=20.56$,[9] $\eta=0.3052$; for MEK $\varepsilon=18.01$,[10] $\eta=0.3803$; for MIBK $\varepsilon=12.8$,[11] $\eta=0.5478$.

Results

The conductances Λ(S cm^2 mol^{-1}) at six to nine concentrations, C(mol dm^{-3}) of $[Co(\beta\text{-dik})_2(diamine)]ClO_4$ and Et_4NClO_4 covering the range from 4.2×10^{-3} to 10^{-5} mol dm^{-3} in the alcohols and the ketones were measured at 25 °C.[12] The data were analyzed by the Fuoss-Hsia equation with $E=E_1\Lambda_0-2E_2$ in the form,[13]

$$\Lambda = \Lambda_0 - SC^{1/2}\gamma^{1/2} + EC\gamma\log C\gamma + J_1(d)C\gamma - J_2(d)C^{3/2}\gamma^{3/2} - K_aC\gamma f_\pm^2\Lambda, \tag{1}$$

where Λ_0 and K_a refer to the limiting conductance and the ionic association constant, respectively, and the other symbols have their usual meanings. The procedure for fitting in terms of Λ_0, K_a, and the distance parameter d has been described previously.[1]

The obtained conductance parameters are given in Tables 1 and 2 for the alcohols and the ketones,

Table 1. Conductance Results in Alcohols at 25 °C

Electrolyte	Solvent	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	d[a)] Å	σ_Λ[b)]
$[Co(acac)_2(en)]ClO_4$	MeOH	106.08±0.06	37±12	8.5	0.020
Et_4NClO_4		131.0 ±0.1	60±16	8.8	0.028
$[Co(acac)_2(en)]ClO_4$	EtOH	48.68±0.02	147± 8	13.7	0.012
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$		53.36±0.01	180± 3	14.4	0.009
$[Co(acacBr)_2(en)]ClO_4$		46.68±0.01	179± 2	14.6	0.003
$[Co(acacNO_2)_2(en)]ClO_4$		46.06±0.05	297± 6	18.0	0.012
Et_4NClO_4		61.31±0.16	295±30	11.4	0.008
$[Co(acac)_2(en)]ClO_4$[c)]	*n*-PrOH	25.81±0.02	411±45	14.1	0.011
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$[c)]		28.57±0.02	480±15	16.4	0.015
Et_4NClO_4		31.50±0.02	895±19	19.3	0.015
$[Co(acac)_2(en)]ClO_4$	*i*-PrOH	23.67±0.02	812±36	14.4	0.016
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$		26.63±0.05	837± 9	22.9	0.026

a) Distance parameter with a minimum σ_Λ value in Eq. 1. b) Standard deviation of Λ ($\sigma_\Lambda=[\sum(\Lambda_{calcd}-\Lambda_{obsd})^2/(n-3)]^{1/2}$). c) Ref. 3.

Table 2. Conductance Results in Ketones at 25 °C

Electrolyte	Solvent	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	d[a)] Å	σ_Λ[b)]
$[Co(acac)_2(en)]ClO_4$[c)]	Me_2CO	180.03±0.09	180± 4	14.0	0.06
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$[c)]		186.40±0.04	137± 2	13.1	0.03
$[Co(acacBr)_2(en)]ClO_4$		175.84±0.07	231± 4	15.0	0.06
$[Co(acacNO_2)_2(en)]ClO_4$		174.74±0.08	368± 4	15.6	0.06
Et_4NClO_4		208.85±0.09	210± 5	13.6	0.08
$[Co(acac)_2(en)]ClO_4$	MEK	140.44±0.03	374± 4	16.6	0.02
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$		145.3 ±0.1	253± 9	16.2	0.15
$[Co(acacBr)_2(en)]ClO_4$		136.93±0.06	524± 7	17.2	0.04
$[Co(acacNO_2)_2(en)]ClO_4$		136.52±0.07	981± 14	18.2	0.05
Et_4NClO_4		164.40±0.04	455± 7	16.8	0.04
$[Co(acac)_2(en)]ClO_4$	MIBK	93.5 ±0.1	3120±150	22.6	0.09
$[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$		97.71±0.08	1710± 40	22.2	0.10
Et_4NClO_4		109.5 ±0.2	4190±130	20.8	0.20

a) and b) are the same as in Table 1. c) Ref. 3.

respectively, together with those in 1-propanol (*n*-PrOH) and acetone (Me_2CO). The limiting conductances (λ_0^+/S cm^2 mol^{-1}) and Walden products ($\lambda_0^+\cdot\eta$/S cm^2 mol^{-1} 10^{-1} Pa s) of the chelate cations are given in Table 3, together with those in *n*-PrOH, Me_2CO, nitrobenzene ($PhNO_2$), and 1,2-dichloroethane (1,2-DCE) for comparison. The data were obtained from the limiting conductances of the perchlorate ion, λ_0^- (ClO_4^-): in MeOH, 70.94;[6)] in EtOH, 32.04;[7)] in *i*-PrOH, 15.24;[8)] in Me_2CO, 118.35;[9)] in MEK, 93.0;[10)] in MIBK, $\lambda_0^-\cdot\eta$=0.34.[14)]

Discussion

(1) Solvation and Association of $[Co(acac)_2(diamine)]ClO_4$. (a) Ionic Mobility: Figure 1 shows the Walden products ($\lambda_0^+\cdot\eta$) for $[Co(acac)_2(en)]^+$ and $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ in each solvent. It is clear that $\lambda_0^+\cdot\eta$ for $[Co(acac)_2(en)]^+$ is much smaller than that for $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ except for the result in 1,2-DCE, although the size of $[Co(acac)_2(en)]^+$ is smaller than $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$

Table 3. Ionic Mobilities and Walden Products of [Co(β-dik)$_2$(diamine)]$^+$ in Organic Solvents at 25 °C

Chelate Cation	Solvent	λ_0^+ S cm^2 mol^{-1}	$\lambda_0^+\cdot\eta$ S cm^2 mol^{-1} 10^{-1} Pa s
[Co(acac)$_2$(en)]$^+$	MeOH	35.14	0.192
[Co(acac)$_2$(en)]$^+$	EtOH	16.64	0.180
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^+$		21.32	0.231
[Co(acacBr)$_2$(en)]$^+$		14.64	0.158
[Co(acacNO$_2$)$_2$(en)]$^+$		14.02	0.152
[Co(acac)$_2$(en)]$^{+a)}$	*n*-PrOH	9.39	0.183
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^{+a)}$		12.15	0.237
[Co(acac)$_2$(en)]$^+$	*i*-PrOH	8.43	0.175
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^+$		11.39	0.237
[Co(acac)$_2$(en)]$^{+a)}$	Me$_2$CO	61.63	0.188
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^{+a)}$		68.0	0.208
[Co(acacBr)$_2$(en)]$^+$		57.44	0.175
[Co(acacNO$_2$)$_2$(en)]$^+$		56.34	0.172
[Co(acac)$_2$(en)]$^+$	MEK	47.44	0.180
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^+$		52.3	0.199
[Co(acacBr)$_2$(en)]$^+$		43.93	0.167
[Co(acacNO$_2$)$_2$(en)]$^+$		43.52	0.166
[Co(acac)$_2$(en)]$^+$	MIBK	—	0.17
[C(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^+$		—	0.19
[Co(acac)$_2$(en)]$^{+b)}$	PhNO$_2$	10.9	0.201
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^{+b)}$		11.9	0.220
[Co(acacBr)$_2$(en)]$^{+c)}$		9.77	0.180
[Co(acacNO$_2$)$_2$(en)]$^{+c)}$		9.29	0.172
[Co(acac)$_2$(en)]$^{+b)}$	1,2-DCE	25.7	0.201
[Co(acac)$_2$(*N*,*N*,*N′*,*N′*-tmen)]$^{+b)}$		26.0	0.204

a) Ref. 3. b) Ref. 1. c) Ref. 5.

with four *N*-methyl groups.[15] The difference in $\lambda_0^+\cdot\eta$ is larger in the alcohols than in the other solvents.

These are in opposition to the results for tetraalkylammonium ion (R$_4$N$^+$), for which $\lambda_0^+\cdot\eta$ decreases with increasing the ionic size in the order $\mathrm{Et_4N^+} < \mathrm{Pr_4N^+} < \mathrm{Bu_4N^+} < (i\text{-Am})_3\mathrm{BuN^+}$ in each solvent, as is hydrodynamically expected.[1,6–10,16]

It is considered that there exist three main factors for solute-solvent interactions of [Co(acac)$_2$(diamine)]$^+$: (1) Lewis acid-base interaction ; (2) an ion-dipole interaction; and (3) van der Waals interactions. Table 4 gives the solvent properties: (1-a) donor number (DN),[17] (1-b) acceptor number (AN);[17] (2) dipole moment (μ);[11] (3) solubility parameter (δ).[18] These parameters correspond to the above factors (1—3), respectively.

Table 4. Solvent Parameters

Solvent	DN$^{a)}$	AN$^{b)}$	$\mu^{c)}$	$\delta^{d)}$
MeOH	19	41.3	1.70	14.5
EtOH	20	37.9	1.69	12.7
n-PrOH	—	—	1.68	11.9
i-PrOH	—	33.5	1.66	11.5
Me$_2$CO	17	12.5	2.88	9.9
MEK	—	—	2.74	9.3
MIBK	—	—	2.79	8.4
PhNO$_2$	4.4	14.8	4.22	10.0
1,2-DCE	0	16.7	1.40	9.8

a) Donor number (DN), Ref. 17. b) Acceptor number (AN), Ref. 17. c) Dipole moment (μ), Ref. 11. d) Solubility parameter (δ), Ref. 18.

The alcohols have both basic (oxygen atom) and acidic (OH proton) parts for which the corresponding parameters are DN and AN, respectively (Table 4).

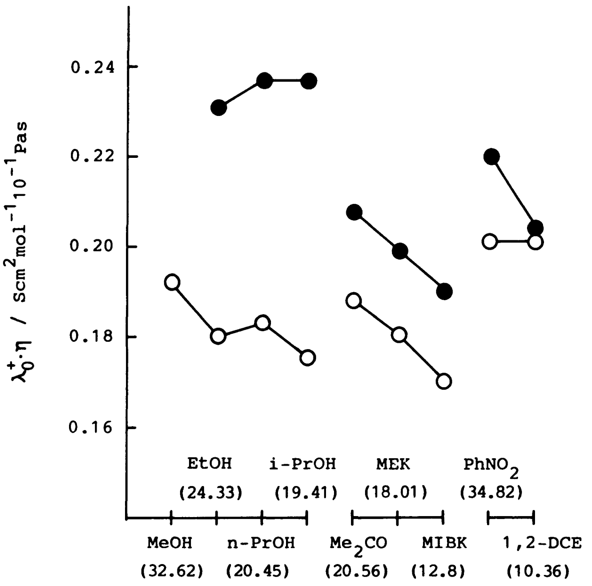

Fig. 1. Walden products for ○, $[Co(acac)_2(en)]^+$ and ●, $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$. The values in parentheses are the dielectric constant (ε) of each solvent.

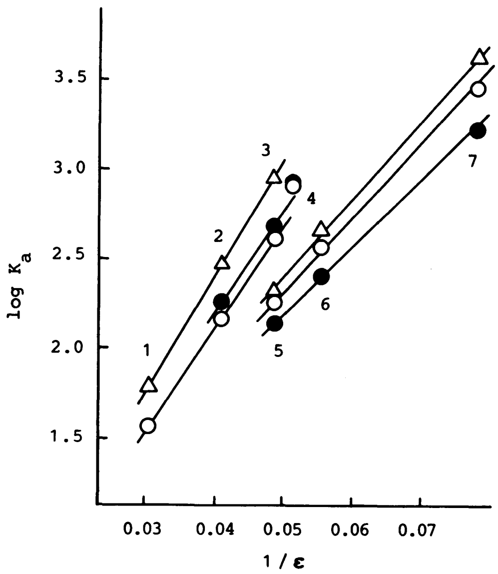

Fig. 2. Plots of log K_a with $1/\varepsilon$ for ○, $[Co(acac)_2(en)]ClO_4$; ●, $[Co(acac)_2(N,N,N',N'\text{-tmen})]ClO_4$; and △, Et_4NClO_4.
Alcohols: 1, MeOH; 2, EtOH; 3, *n*-PrOH;[3] 4, *i*-PrOH. Ketones: 5, Me_2CO;[3] 6, MEK; 7, MIBK.

Thus, they can solvate the NH protons of the ligand en and the oxygen atoms of the ligand acac in $[Co(acac)_2(en)]^+$. A molecular model for the solvation of $[Co(acac)_2(en)]^+$ by one alcohol molecule is possible without crowding. This acid-base interaction contributes to a lower mobility in the alcohols than in the ketones. The effect of an ion-dipole interaction (factor 2) in the alcohols is small due to their lower dipole moments. This was confirmed from the result in 1,2-DCE with low polarity, in which the mobility of $[Co(acac)_2(en)]^+$ was comparable to that of $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$.[1]

The ketones have a basic (CO group) part and act as a hydrogen bonding donor for the NH protons in $[Co(acac)_2(en)]^+$ (factor 1-a). This solvation may result in a lower mobility. However, since the μ values of the ketones are smaller than that of $PhNO_2$ which strongly solvates the NH protons by an ion-dipole interaction,[1] factor 2 is not so effective.

Further, it is noteworthy that the Walden products for $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ in the ketones are much smaller than in the alcohols, as is shown in Table 3. On the other hand, for Bu_4N^+ there is no appreciable change with solvents: $\lambda_0^+\cdot\eta$ is 0.212,[6] 0.213,[7] 0.209,[7] and 0.211[8] for MeOH, EtOH, *n*-PrOH, and *i*-PrOH, and 0.201[9] and 0.199[10] for Me_2CO and MEK, respectively.

Since $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ has no NH protons, another factor should be considered regarding the decreased mobility in the ketones. Van der Waals forces between $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ and the ketones/alcohols may be operative compared to $[Co(acac)_2(en)]^+$, because the charge of Co(III) is shielded by the bulky ligands, *N,N,N′,N′*-tmen and acac. The solubility parameter, δ is an indication for the van der Waals interactions. Although δ values of charged species are not available, δ values of $[Co(acac)_3]$ (9.72, 10.12, and 10.7)[19] are more close to those of the ketones than the alcohols (Table 4), suggesting that the ketone molecules solvate more strongly $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$. Furthermore, the fact that the chelate electrolyte is more soluble in the ketones than the alcohols supports the above view. Another factor may be dipole (ion)–dipole (solvent) interactions, because of the polarity of this cation, in addition to ion–dipole (solvent) interactions. These effects are also larger for ketones with high polarity.

(b) Ionic Association: Figure 2 shows that the variation of K_a with $1/\varepsilon$ for $[Co(acac)_2(diamine)]ClO_4$ and Et_4NClO_4. With good approximations, straight lines are obtained for all electrolytes, as is expected from the coulombic theory of ionic association,[20]

$$\log K_a = e^2 / akT \cdot 1 / \varepsilon + \log K_a^\circ, \qquad (2)$$

where a is the contact distance between the cation and the anion, k is the Boltzman constant and T is the absolute temperature. K_a° contains the contribution to the association for all factors, except for the long-range coulombic interaction.

Two trends are shown: (i) Each electrolyte is more associated in the alcohols than the ketones at the same dielectric constant and (ii) the slope of log K_a vs. $1/\varepsilon$ is a little larger in the alcohols than the ketones. Trend (i) has been observed for tetraalkylammonium perchlorates:[7–9] The larger association constant in the alcohols could be explained in terms of (1) diminution in dielectric constant in the vicinity of an ion pair and (2) a multiple-step association process with solvation and desolvation of ClO_4^- by the alcohol molecules. The increasing effect of K_a due to this multiple-step association process[8,9] increases in the order MeOH< EtOH<*n*-PrOH<*i*-PrOH, which may be responsible for trend (ii).

The different pattern of K_a for [Co(acac)$_2$(diamine)]ClO$_4$ was observed. In the ketones, K_a for [Co(acac)$_2$(en)]ClO$_4$ is larger than that for [Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]ClO$_4$. In the alcohols, on the other hand, the reverse trend is observed although the difference in K_a is small. Since [Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]$^+$ has a large molal volume compared to [Co(acac)$_2$(en)]$^+$, its cation charge may be more shielded. Therefore, K_a for [Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]ClO$_4$ should be smaller than that for [Co(acac)$_2$(en)]ClO$_4$, though this is not the case in alcohols.

An explanation is based on the strong solvation of [Co(acac)$_2$(en)]$^+$ by the alcohols: solvation of the NH protons (en) by the oxygen atom of alcohols and of the oxygen atoms (acac) by the OH proton of the alcohols through hydrogen bonding, as is discussed in the preceding section. This leads to the formation of strongly solvated cation and the cation may be behave as a distinct entity which has a larger molal volume compared to [Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]$^+$. However, the steric structure of the chelate cation would not be affected, even if the alcohols solvate the cation firmly. This has been confirmed from a result which showed that the absorption spectra of $^1A_{1g}$–$^1T_{1g}$ have no appreciable change with solvents.[15] In the ketones, the NH protons in [Co(acac)$_2$(en)]$^+$ are solvated by the oxygen atom of the CO group. However, since they have no acidic part for solvation of the acac in [Co(acac)$_2$(en)]$^+$, the solvation may not be so effective compared to that by the alcohols.

The K_a values in *i*-PrOH are larger than those expected from the line of the plots of the primary alcohols, showing weaker solvation by *i*-PrOH, which may result from its lower acidity or steric hindrance.

(2) Solvation and Association of [Co(β-dik)$_2$(en)]ClO$_4$: The coordinated acac in this type of metal-chelate cations is of pseudo aromatic character with a ring current[21] and has a electron-mediating ability. Therefore, it is expected that the introduction of the electron-withdrawing substituents, Br and NO$_2$ at the C-3 position of the acac in [Co(acac)$_2$(en)]$^+$ increases the relative acidity of the NH protons of the ligand en through the pseudo aromatic chelate ring, although these are far from the substituents. This is justified from the result that the rate of H–D exchange of the NH protons in a deuterium oxide/dimethyl-*d*$_6$-sulfoxide mixture (weight ratio 1:3.9) by ^{1}H NMR measurement increase in the sequence acac<acacBr< acacNO$_2$,[5] in accordance with Hammett's σ_P values of electron-withdrawing tendency of the substituents.

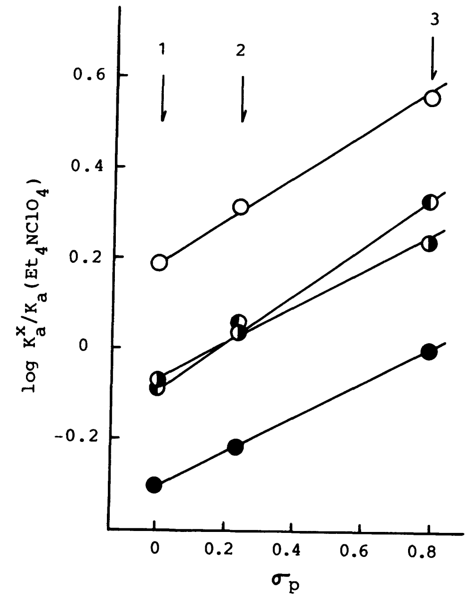

Fig. 3. Hammett's relationship for the ratio of K_a for [Co(β-dik)$_2$(en)]ClO$_4$ to Et$_4$NClO$_4$.
β-dik: 1, acac; 2, acacBr; 3, acacNO$_2$. Organic solvents: ●, EtOH; ◑, Me$_2$CO; ◐, MEK; ○, PhNO$_2$.[1,5]

Figure 3 shows a plot of the ratio of K_a for [Co(β-dik)$_2$(en)]ClO$_4$ to Et$_4$NClO$_4$ vs. Hammett's σ_p value. Since the Et$_4$N$^+$ ion has no specific site for solvation or ion pair formation in each solvent, the change in the ratio of K_a may suggest specific interactions of the chelate electrolytes. The trends indicated in Fig. 3 show two characteristics: (i) The ratio of K_a for [Co(acac)$_2$(en)]ClO$_4$ to Et$_4$NClO$_4$ increases in the order EtOH<MEK≈Me$_2$CO<PhNO$_2$, and (ii) the ratio increases in the same order [Co(acac)$_2$(en)]ClO$_4$< [Co(acacBr)$_2$(en)]ClO$_4$<[Co(acacNO$_2$)$_2$(en)]ClO$_4$ as the rate of H–D exchange. Furthermore, a linear relationship with a similar slope is obtained for all the solvent systems.

For [Co(acac)$_2$(en)]ClO$_4$, a solvent-separated ion pair is formed in the alcohols and ketones and the solvation of the cation by the alcohols is much stronger. On the other hand, a contact ion pair between the NH protons and ClO_4^- is formed in PhNO$_2$ by a partial exclusion of nitrobenzene molecules, leading to a larger K_a value.[1] These correspond to the order of the ratio of K_a for [Co(acac)$_2$(en)]ClO$_4$ to Et$_4$NClO$_4$, EtOH<MEK≈Me$_2$CO<PhNO$_2$.

For the introduction of substituents, Br and NO$_2$, the two effects on the increase in K_a should be considered: (1) The increase in the relative acidity of the NH protons in the ligand en, leading to a stronger interaction between the NH protons and ClO_4^- and (2) the increase in the polarity of the chelate cations, leading to a stronger cation–anion interaction. At the same time, the two effects also enhance the solvation of the cations, leading to a decrease in K_a. The increased solvation of the cations is supported by the fact that the introduction of Br and NO_2 largely decreases the mobility of the cations in the order acac>acacBr>acacNO_2 (Table 3). In practice, however, since K_a values are increased by the introduction of Br and NO_2, the decreasing effect of solvation on K_a is overcome by the increasing effects, (1) and (2). In EtOH, since the $[Co(acac)_2(en)]^+$ cation is strongly solvated, the increase in K_a by the introduction of Br and NO_2 is attributed to effect (2). In Me_2CO and MEK, a solvent-separated ion pair is similarly formed, although the solvation is not so effective compared to that in EtOH. Thus, it seems that the contribution of effect (1) is small and that of effect (2) is large. In $PhNO_2$, where a contact ion pair between the NH protons and ClO_4^- is formed, the contribution of both effects (1) and (2) is considered. However, in view of the fact that the slope for $PhNO_2$ is similar to that for EtOH (Fig. 3), it is likely that effect (2) is predominant.

References

1) K. Ito, *Inorg. Chem.*, **22**, 2872 (1983).

2) K. Ito, E. Iwamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 3190 (1982).

3) K. Ito, E. Iwamoto, S. Suehisa, H. Isono, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **59**, 3841 (1986).

4) K. Ito, E. Iwamoto, K. Hasegawa, M. Yamamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **58**, 1287 (1985).

5) K. Ito, H. Isono, E. Iwamoto, and Y. Yamamoto, *Inorg. Chem.*, **23**, 850 (1984).

6) R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965); R. L. Kay, D. F. Evans, and G. P. Cunningham, *ibid.*, **73**, 3322 (1969).

7) D. F. Evans and P. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968). $\lambda_0^-(ClO_4^-)=32.04$ was obtained from Λ_0 (Et_4NClO_4) and λ_0^+ (Et_4N^+).

8) S. M. A. Matesich, J. A. Nadas, and D. F. Evans, *J. Phys. Chem.*, **74**, 4568 (1970).

9) D. F. Evans, J. Thomas, J. A. Nadas, and S. M. A. Matesich, *J. Phys. Chem.*, **75**, 1714 (1971).

10) S. R. C. Hughes and D. H. Price, *J. Chem. Soc. A*, **1967**, 1093. λ_0^- $(ClO_4^-)=93.0$ was obtained from Λ_0 (Et_4NClO_4) and λ_0^+ (Et_4N^+).

11) "Handbook of Chemistry and Physics," 64th ed., ed. by R. C. West, CRC Press: Florida (1983). The dielectric constant (ε=12.8) for MIBK at 25 °C was estimated from 13.11 (ε) for MIBK at 20 °C and the temperature dependence of the dielectric constants for Me_2CO and MEK.

12) The equivalent conductance data at various concentrations of $[Co(\beta\text{-dik})_2(\text{diamine})]ClO_4$ and Et_4NClO_4 in the alcohols and the ketones at 25 °C can be ordered directly to the author (K.I.).

13) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1550 (1967); R. Fernández-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).

14) λ_0^- $(ClO_4^-)\cdot\eta$ (=0.34) in MIBK was estimated from (a) 0.36 for λ_0^- $(ClO_4^-)\cdot\eta$ in Me_2CO and 0.35 in MEK and (b) $\Lambda_0\cdot\eta$ for the chelate electrolytes in Me_2CO, MEK, and MIBK.

15) This is further confirmed from the result that the *N*-methylation lengthens the Co–N bond length, which is justified from the absorption peak in the visible region of $^1A_{1g}$–$^1T_{1g}$ red-shifted with *N*-methylation (541 and 542 nm for $[Co(acac)_2(en)]^+$ and 598 and 596 nm for $[Co(acac)_2(N,N,N',N'\text{-tmen})]^+$ in *n*-PrOH and Me_2CO, respectively, in analogy with the results in $PhNO_2$ and 1,2-DCE (Ref. 1)).

16) R. Fernández-Prini, "Physical Chemistry of Organic Solvent Systems," ed. by A. K. Covington and T. Dickson, Plenum Press, London (1973), Chap. 5.

17) V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions," Plenum Press, New York (1978).

18) A. F. M. Barton, *Chem. Rev.*, **75**, 731 (1975).

19) M. Yamamoto and Y. Yamamoto, *Anal. Chim. Acta*, **87**, 375 (1976); J. F. Huber, F. C. Kraak, and H. Veening, *Anal. Chem.*, **44**, 1554 (1972).

20) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956); R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

21) J. J. Bellary and R. F. Branch, *J. Chem. Soc.*, **1945**, 4491; J. P. Colemann, R. L. Marchall, and W. L. Young III, *Chem. Ind.* (*London*), **1962**, 1380.