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Relative Acidity of Bis(2,4-pentanedionato)(diamine)cobalt(III) Complexes in Lower Dielectric Solvents

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The conductances of bis(2,4-pentanedionato)(diamine)cobalt(III) complexes ([Co(acac)$_2$(diamine)]X, diamine: ethylenediamine (en) and *N,N'*-dimethylethylenediamine (*N,N'*-dmen), X=Br^- and ClO_4^-) were measured in aprotic solvents covering the approximate range of dielectric constant 5—28 at 25 °C. It was found that a) in spite of the larger size of the methyl derivative the ionic association constants (K_a) for [Co(acac)$_2$(*N,N'*-dmen)]$^+$ complexes are larger than those for [Co(acac)$_2$(en)]$^+$ complexes in all the composition of nitrobenzene ($PhNO_2$)-carbon tetrachloride (CCl_4) mixtures (wt % CCl_4: 20, 40, 60, 70). b) The reverse trend was obtained in dichloromethane (DCM), 1,1,2,2-tetrachloroethane (1,1,2,2-TCE), and chloroform ($CHCl_3$). These results were explained in terms of hydrogen bonding between the NH protons in the chelate cations and the anions ClO_4^- and Br^-, selective solvation of the NH group side by nitrobenzene, and the desolvation due to the introduction of the *N*-methyl groups. The relative acidity of NH protons which is controlled by solvation plays an important role in ionic association for the chelate cations with NH protons.

It is known that when *N*-alkyl groups are introduced into some amines coordinated to a metal ion, the acidity of the residual NH protons increases.[1,2] For example, the acid dissociation constant (pK_a=7.2) of $[Pt(NH_3)_6]^{4+}$ in water increases with the replacement of ammonia (NH_3) by ethylenediamine (en) (pK_a: 5.5 for $[Pt(en)_3]^{4+}$). However, the source of the increasing acidity is not clear although the basicity of *N*-methyl-substituted amines and polyamines has been examined in great deal by vapor pressure, EMF, calorimetry, UV, NMR measurements, and *ab initio* calculation.[3]

In our previous studies,[4—6] we have employed a series of bis(*β*-diketonato)(diamine)cobalt(III) complexes as probes to obtain the information on solute-solvent interactions in electrolyte solutions. It is interesting to note that the ionic association constants (K_a) for [Co(acac)$_2$(*N,N'*-dmen)]X (X=ClO_4^- and Br^-) in $PhNO_2$ are larger than those for [Co(acac)$_2$(en)]X in spite of decreasing the number of the NH protons capable of hydrogen bonding with the anions. We have proposed that the results can be interpreted in terms of the difference in acidities of the NH protons owing to an ion-solvent dipole interaction. Therefore, it is considered that the properties of mixed solvents become much clear using the ion association processes of [Co(acac)$_2$(en)]$^+$ and [Co(acac)$_2$(*N,N'*-dmen)]$^+$ complexes.

In this study, we applied these ideas to the mixed solvents of nitrobenzene ($PhNO_2$) and carbon tetrachloride (CCl_4), and pure solvents dichloromethane (DCM), 1,1,2,2-tetrachloroethane (1,1,2,2-TCE), and chloroform ($CHCl_3$). Carbon tetrachloride is nonpolar aprotic and the properties of $PhNO_2$–CCl_4 mixtures (dielectric constant, viscosity, and specific gravity) change linearly with the increase in a fraction of CCl_4, so carbon tetrachloride acts only as a diluent.[7]

Experimental

The metal chelate electrolytes, [Co(acac)$_2$(en)]X and [Co(acac)$_2$(*N,N'*-dmen)]X (X=Br^- and ClO_4^-) were prepared and purified as described previously.[4,5] All the solvents employed were commercial products (Wako Pure Chemical Industries, Ltd.). Reagent grade carbon tetrachloride (CCl_4) was distilled under nitrogen atmosphere, after being shaken with $NaHCO_3$ solution, then with water, and dried over $CaCl_2$. The middle fraction was collected. Dichloromethane (DCM) was washed with $NaHCO_3$ solution and then with water, dried over $CaCl_2$, and fractionally distilled. The method of purification of nitrobenzene ($PhNO_2$) has been described previously.[5] Spectrograde chloroform was washed with water and passed through a molecular sieve (4A) ($CHCl_3$: Density 1.4799 g cm^{-3}, viscosity 0.5470 mPa s at 25 °C). Reagent grade 1,1,2,2-tetrachloroethane was used without further purification (1,1,2,2-TCE: Density 1.5866 g cm^{-3}, viscosity 1.610 mPa s at 25 °C).

Conductance measurements were carried out by a LCR-type bridge (Ando Electric Company Ltd.) having a frequency of 1592 Hz. The procedure used for the conductance measurements and other measurements (viscosity and density of solvent) have been described previously.[5] The solvent mixtures of nitrobenzene and carbon tetrachloride were prepared by weight (corrected to vaccum) under nitrogen atmosphere in a dry box. The dielectric constant (ε) and viscosity (η in mPa s) of the solvent mixtures used for analysis were obtained from interpolation of those determined by Fuoss *et al.*;[7] wt % CCl_4 20, ε=27.9, η=1.612; 40, ε=21.2, η=1.400; 60, ε=14.5, η=1.201; 70, ε=11.4, η=1.105. The dielectric constant[8] and viscosity of pure solvents are as follows: DCM, ε=8.90, η=0.416; 1,1,2,2-TCE, ε=8.01, η=1.610; $CHCl_3$, ε=4.72, η=0.5470.

Results and Discussion

The measured molar conductances Λ (S cm^2 mol^{-1}) and corresponding electrolyte concentrations C (mol dm^{-3}) at 25 °C were given in Tables 1 and 2 for [Co(acac)$_2$(diamine)]Br in $PhNO_2$–CCl_4 mixtures and [Co(acac)$_2$(diamine)]ClO_4 in chloroalkane solvents and $PhNO_2$–CCl_4 (wt % 70) mixture, respectively. The data were analyzed by using the expanded Fuoss-Hsia equation with $E=E_1\Lambda_0-2E_2$ as in the following[9]

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + J_1C\gamma - J_2(C\gamma)^{3/2} - K_aC\gamma f_\pm^2\Lambda \qquad (1)$$

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Table 1. Molar concentrations, C/mol dm^{-3}, and molar conductances, Λ/S cm^2 mol^{-1} of [Co(acac)$_2$(diamine)]Br in nitrobenzene-carbon tetrachloride (wt% CCl$_4$) mixtures at 25 °C

20 %				60 %	
[Co(acac)$_2$(en)]Br		[Co(acac)$_2$(N,N'-dmen)]Br		[Co(acac)$_2$(en)]Br	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
3.866	26.36	4.407	23.73	3.400	12.50
2.627	27.85	3.101	24.99	1.694	15.99
1.924	28.89	2.201	26.50	0.9079	19.55
1.406	29.78	1.633	27.73	0.4258	24.11
0.9600	30.69	1.205	28.86	0.2069	28.24
0.6072	31.57	0.8105	30.11	0.1222	30.95

40 %			
[Co(acac)$_2$(en)]Br		[Co(acac)$_2$(N,N'-dmen)]Br	
$C\times10^4$	Λ	$C\times10^4$	Λ
3.327	22.89	4.350	18.35
1.877	25.84	3.130	20.04
1.529	26.83	2.262	21.79
1.185	27.96	1.548	23.78
0.9316	28.96	1.104	25.97
0.6368	30.38	0.6751	27.96
0.3981	31.87	0.4101	30.16

Table 2. Molar concentrations, C/mol dm^{-3}, and molar conductances, Λ/S cm^2 mol^{-1} of [Co(acac)$_2$(diamine)]ClO$_4$ in aprotic solvents at 25 °C

DCM				1,1,2,2-TCE			
[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
2.329	22.34	2.519	30.27	1.009	9.662	1.024	12.03
1.147	29.71	1.216	39.44	0.4224	12.95	0.7411	13.26
0.7128	35.86	0.7432	46.77	0.2365	15.31	0.4333	15.43
0.4006	44.52	0.4122	56.56	0.1156	18.04	0.2263	17.99
0.1952	57.24	0.2399	66.37	0.0545	20.33	0.1083	20.61
0.0867	73.38	0.1228	78.95			0.0311	22.73
0.0536	82.69						

PhNO$_2$-CCl$_4$ (wt% 70)				CHCl$_3$			
[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
2.306	16.29	3.843	13.26	4.140	0.222	54.86	0.230
1.563	18.40	2.465	15.38	3.006	0.245	45.56	0.227
1.030	20.76	1.720	17.23	1.895	0.290	33.46	0.225
0.6914	23.05	1.269	18.88	1.221	0.340	14.93	0.248
0.4782	25.12	0.8714	20.99	0.618	0.447	11.23	0.263
0.3206	27.28	0.5611	23.51	0.246	0.669	6.533	0.307
0.2168	29.12	0.3688	25.84			3.883	0.363
		0.2154	28.65			2.437	0.433
		0.1413	30.48			0.731	0.700

where K_a is the ionic association constant and Λ_0 is the limiting conductance. The molar conductances of [Co(acac)$_2$(N,N'-dmen)]ClO$_4$ in CHCl$_3$ indicated a minimum conductance Λ_{min} at *ca.* 3.5×10^{-3} mol dm^{-3} (Table 2). The Fuoss-Kraus theory[10] of triple ion formation showed that the position C_{min} of Λ_{min} is the product of K_{a3} by electrostatic theory and Λ_0/Λ_{03}. This relation coincides with the empirical rule, $C_{min}\simeq(\varepsilon^3/3)\times10^{-4}$, discoverd by Walden.[10] The solubility of [Co(acac)$_2$(en)]ClO$_4$ is too small to obtain a minimum

TABLE 3. CONDUCTANCE RESULTS FOR [Co(acac)$_2$(diamine)]Br IN NITROBENZENE–CARBON TETRACHLORIDE MIXTURES AT 25 °C

CCl_4 (wt %)	Electrolyte	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	d Å	K_a(en)[a)] / K_a(N,N'-dmen)
0	[Co(acac)$_2$(en)]Br[b)]	32.23±0.03	449±7	18.1	0.60
	[Co(acac)$_2$(N,N'-dmen)]Br[b)]	32.34±0.08	749±65	8.4	
20	[Co(acac)$_2$(en)]Br	33.62±0.08	840±140	11	0.57
	[Co(acac)$_2$(N,N'-dmen)]Br	33.79±0.29	1480±360	11	
40	[Co(acac)$_2$(en)]Br	35.28±0.19	2610±320	13	0.60
	[Co(acac)$_2$(N,N'-dmen)]Br	34.85±0.73	4310±960	12	
60	[Co(acac)$_2$(en)]Br	37.38±0.36	20500±900	17	—

a) Ratio of K_a for [Co(acac)$_2$(en)]Br to that for [Co(acac)$_2$(N,N'-dmen)]Br. b) From Ref. 4.

TABLE 4. CONDUCTANCE RESULTS FOR [Co(acac)$_2$(diamine)]ClO$_4$ IN APROTIC SOLVENTS AT 25 °C

Solvent	Electrolyte	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	d Å	K_a(en)[a)] / K_a(N,N'-dmen)
1,2-DCE	[Co(acac)$_2$(en)]ClO$_4$[b)]	64.85±0.40	16600±600	20.2	1.50
	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$[b)]	64.33±0.40	11100±900	20.4	
1,1,2,2-TCE	[Co(acac)$_2$(en)]ClO$_4$	24.60±0.18	46000±800	—	1.82
	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	24.84±0.38	25300±1500	—	
DCM	[Co(acac)$_2$(en)]ClO$_4$	120.6±1.5	130100±3000	25	2.40
	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	113.0±2.9	54100±3600	23	
$CHCl_3$	[Co(acac)$_2$(en)]ClO$_4$	—	(6.92±0.18)×10^8[c)] 950±70[d)]	—	3.66
	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	—	(1.89±0.07)×10^8[c)] 280±10[d)]	—	
$PhNO_2$	[Co(acac)$_2$(en)]ClO$_4$[b)]	31.770±0.007	56±1	12.0	0.95
	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$[b)]	31.90±0.02	59±1	11.7	
$PhNO_2$–CCl_4	[Co(acac)$_2$(en)]ClO$_4$	36.74±0.10	15000±400	32	0.93
(70 %)	[Co(acac)$_2$(N,N'-dmen)]ClO$_4$	36.50±0.22	16200±500	19	

a) Ratio of K_a for [Co(acac)$_2$(en)]ClO$_4$ to that for [Co(acac)$_2$(N,N'-dmen)]ClO$_4$. b) From Ref. 5. c) Values were obtained from Fuoss-Kraus theory. d) Values of triple ion formation constant, K_{a3}.

conductance. The data were analyzed by using the Fuoss-Kraus equation[10)]

$$\Lambda C^{1/2}g(C) = \Lambda_0/K_a^{1/2} + (\Lambda_{03}K_{a3}/K_a^{1/2})(1-\Lambda/\Lambda_0)C \quad (2)$$

where $g(C)$ is given by $g(C)=\exp[-2.303\,A_f(C\Lambda/\Lambda_0)^{1/2}]/[1-A_\lambda(C\Lambda/\Lambda_0)^{1/2}/\Lambda_0]\ (1-\Lambda/\Lambda_0)^{1/2}$, K_{a3} is the triple ion formation constant and Λ_{03} is the sum of the limiting conductances of the two kinds of triple ions. A_f and A_λ are the limiting slopes of the Debye-Hückel theory and of the Onsager theory, respectively. In this study, $\Lambda_{03}/\Lambda_0=1/2$[11)] was assumed and Λ_0 was estimated from the average Walden product of each chelate electrolyte in 1,2-DCE, DCM, and 1,1,2,2-TCE. The conductance parameters are given in Table 3 ([Co(acac)$_2$(en)]Br and [Co(acac)$_2$(N,N'-dmen)]Br in $PhNO_2$–CCl_4 mixtures) and Table 4 ([Co(acac)$_2$(en)]ClO$_4$ and [Co(acac)$_2$(N,N'-dmen)]ClO$_4$ in chloroalkane solvents and $PhNO_2$–CCl_4 (wt%70) mixture).

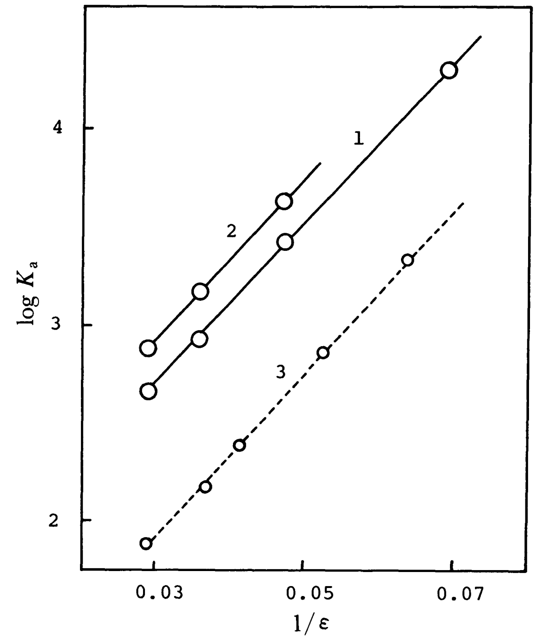

Fig. 1. Dependence of ionic association constant on dielectric constant in $PhNO_2$–CCl_4 mixtures at 25 °C. 1, [Co(acac)$_2$(en)]Br; 2, [Co(acac)$_2$(N,N'-dmen)]Br; 3, n-Bu$_4$NBr.[7)]

Figure 1 shows that the K_a values for [Co(acac)$_2$(diamine)]Br in $PhNO_2$–CCl_4 mixtures are much larger than those for n-Bu$_4$NBr,[7)] this being attributed to hydrogen bonding between the NH protons of the chelate cations and the Br^- ion. However, the K_a values for [Co(acac)$_2$(N,N'-dmen)]Br are larger than those for [Co(acac)$_2$(en)]Br in spite of decreasing the number of the NH protons from four to two. Similar results were obtained for $[Co(acac)_2(en)]ClO_4$ and $[Co(acac)_2(N,N'\text{-}dmen)]ClO_4$ in $PhNO_2$–CCl_4 (wt% 70) mixture although the difference is small owing to the weakness of hydrogen bonding ability of the ClO_4^- ion.[5,6] On the other hand, in chloroalkane solvents (1,2-DCE, DCM, 1,1,2,2-TCE, and $CHCl_3$) the K_a values for $[Co(acac)_2(en)]ClO_4$ are all larger than those for $[Co(acac)_2(N,N'\text{-}dmen)]ClO_4$ (Table 4).

The dipole moment of $PhNO_2$ (μ=4.22) is larger than that of 1,2-DCE, DCM, 1,1,2,2-TCE, and $CHCl_3$ (1,40, 1.60, 1.32, and 1.01, respectively).[8] The NH protons of the $[Co(acac)_2(en)]^+$ ion in $PhNO_2$ are solvated by an ion–solvent dipole interaction and the introduction of *N*-methyl groups removes partly the solvation sheath of the residual protons by steric hindrance, resulting in the increasing K_a.[5] This view is valid in $PhNO_2$–CCl_4 mixtures in which CCl_4 acts only as a diluent. Thus, the significant difference in K_a between $PhNO_2$–CCl_4 mixtures and the chloroalkane solvents is attributed to the selective solvation by nitrobenzene molecules: For the ionic association of *n*-Bu_4NBr and *n*-Bu_4NI in $PhNO_2$–CCl_4 mixtures,[7] the selective solvation of the cation by nitrobenzene was not observed. In addition, the ion pair extraction of R_4NI (R=Et, *n*-Pr, *n*-Bu, and *i*-C_5H_{11} from water to $PhNO_2$–CCl_4 mixtures can be interpreted mainly in terms of the dielectric constant and solubility parameter.[12] These are because of the long-range ion–solvent interaction between the cation R_4N^+ and nitrobenzene molecules. On the other hand, the selective solvation of the chelate cations by nitrobenzene molecules is due to the active NH groups in the coordinated diamine.

In $PhNO_2$–CCl_4 mixtures, the ratios of K_a for $[Co(acac)_2(en)]Br$ to that for $[Co(acac)_2(N,N'\text{-}dmen)]Br$ (Table 3) are almost equal and the plots of $\log K_a$ *vs.* $1/\varepsilon$ for these two salts are linear (Fig. 1), suggesting the similar effective size (5.9 Å, ionic distance parameter from the Fuoss equation).[13] In the chloroalkane solvents, the correlation of plots for $[Co(acac)_2(en)]ClO_4$ and $[Co(acac)_2(N,N'\text{-}dmen)]ClO_4$ is not good (Fig. 2). However, the ratios of K_a for the en complex to the *N,N′*-dmen complex in each solvent are increased with the increase in K_a (Table 4). The K_a values for each salt in 1,1,2,2-TCE are smaller than those in DCM although the bulk dielectric constants of both solvents are nearly equal, suggesting that the effective dielectric constant of 1,1,2,2-TCE is larger than that of DCM. This is due to that the effective dielectric constant of 1,2-DCE[14] and 1,1,2,2-TCE in the vicinity of an ion is appreciably greater than the macroscopic dielectric constant due to the conversion of gauche to trans molecules. The ionic distance parameters obtained tentatively from the slopes between 1,2-DCE and $CHCl_3$ are 6.1 Å for $[Co(acac)_2(en)]ClO_4$ and 6.5 Å for $[Co(acac)_2(N,N'\text{-}dmen)]ClO_4$. This result indicates that the effective size of $[Co(acac)_2(N,N'\text{-}dmen)]^+$ is larger than that of $[Co(acac)_2(en)]^+$ by the volume of two methyl groups in the chloroalkane solvents whcih have lower solvation ability.

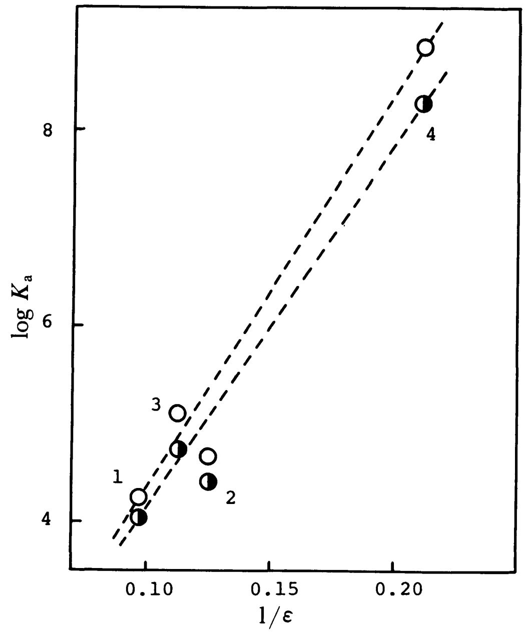

Fig. 2. Dependence of ionic association constant on dielectric constant in chloroalkane solvents at 25 °C. ○, $[Co(acac)_2(en)]ClO_4$; ◑, $[Co(acac)_2(N,N'\text{-}dmen)]ClO_4$.
1, 1,2-DCE; 2, 1,1,2,2-TCE; 3, DCM; 4, $CHCl_3$.

In conclusion, the increasing acidity of the residual NH protons due to *N*-methylation in $PhNO_2$–CCl_4 mixtures is attributed to the appearance of the naked nitrogen protons by the steric hindrance rather than to the reduction in electron density of the protons. Thus, this leads to the results that the K_a values for $[Co(acac)_2(N,N'\text{-}dmen)]X$ are larger than those for $[Co(acac)_2(en)]X$ in solvents with stronger solvation ability for the NH protons, in spite of the larger size and the decrease in the number of the protons for the former salt.

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