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Effects of *N*-Methylated Diamine on Ion Pair Formation of Bis(2,4-pentanedionato)(diamine) Cobalt(III) Bromides in Nitrobenzene by Conductometry

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The conductometric study of bis(2,4-pentanedionato)(diamine) cobalt(III) bromides in nitrobenzene at 25 °C indicated that the ion association constant of the chelate salts increases in the order, $[Co(acac)_2(N,N,N',N'\text{-tmen})]Br < Bu_4NBr < [Co(acac)_2(N,N\text{-dmen})]Br < [Co(acac)_2(en)]Br < [Co(acac)_2(N,N'\text{-dmen})]Br$ (acac = 2,4-pentanedione anion, diamine: en = ethylenediamine, *N,N*-dmen = *N,N*-dimethylethylenediamine, *N,N'*-dmen = *N,N'*-dimethylethylenediamine, *N,N,N',N'*-tmen = *N,N.N',N'*-tetramethylethylenediamine). The results were discussed from the view points of hydrogen bonds through the N–H protons of the chelate cations to the bromide anion and cation-solvent interactions.

The outer-sphere ion association of $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$ (M = Co and Cr) with some anions in aqueous[1-7] and nonaqueous solutions[8,9] has been determined by the conductometric and spectrophotometric methods. The results in aqueous solution indicated that the ion association of $[M(en)_3]^{3+}$ is promoted for the chloride ion,[1,5] but is reduced for the SO_4^{2-} and $C_2O_4^{2-}$ ions,[1-3,6] compared to that of $[M(NH_3)_6]^{3+}$. This result cannot be accounted for by the electrostatic theory of ionic association, suggesting the importance of the following ion-solvent interactions: hydration of the N–H protons of $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$, Cl^-, SO_4^{2-}, and $C_2O_4^{2-}$ and the dehydration accompanied by the ion pair formation. On the other hand, ion association of $[Co(en)_3]^{3+}$ salts in nonaqueous solvents such as DMSO is affected by the basicity of the solvents.[8,9]

The present study deals with the conductance of bis(2,4-pentanedionato)(diamine) cobalt(III) bromides($[Co(acac)_2(diamine)]Br$) in nitrobenzene at 25 °C to understand the effects of the replacement of the N–H protons by the CH_3 groups on ion pair formation. Nitrobenzene is dipolar aprotic (dielectric constant = 34.82) and poorly basic (Gutmann's donor number = 4.4). Thus, the ion pair formation of the chelate salts is affected by the ion-dipole interaction between the chelate cations and nitrobenzene molecules. The title compounds, which were confirmed to be stable in nitrobenzene by both spectrophotometry and conductometry, are 1 : 1 electrolytes and advantageous to elucidate the ligand and solvent effects on ion pair formation from conductance data.

Experimental

Four bis(2,4-pentanedionato)(diamine)cobalt(III) perchlorates were prepared by mixing $Na[Co(acac)_2(NO_2)_2]$ with equimolar amounts of the corresponding diamine, followed by addition of an aqueous solution of $NaClO_4$.[10] After triple recrystallizations, these samples were converted into the bromide salts by anion exchange resin in the Br^- form, and purified by recrystallizing twice from acetone (or ethanol)–ether. The purity of samples was checked by chemical analysis of C, H, and N, potentiometric titration of the bromide ion with silver nitrate, and the coulometric determination of water content by a Hiranuma AQ-3 aquacounter. Nitrobenzene was purified by shaking with sodium hydroxide, sulfuric acid, and distilled water, successively, and then by distillation under reduced pressure after drying over calcium chloride.

Conductances were measured at 1592 Hz by a LCR 10 type bridge (Ando Electric Co. Ltd.) which was calibrated with a standard resistance box(Shimadzu Seisakusho Co.). The cell was of the Kraus-Erlenmeyer type which was calibrated by fitting the conductance of KCl solutions (0.001—0.01 mol dm^{-3}) to the equation due to Lind, Zwolenik, and Fuoss.[11] The density and viscosity (0.01847 P) were measured with a digital density meter (Anton Paar Model DMA 02D) and Ubbelohde viscometer modified for use in a closed, dry atmosphere, respectively. All measurements were carried out in a water bath thermostated to 25±0.005 °C.

Results and Discussion

The measured equivalent conductances, Λ and

Table 1. Molar concentrations, C/mol dm^{-3}, and molar conductances, Λ/Ω^{-1} cm^2 mol^{-1} in nitrobenzene at 25 °C

$[Co(acac)_2(en)]Br$		$[Co(acac)_2(N,N'\text{-dmen})]Br$	
$C\times10^4$	Λ	$C\times10^4$	Λ
17.662	21.207	15.383	19.348
13.757	22.441	11.946	20.604
9.7454	24.038	9.2914	21.847
6.9643	25.452	7.0486	23.170
4.6252	26.942	5.0765	24.610
3.3591	27.935	3.6338	26.008
2.4302	28.787	2.9198	26.842
1.4775	29.793	1.8535	28.319
0.6445	30.951	1.0947	29.704

$[Co(acac)_2(N,N\text{-dmen})]Br$		$[Co(acac)_2(N,N,N',N'\text{-tmen})]Br$	
$C\times10^4$	Λ	$C\times10^4$	Λ
23.391	21.253	25.104	30.074
18.277	22.492	15.491	30.812
14.116	23.740	12.177	31.102
10.347	25.130	7.5076	31.628
7.5084	26.440	3.1540	32.273
5.5730	27.496	1.6923	32.557
3.5078	28.887	0.8918	32.798
2.1521	30.007		
1.2072	30.941		
0.5627	31.797		

TABLE 2. DERIVED PARAMETERS

Electrolyte	Λ_o / Ω^{-1} cm^2 mol^{-1}	λ_o^+	K_a / dm^3 mol^{-1}	d / 10^{-1} nm	σ_Λ
$[Co(acac)_2(en)]Br$	32.23±0.03	10.6	449±7	18.1	0.026
[Co(acac)$_2$(*N,N′*-dmen)]Br	32.34±0.14	10.7	749±65	8.4	0.093
[Co(acac)$_2$(*N,N*-dmen)]Br	32.83±0.02	11.2	365±3	18.4	0.022
[Co(acac)$_2$(*N,N,N′,N′*-tmen)]Br	33.47±0.02	11.9	25±2	15.9	0.019
Bu_4NBr[a]	33.27±0.03	11.7	74±2	12.5	0.008

a) From Ref. 15.

corresponding electrolyte concentrations in mol dm^{-3} are given in Table 1 for nitrobenzene solutions of [Co(acac)$_2$(diamine)]Br. The data were analyzed by using the Fuoss-Hsia equation[12a] with Fernández-Prini coefficients[12b] and $E=E_1\Lambda_0-2E_2$,[12c]

$$\Lambda = \gamma[\Lambda_o - SC^{1/2}\gamma^{1/2} + EC\gamma \log C\gamma + J_1(\mathrm{d})C\gamma + J_2(\mathrm{d})C^{3/2}\gamma^{3/2}], \tag{1}$$

where the symbols have their usual meaning:[13] S, E, J_1, and J_2 contain contributions from both the electrophoretic and the relaxation effects, and each depends on Λ_0, and γ is the fraction of free ions. The association constant K_a can be expressed as

$$K_a = (1-\gamma)/\gamma^2 C f_\pm^2, \tag{2}$$

The mean ionic activity coefficient $f_\pm$ is given by the extended Debye-Hückel equation

$$-\log f_\pm = A(C\gamma)^{1/2}/[1+Bd(C\gamma)^{1/2}]. \tag{3}$$

The method of fitting in terms of Λ_0, K_a and the ion-size parameter d is based on that of Hanna *et al.*[14] The values of the standard deviation is defined as

$$\sigma_\Lambda = [\sum(\Lambda_{\mathrm{calcd}}-\Lambda_{\mathrm{obsd}})^2/(n-3)]^{1/2}, \tag{4}$$

where n is the number of experimental points. The results are given in Table 2.

The association constants of the chelate electrolytes show two features: (a) the chelate electrolytes associate more strongly than tetrabutylammonium bromide (Bu_4NBr) ($K_a=74$)[15] except for [Co(acac)$_2$(*N,N,N′,N′*-tmen)]Br, and (b) the K_a value of [Co(acac)$_2$(*N,N′*-dmen)]Br is much larger than those of $[Co(acac)_2(en)]Br$ and [Co(acac)$_2$(*N,N*-dmen)]Br.

Since the chelate electrolytes have approximately the same hydrodynamic size as Bu_4NBr, the electrostatic theory of ionic association predicts that they should have a similar association constant. However, en, *N,N*-dmen, and *N,N′*-dmen complexes have much larger association constants compared with that of Bu_4NBr. This increase in K_a should be attributed to the hydrogen bond between the N–H protons of the chelate cations and the bromide anion. This explains well that K_a of the *N,N*-dmen complex is smaller than that of the en complex due to the decrease in the number of the N–H protons by the introduction of the *N*-methyl groups. Furthermore, this effect was confirmed from the fact that the K_a value of the *N,N,N′,N′*-tmen complex without the N–H protons is much smaller than those of en, *N,N*-dmen, and *N,N′*-dmen complexes, and is further smaller than that of symmetrical Bu_4NBr in spite of the enhanced effect of the unsymmetrical charge distribution in the chelate cation on K_a. This suggests that when there is no hydrogen bonding, the pseudo aromaticity of the acac ligand reduces the ion pair formation, probably due to the repulsion between Br^- and the π electrons or solvation of the acac ligand by nitrobenzene through π-π interaction.

As to observation (b), it has been shown by the studies of the rate of H–D exchange[16] and the acid ionization constant[17] in aqueous solution that the alkyl substitution (CH_3NH– and –CH_2NH_2) in the coordinated amine results in stronger acidity of the residual N–H protons. Therefore, the result (b) suggests that the *N*-methyl groups of the *N,N′*-dmen complex activate the residual N–H protons to associate more strongly with the bromide anion.

As is clear from Table 2, the limiting ionic conductance (λ_o^+) of the chelate cations which was estimated using $\lambda_o^-(Br^-)=21.6$ in nitrobenzene[18] is increased in spite of the increasing size with the introduction of CH_3 groups. Particularly, it is noteworthy that the mobility of the [Co(acac)$_2$(*N,N,N′,N′*-tmen)]$^+$ ion is much larger than that of the $[Co(acac)_2(en)]^+$ ion. This result conflicts with hydrodynamic theory, suggesting specific ion-solvent interactions. Since nitrobenzene is a dipolar aprotic and poorly basic solvent, the chelate cations are considered to be solvated mainly by cation-solvent dipole interaction. In this case, the N–H protons of the $[Co(acac)_2(en)]^+$ ion would be solvated and the introduction of the CH_3 groups promotes the desolvation, leading to the increase in mobility due to the decrease in its effective size. For the [Co(acac)$_2$(*N,N′*-dmen)]$^+$ ion, the methyl substitution (CH_3NH–) prevents the solvation of the residual N–H protons because of the steric hindrance by the nearest neighboring CH_3 groups, which corresponds to the activation of the N–H protons. This leads to the larger association of [Co(acac)$_2$(*N,N′*-dmen)]Br compared to $[Co(acac)_2(en)]Br$ and [Co(acac)$_2$(*N,N*-dmen)]Br in which the methyl groups are too far from the residual N–H protons.

The above discussion explains well the data of $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$ salts: the larger K_a value of $[M(en)_3]Cl^{2+}$ compared to that of $[M(NH_3)_6]Cl^{2+}$[1,5] in spite of the increasing cation size is attributed to the stronger acidity of the N–H protons of $[M(en)_3]^{3+}$, which is considered as the result of the dehydration of the N–H protons by the hydrophobicity of the C_2H_4 groups. On the other hand, for $SO_4{}^{2-}$ and $C_2O_4{}^{2-}$ salts,[1–3,6] the hydrogen bonding of the N–H protons with $SO_4{}^{2-}$ and $C_2O_4{}^{2-}$ is prevented by the strong hydration of divalent anions. This leads to the smaller ionic association of SO_4^{2-} and $C_2O_4^{2-}$ with $[Co(en)_3]^{3+}$ than that with $[Co(NH_3)_6]^{3+}$.

A further study in other solvents is under way to ascertain the above concept.

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