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Solvation and Ionic Association of Bis(2,4-pentanedionato)(diamine)cobalt(III) Perchlorates in 1-Propanol, Acetone, and Their Mixtures

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The conductances of bis(2,4-pentanedionato)(diamine)cobalt(III) perchlorates ([Co(acac)$_2$(diamine)]ClO$_4$, diamine: en=ethylenediamine, pn=1,2-propanediamine, *N,N*-dmen=*N,N*-dimethylethylenediamine, *N,N′*-dmen=*N,N′*-dimethylethylenediamine, *N,N,N′*-trimen=*N,N,N′*-trimethylethylenediamine, *N,N,N′,N′*-tmen=*N,N,N′,N′*-tetramethylethylenediamine) were measured in isodielectric solvents, 1-propanol (*n*-PrOH), acetone (Me$_2$CO), and 60 and 80 mol% acetone in 1-propanol (*n*-PrOH-Me$_2$CO) at 25 °C. In spite of the increase in size of [Co(acac)$_2$(diamine)]$^+$ due to the introduction of *N*-methyl groups, the Walden products ($\lambda_0^+ \cdot \eta$) of the chelate cations were found to increase in all solvents. The contribution per *N*-methyl group was large in *n*-PrOH. The variation in the ionic association constants (K_a) with the number of NH protons in the chelate cations was small in all solvents. The K_a values for [Co(acac)$_2$(*N,N′*-dmen)]ClO$_4$ were larger than those for other chelate salts in all solvents. These results could be explained in terms of the solvation of the NH protons (diamine in [Co(acac)$_2$(diamine)]$^+$) by oxygen atoms of *n*-PrOH and Me$_2$CO, and of oxygen atoms (acac) by the OH proton of *n*-PrOH owing to hydrogen bonding interactions and desolvation resulting from the introduction of the *N*-methyl groups. For [Co(acac)$_2$(en)]$^+$ in *n*-PrOH a solvation model to form a six-membered ring was proposed.

Our previous conductometric studies of [Co(acac)$_2$(en)]X (X$^-$=ClO$_4^-$, I$^-$, and Br$^-$) and their *N*-methyl derivatives in nitrobenzene and 1,2-dichloroethane[1,2] indicated that NH protons in the chelate cations are solvated by the dipolar aprotic solvent nitrobenzene, and that the substitution of *N*-methyl groups for NH protons prevents solvation, leading to an increase in mobility in spite of the increasing size. The *N*-methylation results in an apparent increase in the acidity of the residual and the nearest-neighbor NH protons. These trends were not observed in 1,2-dichloroethane with a lower polarity. The association constants decrease with a decrease in the number of NH protons in both solvents and the change per proton is larger in 1,2-dichloroethane. These solvents are aprotic and weak in basicity but have different dielectric constants and polarities. Thus, it is suggested that ionic association processes of the chelate cations are affected by ion-solvent dipole interactions.

In this study, in an effort to obtain more information concerning the effects of the solvent dipole moment and the solvent acidity and basicity, the conductances of [Co(acac)$_2$(diamine)]ClO$_4$ were measured in the protic solvent 1-propanol, aprotic acetone, and their mixtures. 1-Propanol has acidic and basic sites that are effective for solvation; acetone interacts through its electron lone pair. Since the solvents have nearly the same dielectric constants, the electrostatic interaction energy between a cation and an anion is regarded as constant for a given electrolyte. Solvation of the ClO$_4^-$ ion is weak compared to that of halide ions. Thus, it is considered that specific cation-solvent interactions in ionic association process become much apparent.

Experimental

[Co(acac)$_2$(diamine)]ClO$_4$ was prepared and purified as described previously.[2] 1-Propanol was refluxed over calcium hydride for 2 d and fractionally distilled. Acetone was refluxed over Drierite after dehydration by molecular sieves (4A) for one week and fractionally distilled. The distillation was performed under a flow of N$_2$ gas since the solvents were relatively hygroscopic. Typical densities (d in g cm^{-3}), viscosities (η in mPa s), and specific conductances of pure solvents (κ in S cm^{-1}) at 25 °C and water contents (wc in wt%) are: for *n*-PrOH d=0.79963, η=1.952, κ=2×10^{-8}, and wc=8×10^{-3}; for Me$_2$CO d=0.78426, η=0.3052, κ=2×10^{-8}, and wc=5×10^{-3}.

The procedure for the conductance measurements and other measurements (viscosity and density) have been described previously.[2] The water content was measured coulometrically using a Hiranuma AQ-3 aqua counter. *n*-PrOH-Me$_2$CO mixtures were prepared by weight just before a conductance measurement. The dielectric constant (ε) and viscosity (η in mPa s) of the solvents used for an analysis were as follows: for *n*-PrOH ε=20.45,[3] η=1.952; for Me$_2$CO ε=20.45,[4] η=0.3052; for *n*-PrOH-Me$_2$CO (60 mol% Me$_2$CO) ε=18.64,[4] η=0.463; for 80 mol% Me$_2$CO ε=19.37,[4] η=0.361.

Results and Discussion

The measured molar conductances, Λ (S cm^2 mol^{-1}) and the corresponding electrolyte concentrations, C (mol dm^{-3}) for [Co(acac)$_2$(diamine)]ClO$_4$ in 1-propanol and acetone are given in Table 1 and those in 1-propanol-acetone mixtures (60 and 80 mol% acetone) in Table 2. The data were analyzed by the Fuoss-Hsia equation with $E=E_1\Lambda_0-2E_2$ in the form[5]

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

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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)]ClO$_4$ in 1-Propanol and Acetone at 25 °C

1-Propanol

[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(pn)]ClO$_4$		[Co(acac)$_2$(N,N-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
10.224	19.505	9.5497	19.816	26.123	17.343
8.3805	20.091	7.6345	20.426	21.880	18.019
7.0600	20.556	5.9069	21.055	17.218	18.916
5.9400	21.002	4.4038	21.702	13.272	19.841
4.5408	21.640	2.9868	22.422	9.8481	20.888
3.6357	22.129	1.9922	23.062	6.9774	21.968
2.6764	22.723			4.8040	23.040
2.0269	23.184			2.7621	23.330
0.9446	24.192				

1-Propanol

[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$		[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
18.641	17.180	23.911	16.954	21.551	18.430
14.948	17.982	17.556	18.085	17.192	19.296
11.365	18.945	13.257	19.088	14.563	19.910
8.6067	19.865	10.692	19.830	11.067	20.924
6.4579	20.759	7.6271	20.941	9.2711	21.533
4.9530	21.510	5.5441	21.894	6.3357	22.742
3.1541	22.624	3.7396	22.952	4.5616	23.704
2.3229	23.297	2.4411	23.906	2.3837	25.222

Acetone

[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(pn)]ClO$_4$		[Co(acac)$_2$(N,N-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
31.363	132.71	42.062	128.84	21.253	142.88
26.509	135.75	27.015	136.60	16.675	146.79
22.820	138.35	21.579	140.33	13.340	150.19
17.781	142.65	16.359	144.61	10.833	153.21
13.613	146.85	12.260	148.72	8.6943	156.25
10.152	151.08	9.1657	152.54	5.1964	162.36
6.1533	157.38	6.1154	157.19	3.3321	166.62
3.2943	163.69				

Acetone

[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$		[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ	$C\times10^4$	Λ
33.219	128.76	29.541	136.75	30.991	143.57
26.207	133.47	21.870	142.26	26.797	145.91
19.247	139.43	17.930	145.62	22.438	148.69
15.446	143.42	14.988	148.63	18.055	151.90
12.259	147.66	11.763	152.38	13.876	155.63
9.2749	152.22	9.0216	156.14	10.435	159.30
6.5372	157.02	5.9052	161.42	6.3053	165.10
4.1195	163.14	3.9766	165.62	3.7059	170.06

where K_a is the ionic association constant, Λ_0 is the limiting conductance, and other symbols have their usual meaning.

The conductance parameters obtained for 1-propanol and acetone are given in Table 3 and those for 1-propanol–acetone mixtures in Table 4. 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 [Co(acac)$_2$(diamine)]$^+$ are obtained from the limiting conductances of ClO$_4^-$ (16.42[3] and 118.35 S cm^2 mol^{-1}[4]) in 1-propanol and acetone, respectively) (Table 5).

Ionic Mobility. Figure 1 shows the variation of the

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 1-Propanol–Acetone Mixtures at 25 °C

60 (mol% Acetone)

[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(*N*,*N*-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ
31.273	75.854	33.185	77.649
24.393	78.623	23.971	81.309
19.691	80.955	18.056	84.358
14.878	83.884	14.163	86.894
10.805	86.958	9.4644	90.732
7.7621	89.832	6.2743	94.174
5.3801	92.687	3.7910	97.727
3.3449	95.777	2.5638	99.868

60 (mol% Acetone)

[Co(acac)$_2$(*N*,*N*′-dmen)]ClO$_4$		[Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ
32.162	75.095	27.439	84.765
26.544	77.468	22.923	86.714
20.531	80.527	17.154	89.695
16.227	83.286	13.512	92.072
12.413	86.215	9.5311	95.232
9.2761	89.208	7.2195	97.533
6.6941	92.237	5.3991	99.678
4.0004	96.382	3.7963	101.97

80 (mol% Acetone)

[Co(acac)$_2$(en)]ClO$_4$		[Co(acac)$_2$(*N*,*N*-dmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ
41.089	98.665	36.512	102.89
33.005	101.91	28.838	106.34
25.587	105.75	22.892	109.53
19.780	109.30	17.623	113.05
14.669	113.13	14.183	115.78
10.629	117.09	10.535	119.41
6.6433	122.09	7.6902	122.85
3.8580	126.87	5.0160	126.87

80 (mol% Acetone)

[Co(acac)$_2$(*N*,*N*′-dmen)]ClO$_4$		[Co(acac)$_2$(*N*,*N*,*N*′,*N*′-tmen)]ClO$_4$	
$C\times10^4$	Λ	$C\times10^4$	Λ
36.095	99.126	29.046	112.28
28.375	102.99	23.603	114.97
22.211	106.76	17.865	118.52
17.202	110.48	14.133	121.25
13.539	113.83	10.209	124.84
10.241	117.53	7.7400	127.59
7.5489	121.23	5.1022	131.18
4.4823	126.76	2.8076	135.33

Walden products of [Co(acac)$_2$(diamine)]$^+$ with the introduction of methyl groups in 1-propanol and acetone, compared with that of tetraalkylammonium cations[3,4] for which n refers to the number of carbons in the alkyl group. For tetraalkylammonium ions which have approximately the same size as the chelate cations used here and no specific site for solvation, the Walden product decreases with increasing ionic size, as is hydrodynamically expected. It should be noted that, in contrast, the Walden product of the che-

Table 3. Conductance Results for [Co(acac)$_2$(diamine)]ClO$_4$ in 1-Propanol and Acetone at 25 °C

Electrolyte	Solvent	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	$d^{a)}$ Å	$\sigma_\Lambda$$^{b)}$
[Co(acac)$_2$(en)]ClO$_4$	n-PrOH	25.81±0.02	411±45	14.1	0.011
[Co(acac)$_2$(pn)]ClO$_4$		25.37±0.02	369± 9	20.5	0.008
[Co(acac)$_2$(N,N-dmen)]ClO$_4$		27.86±0.02	467±11	16.2	0.016
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		26.53±0.01	531±12	17.3	0.010
[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$		27.31±0.03	507±36	14.3	0.006
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$		28.57±0.02	480±15	16.4	0.015
[Co(acac)$_2$(en)]ClO$_4$	Me$_2$CO	180.03±0.09	180± 4	14.0	0.06
[Co(acac)$_2$(pn)]ClO$_4$		178.9 ±0.1	161± 3	13.3	0.06
[Co(acac)$_2$(N,N-dmen)]ClO$_4$		183.15±0.06	172±17	13.3	0.06
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		184.1 ±0.2	228±34	12.8	0.17
[Co(acac)$_2$(N,N,N'-trimen)]ClO$_4$		184.02±0.08	181± 4	14.2	0.05
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$		186.40±0.04	137± 2	13.1	0.03

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

Table 4. Conductance Results for [Co(acac)$_2$(diamine)]ClO$_4$ in 1-Propanol-Acetone Mixtures at 25 °C

Electrolyte	mol% Acetone	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	$d^{a)}$ Å	$\sigma_\Lambda$$^{b)}$
[Co(acac)$_2$(en)]ClO$_4$	60	107.37±0.09	243±6	15.1	0.06
[Co(acac)$_2$(N,N-dmen)]ClO$_4$		110.1 ±0.1	236±8	14.8	0.11
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		110.41±0.07	288±5	14.8	0.05
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$		114.17±0.07	208±5	14.8	0.05
[Co(acac)$_2$(en)]ClO$_4$	80	142.3 ±0.1	209±4	14.1	0.09
[Co(acac)$_2$(N,N-dmen)]ClO$_4$		144.7 ±0.1	202±6	13.6	0.07
[Co(acac)$_2$(N,N'-dmen)]ClO$_4$		145.06±0.03	249±2	13.7	0.02
[Co(acac)$_2$(N,N,N',N'-tmen)]ClO$_4$		147.6 ±0.1	165±5	14.8	0.09

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

Table 5. Ionic Mobilities and Walden Products in 1-Propanol and Acetone at 25 °C

	λ_0^+/S cm^2 mol^{-1} ($\lambda_0^+\cdot\eta$/S cm^2 mol^{-1} 10^{-1} Pa s)	
	1-Propanol	Acetone
[Co(acac)$_2$(en)]$^+$	9.39(0.183)	61.63(0.188)
[Co(acac)$_2$(pn)]$^+$	8.95(0.174)	60.5 (0.185)
[Co(acac)$_2$(N,N-dmen)]$^+$	11.44(0.223)	64.75(0.198)
[Co(acac)$_2$(N,N'-dmen)]$^+$	10.11(0.197)	65.7 (0.201)
[Co(acac)$_2$(N,N,N'-trimen)]$^+$	10.89(0.212)	65.62(0.200)
[Co(acac)$_2$(N,N,N',N'-tmen)]$^+$	12.15(0.237)	68.0 (0.208)

late cations in both 1-propanol and acetone roughly increases with the N-methylation of NH protons in spite of the increase in the size of the cations. Similar results were also obtained in nitrobenzene which has a poor basicity and can be explained in terms of the solvation of the NH proton site by nitrobenzene through an ion-solvent dipole interaction and desolvation by N-methylation.[1,2]

However, this N-methylation effect in 1-propanol is more marked than in nitrobenzene. The difference in the Walden products between N,N,N',N'-tmen and en complexes in acetone, 0.020 S cm^2 mol^{-1} 10^{-1} Pa s is comparable with that in nitrobenzene; however, a large difference of 0.054 S cm^2 mol^{-1} 10^{-1} Pa s was observed in 1-propanol. A small difference of 0.003 S cm^2 mol^{-1} 10^{-1} Pa s was obtained in 1,2-dichloroethane.[2] The large variation of the Walden product with the substituted groups in diamine for the 1-propanol system is suggestive of a specific solvation of the chelate cations.

The dipole moment of acetone, 1-propanol, nitrobenzene, and 1,2-dichloroethane is 2.88, 1.68, 4.22, and 1.40 in Debye, respectively,[6] and the large variation in the Walden products in 1-propanol can not be explained by only the dipole moment.

The following two specific interactions for the solvation of chelate cations are considered: A hydrogen-bonding interaction between the NH protons in [Co(acac)$_2$(diamine)]$^+$ and the oxygen atom of 1-propanol and acetone which act as hydrogen bonding acceptor. The second is the hydrogen-bonding of the oxygen atom of the coordinated acac ligand with the

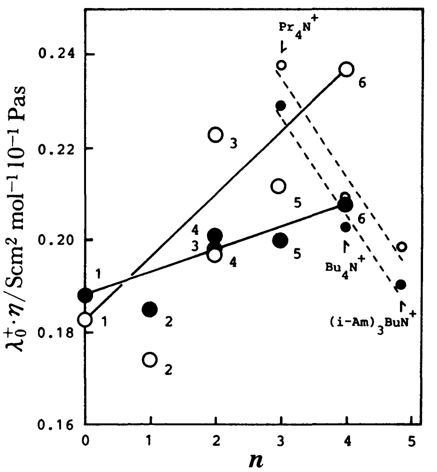

Fig. 1. Walden products of [Co(acac)$_2$(diamine)]$^+$ as a function of the increased carbon number, **n** compared to [Co(acac)$_2$(en)]$^+$. ○: in *n*-PrOH, ●: in Me$_2$CO. Diamine, 1: en, 2: pn, 3: *N,N*-dmen, 4: *N,N'*-dmen, 5: *N,N,N'*-trimen, 6: *N,N,N',N'*-tmen. For onium salts, **n** refers to the number of carbon in the alkyl group and the data are from Refs. 3 and 4.

OH proton of 1-propanol which acts as a hydrogen-bonding donor.

The hydrogen-bonding acceptor ability or donicity is evaluated by the Gutmann donor number. The donor numbers (DN) of acetone, nitrobenzene, and 1,2-dichloroethane are 17, 4.4, and 0.0, respectively.[7] The DN value of 1-propanol, although not available in the literature, was reasonably estimated to be around 20, since that of methanol and ethanol is 19 and 20, respectively. The ^{59}Co NMR for [Co(en)$_3$]$^{3+}$ was measured in several organic solvents and the signal was shifted to a higher field upon increasing the donicity of the solvents.[8] This was interpreted as the result of a donor solvent attack on the NH protons. Although an ion-dipole interaction for acetone is weaker than that for nitrobenzene, the solvation of NH protons by acetone is strengthened by its stronger donicity, resulting in a comparable difference in the Walden product between acetone and nitrobenzene.

A relatively large increase in the mobility by the *N*-methylation in 1-propanol indicates the strong solvation power of 1-propanol. The IR spectra of methanol in the carbon tetrachloride solutions of bis- and tris (2,4-pentanedionato) complexes such as Be(acac)$_2$ and Cr(acac)$_3$ showed that for Cr(acac)$_3$ hydrogen bonding occurrs between the oxygen atom of acac and the OH proton of methanol but does not occur for Be(acac)$_2$ because of a steric hindrance.[9] The ^{1}H NMR study of paramagnetic Cr(acac)$_3$ indicated that the OH group of methanol is closer to the central metal Cr(III) than the CH$_3$ group of methanol.[10] Furthermore, the X-ray study of [Cr(acac)$_2$(tn)]I (tn=1,3-propanediamine)[11] showed that the intramolecular distance between the NH protons and oxygen atoms of the acac is 2.5 and 2.6 Å. A molecular model of [Co(acac)$_2$(en)]$^+$ indicates that it possesses spaces enough to accomodate the OH group of 1-propanol. Thus, it is possible that [Co(acac)$_2$(en)]$^+$ is solvated by 1-propanol through hydrogen bonding to form a six-membered ring.

In 1-propanol-acetone mixtures (Table 4) the mobility of the complex ions increases with the *N*-methylation in a similar manner. The differences in the Walden product between *N,N,N',N'*-tmen and en complexes are 0.031 and 0.019 S cm^2 mol^{-1} 10^{-1} Pa s in 60 and 80 mol% acetone in 1-propanol, respectively. These values are closer to the value for acetone (0.020) than that for 1-propanol (0.054), thereby suggesting that the selective solvation of [Co(acac)$_2$(en)]$^+$ by 1-propanol is not seen in the mixed solvents.

The methylation effect on the mobility depends on the substituted position. As can be seen for [Co(acac)$_2$(pn)]$^+$, the *C*-methylation leads to a decrease in the mobility. A similar result was obtained in nitrobenzene and 1,2-dichloroethane.[2] This shows that the methyl group does not prevent the solvation of NH protons, but contributes only to a decrease in mobility by increasing the size. It is interesting to compare the Walden product between [Co(acac)$_2$(*N,N*-dmen)]$^+$ and [Co(acac)$_2$(*N,N'*-dmen)]$^+$ in 1-propanol: the *N,N*-dmen ligand increases more the mobility than the *N,N'*-dmen ligand, compared with the ligand en. Therefore, it is likely that the mono-methylation of the two NH protons does not have a large desolvation effect; however, the doble-methylation completely prevents solvation by 1-propanol with a six-membered ring and compensates for the effect of an increasing size on mobility. This can be also seen in the decrease in the mobility from *N,N*-dmen to *N,N,N'*-trimen and an increase in the mobility from *N,N'*-dmen to *N,N,N'*-trimen and *N,N,N',N'*-tmen.

Ionic Association. The association constants of the chelate electrolytes show three features: (a) the K_a value in 1-propanol is much larger than that in acetone. (b) The variation of K_a with the number of NH protons in [Co(acac)$_2$(diamine)]$^+$ is small in all solvents. (c) The K_a value of [Co(acac)$_2$(*N,N'*-dmen)]$^+$ is larger than that of [Co(acac)$_2$(en)]$^+$ in all the systems.

Observation (a) held for Bu$_4$NClO$_4$[4]: Although the dipole moment of 1-propanol (1.68 Debye) is small compared to that of acetone (2.88 Debye), the magnitude of the bulk dielectric constant of 1-propanol which is similar to that of acetone is due to the structure arising from hydrogen bonding. However, in the vicinity of the ion pairs, the structure is destroyed by the solvation of the chelate cations, leading to a diminution of the local dielectric constant. Thus, ionic association constants in 1-propanol are larger than those in acetone.

(b) The ratio of K_a for [Co(acac)$_2$(en)]ClO$_4$ to [Co(acac)$_2$(*N,N,N',N'*-tmen)]ClO$_4$ is 0.9 and 1.3 for 1-propanol and acetone, respectively. These values are smaller than those for 1,2-dichloroethane (7.9) and nitrobenzene (2.4).[2] The NH protons in $[Co(acac)_2(en)]^+$ associates with ClO_4^- by hydrogen bonding in 1,2-dichloroethane, leading to the larger K_a value for $[Co(acac)_2(en)]ClO_4$. In nitrobenzene, the protons are solvated due to the high polarity of the nitrobenzene molecule. However, the ion pair, $[Co(acac)_2(en)]ClO_4$ is a contact ion pair, formed by the partial exclusion of nitrobenzene molecules. On the other hand, in 1-propanol and acetone the protons are solvated owing to an acid-base interaction. Especially, the solvation is large in 1-propanol because $[Co(acac)_2(en)]^+$ is specifically solvated by the 1-propanol molecule as discussed in the preceding section. This leads to the formation of solvent-separated ion pairs and observation (b).

Previous studies showed that the trend of observation (c) was also seen in nitrobenzene and nitrobenzene-carbon tetrachloride mixtures but chloroalkane solvents such as 1,2-dichloroethane and dichloromethane, and that the results could be ascribed to a difference in polarity of the solvent.[12] For the $[Co(acac)_2(N,N'\text{-dmen})]^+$ ion in solvents which provide observation (c), the methyl substitution (CH_3-NH-) interferes with the solvation of the residual NH protons due to a steric hindrance. This leads to an increase in the acidity of the NH protons and to a larger association of $[Co(acac)_2(N,N'\text{-dmen})]ClO_4$ compared with $[Co(acac)_2(en)]ClO_4$. The K_a value of $[Co(acac)_2(N,N,N'\text{-trimen})]ClO_4$ is larger than that of $[Co(acac)_2(N,N\text{-dmen})]ClO_4$ in a similar manner. It can be said that the existence of a relatively strong specific solvation of NH protons such as solvations due to ion-dipole and hydrogen-bonding interactions gives the pattern shown in (c).

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