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Conductometric Investigations on Solvatochromic Nickel(II) Complexes in Dichloromethane and *N,N*-Dimethylformamide

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Abstract

Conductivity measurements have been performed on solutions of mixed Ni(II) complexes with tetramethylethylenediamine and substituted β-diketones in dichloroethane (DCE) and *N,N*-dimethylformamide (DMF). The data have been analysed with the Fuoss–Justice conductivity equation to estimate ion-pair association constants. The results show that even the weak coordinating ClO_4^- and BPh_4^- anions appear to be coordinated to the complexes in a square-planar form in DCE. Complexes dissolved in the strong donor solvent DMF are octahedrally coordinated and show much less tendency for ion pair formation.

Introduction

Mixed tetramethylethylenediamine (tmen) Ni(II) complexes with β-diketones (β-dik), such as acetylacetonate (acac), benzoylacetonate (bzac) and dibenzoylmethanate (dbzm), are known to show simultaneously solvatochromic and thermochromic behaviour [1–6]. Both effects have been interpreted as due to the reaction

$$[Ni(tmen)(\beta\text{-dik})]^+ + 2L \longrightarrow [Ni(tmen)(\beta\text{-dik})L_2]^+ \qquad (1)$$

where $[Ni(tmen)(\beta\text{-dik})]^+$ is a red coloured square-planar complex, L represents solvent molecules (such as electron pair donors, and $[Ni(tmen)(\beta\text{-dik})L_2]^+$ is the corresponding blue coloured octahedral form of the complex involving two donor molecules L. Spectral analysis has shown [1] that in dichlorethane (DCE) only the tetrahedral form exists, whereas in *N,N*-dimethylformamide (DMF) only the octahedral form is present. Knowledge of the association between the complex cations and their anions is necessary for the interpretation of the mentioned thermochromic and solvatochromic properties when the complexes are used as colour indicators for solvent parameters [7]. Conductivity measurements on solutions of the complexes in DCE and DMF should, when analysed by suitable conductivity equations, yield information about the association constants [8, 9]. For the present investigation perchlorate (ClO_4^-) and tetraphenyloborate (BPh_4^-) have been used as anions as they are known to show less coordinative properties than other ions.

Experimental

For the preparation of $Ni(tmen)(\beta\text{-dik})ClO_4$ the method of Fukuda [2] was used. $Ni(tmen)(\beta\text{-dik})BPh_4$ has been prepared in a slightly modified way: $Ni(NO_3)_2 \cdot 6H_2O$ was pre-dried over P_2O_5 for 15 h under reduced pressure. 200 ml of a 0.5 molar solution of tmen and the equimolar amount of the appropriate β-dik in dry dichlorethane was added dropwise to 100 ml of a 0.1 molar solution of this Ni compound in dry ethanol. After addition of dry Na_2CO_3 the solution was refluxed for 3 h. After removing the aqueous phase the DCE was evaporated. The product $Ni(tmen)(\beta\text{-dik})(NO_3)$ was recrystallized from DCE. Sodium tetraphenyloborate was added to a solution of the nitrate in DCE until the colour changed from greenish-blue to red. The product was recrystallized twice from DCE.

The solvent (DCE and DMF) for the conductivity measurements were purified according to standard procedures [10–12]. The water content in the solvents was measured by Karl–Fischer titration and was usually found to be below 30 mg/l.

The conductivity measurements were made by means of a Wayne Kerr Autobalance Universal Bridge 642 at 25 ± 0.05 °C under nitrogen atmosphere and at a frequency of 1591.5 Hz. Polished platinum electrodes were used. The cell constant was calibrated with aqueous KCl solution and was found to be slightly dependent on the measured conductivity. A value of $42.51 \pm 2.227 \times 10^{-4}\, c\ m^{-1}$ was used where c is the molar concentration of the electrolyte.

Stock solutions of the compounds were prepared in a dry box to exclude oxygen and water. These solutions were placed in air-tight syringes with the tip closed by silicone rubber discs. About 50 ml of pure

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solvent was placed in the conductivity cell and the cell was closed. Both the cell and the syringes were removed from the glove box and weighed to determine the exact amount of the solvent and the stock solution. After thermostatting the cell, weighed additions of the stock solutions were made by pushing the needle of the syringe through a silicone septum attached to the conductivity cell. The conductivity cell was purged with nitrogen during each run.

Results and Discussion

Equivalent conductivities (λ_c) and molar concentrations for the systems measured are listed in Table I. The results were analysed by the Fuoss–Justice equation [13, 14] using a fitting procedure. The λ_0, K_A and r values obtained from this procedure are given in Table II. Variation of the distance parameter r by about 50 pm in the neighbourhood of the optimal parameter had no significant effect on the reported λ_0 and K_A values. The distance parameter derived from the conductivity measurements differs obviously from crystallographic values as the former is more closely related to the distance at which the electrostatic interaction between two ions reaches a critical value. This distance increases rapidly as the dielectric constant decreases. The Bjerrum distances are calculated as 2630 pm for DCE and 763 pm for DMF and are somewhat higher than the parameters fitted to the Fuoss–Justice equation, which are about 1860 pm for DCE and 608 pm for DMF. The ratio of the fitted r parameters for the DMF and DCE results are in agreement with the ratios of the Bjerrum distances.

The limiting conductivities are higher for ClO_4^- species than for the BPh_4^- species. The differences increase with increasing size of the β-diketone ligands (see Table I). Limiting ionic conductances for the ClO_4^- and the BPh_4^- ion are either taken from the literature [8, 15] or approximated from Walden's rule [16] (based on available data in formamide) have been used to calculate the limiting conductances for the complex cations. They are given in Table III. It is found that they are in agreement with Walden's rule which suggests that the approximations used are valid. (It has been shown that the Walden rule itself gives good approximations for such large ions [8].) The values for the cations are not significantly different when different anions are used for the calculation, so that mean values for the ClO_4^- and BPh_4^- species are given. They can be used to estimate hydrodynamic radii (Stokes radii) of the solvated ions by means of eqn. (2).

$$r_s = Ne^2/6\pi\lambda_0\eta \qquad (2)$$

Pauling radii [17] for the surrounding spheres are approximately 750 pm for $[Ni(tmen)(acac)]^+$, 930 pm for $[Ni(tmen)(acac)]^+$, 1100 pm for $[Ni(tmen)(dbzm)]^+$, 190 pm for ClO_4^- [15], and 640 pm for

TABLE I. Molar Concentration (c) and Molar Conductivities (λ_c) of the Nickel Complexes in DCE and DMF

$10^{-4} \times c$ (mol dm^{-3})	λ_c (Ω^{-1} cm^2 mol^{-1})	$10^{-4} \times c$ (mol dm^{-3})	λ_c (Ω^{-1} cm^2 mol^{-1})
$Ni(tmen)(acac)ClO_4$ in DCE		$Ni(tmen)(acac)BPh_4$ in DCE	
7.284	48.57	1.787	40.63
19.45	51.66	5.235	41.71
37.81	51.53	8.996	40.72
60.13	50.19	16.62	38.59
121.8	46.21	27.24	36.15
234.9	41.69	33.31	34.36
416.3	37.30	48.52	32.57
1067	28.62	63.71	31.10
1522	26.65	90.51	29.14
2478	23.56	125.2	27.38
4190	20.53	163.1	25.39
6922	18.14	206.4	24.33
9895	16.72	256.7	23.30
12690	15.78	313.1	22.36
14320	15.40		
$Ni(tmen)(bzac)ClO_4$ in DCE		$Ni(tmen)(bzac)BPh_4$ in DCE	
2.289	54.30	1.346	50.93
4.596	52.19	3.484	50.53
6.836	50.36	9.920	46.49
9.042	48.60	16.37	43.04
17.28	43.21	22.64	41.67
34.31	37.28	32.03	39.57
49.71	34.01	48.27	36.69
74.93	30.93	80.45	32.66
107.9	27.84	115.7	29.96
137.8	26.10	144.9	28.35
176.7	24.24	170.3	27.22
274.5	21.58	223.6	25.45
388.0	19.68	381.1	22.01
547.2	18.00	551.0	19.85
730.3	16.73	707.9	18.61
930.7	15.73	874.5	17.60
1102	15.13	1035	16.92
		1238	16.22
$Ni(tmen)(dbzm)ClO_4$ in DCE		$Ni(tmen)(dbzm)BPh_4$ in DCE	
1.849	67.48	9.53	33.98
3.669	68.03	27.17	37.76
5.38	68.00	44.47	38.13
7.105	67.75	86.61	37.36
8.939	67.71	142.3	35.83
10.66	67.67	226.7	33.12
28.87	66.19	394.6	30.74
48.63	65.53	565.4	29.01
64.71	65.04	958	26.26
82.44	64.47	1520	23.86
99.22	63.78	2193	22.11
117.1	63.58	3018	20.66
271.3	61.11	5043	18.48
440.8	59.17	7575	16.89
587.0	57.85		
741.4	56.48		
887.1	55.69		

(continued)

TABLE I. *(continued)*

$10^{-4} \times c$ (mol dm^{-3})	λ_c (Ω^{-1} cm^2 mol^{-1})	$10^{-4} \times c$ (mol dm^{-3})	λ_c (Ω^{-1} cm^2 mol^{-1})
Ni(tmen)(acac)ClO_4 in DMF		Ni(tmen)(acac)BPh_4 in DMF	
2.192	49.49	1.998	51.68
6.572	49.76	2.193	49.49
10.88	49.91	4.049	52.08
16.89	49.26	6.572	49.76
25.63	48.87	8.347	51.71
37.84	47.97	10.89	49.91
58.89	47.11	15.79	50.74
80.77	46.33	16.89	49.26
127.7	45.33	25.63	49.64
167.0	44.42	25.63	48.87
215.6	43.75	37.84	47.97
301.9	42.54	39.02	48.65
420.0	41.33	58.9	47.11
565.3	40.11	62.69	47.61
764.4	38.87	80.78	46.33
1014	37.14	84.3	46.98
1221	36.12	123.1	46.00
1387	35.32	127.7	45.33
		167.1	44.42
		170.0	45.10
		215.4	43.96
		215.7	43.75
		295.9	42.70
		302.0	42.54
		418.1	41.43
		420.1	41.33
		547.0	40.01
		565.4	40.11
		749.2	38.56
		764.4	38.87
		964.6	36.93
		1014	37.14
		1168	35.86
		1222	36.12
		1388	34.79
		1388	35.32
Ni(tmen)(bzac)ClO_4 in DMF		Ni(tmen)(bzac)BPh_4 in DMF	
1.509	72.54	1.807	45.32
4.505	71.07	3.576	45.90
9.247	73.42	5.18	46.09
14.12	73.35	6.866	46.07
18.73	72.97	8.493	45.96
27.97	71.84	10.11	45.86
44.83	70.63	21.36	45.24
73.39	69.44	35.68	44.29
104.2	68.17	50.62	43.60
131.8	67.57	65.55	43.13
155.2	66.63	81.52	42.73
235.3	65.43	93.58	42.49
361.1	63.00	205.1	40.84
484.3	61.43	348.3	39.29
606.8	60.16	488.7	38.17
721.2	59.06		
909.7	57.46		
1075	56.24		
1284	55.09		
Ni(tmen)(dbzm)ClO_4 in DMF		Ni(tmen)(dbzm)BPh_4 in DMF	
2.655	73.99	1.746	44.61
7.463	76.49	4.077	46.52
10.39	76.46	7.994	48.66
15.16	76.38	11.76	48.70
23.50	76.48	15.33	48.83
34.95	75.08	25.27	47.48
52.56	74.16	43.63	46.29
74.53	73.26	53.19	45.77
106.6	72.56	70.80	45.24
159.1	71.34	102.8	44.54
249.2	69.50	139.8	43.93
415.8	67.55	214.1	42.62
505.3	66.61	374.5	41.09
663.2	65.37	676.2	39.00
		1033	37.13

BPh_4^-. The fact that the Stokes radii are smaller than the Pauli radii may be due to the approximations used in the conductivity model used in the fitting procedure and to the non-spherical symmetry. However, the use of a more complex expression, *e.g.* that derived by Fernandez-Pirni and Atkinson [9] does not alter the following qualitative interpretation. The Stokes radii of the complex cations increase when the solvent is changed from DCE to DMF. In DMF they also increase in the order (acac), (bzac) and (dbzm). Both may be explained by increasing radii of the surrounding spheres, in the former case due to the formation of the octahedral species, in the latter due to increasing size of the β-diketone substituents. The nearly unchanged Stokes radii for the complex cations in DCE can be explained by the 'disc-like' shape of the square-planar complex.

The ion pair association constants found are much larger for DCE than for DMF. In DCE the values are greater for ClO_4^- than for the BPh_4^- species. The ion-pair association constants derived from the analysis of the conductivity data refer to the limit of infinite dilution and thus unit activity. They can be compared to approximate values calculated from:

$$K = 4\pi N^3/(3 \times 10^{-3}) \exp(-Z_1 Z_2 e^2 N/\varepsilon r R T)$$

for the case of zero ionic strength (given in esu units).

TABLE II. Fitting Parameters for the Complexes in DCE and DMF at 25 °C using the Fuoss–Justice Equation

Solvent	Complex	λ_0 (Ω^{-1} cm^2 mol^{-1})	K_A (dm^3 mol^{-1})	r (pm)	σ (Ω^{-1} cm^2 mol^{-1})
DCE	$\mathrm{Ni(tmen)(acac)ClO_4}$	59.73	3350	1750	0.93
DCE	$\mathrm{Ni(tmen)(acac)BPh_4}$	53.66	2280	1750	1.05
DCE	$\mathrm{Ni(tmen)(bzac)ClO_4}$	57.06	2630	1900	1.05
DCE	$\mathrm{Ni(tmen)(bzac)BPh_4}$	47.29	1770	2100	0.50
DCE	$\mathrm{Ni(tmen)(dbzm)ClO_4}$	61.41	4070	1800	0.58
DCE	$\mathrm{Ni(tmen)(dbzm)BPh_4}$	43.14	1740	1850	0.49
DMF	$\mathrm{Ni(tmen)(acac)ClO_4}$	68.99	12.7	650	0.15
DMF	$\mathrm{Ni(tmen)(acac)BPh_4}$	51.36	25.8	550	0.54
DMF	$\mathrm{Ni(tmen)(bzac)ClO_4}$	78.21	13.5	600	0.35
DMF	$\mathrm{Ni(tmen)(bzac)BPh_4}$	49.41	15.1	600	0.56
DMF	$\mathrm{Ni(tmen)(dbzm)ClO_4}$	74.36	23.4	550	0.43
DMF	$\mathrm{Ni(tmen)(dbzm)BPh_4}$	46.93	17.0	700	0.27

TABLE III. Limiting Ionic Conductances (λ_0) and Stokes Radii r_s for Complex Ions in DCE and DMF

Solvent	Ion	λ_0 (Ω^{-1} cm^2 mol^{-1})	r_s (pm)
DCE	$\mathrm{Ni(tmen)(acac)^+}$	37.57	137
DCE	$\mathrm{Ni(tmen)(bzac)^+}$	35.05	147
DCE	$\mathrm{Ni(tmen)(dbzm)^+}$	35.14	145
DCE	$\mathrm{ClO_4^-}$ [a]	23.17	222
DCE	$\mathrm{BPh_4^-}$ [a]	11.08	464
DMF	$\mathrm{Ni(tmen)(acac)^+}$	29.75	172
DMF	$\mathrm{Ni(tmen)(bzac)^+}$	25.09	205
DMF	$\mathrm{Ni(tmen)(dbzm)^+}$	21.92	235
DMF	$\mathrm{ClO_4^-}$ [a]	52.40	222
DMF	$\mathrm{BPh_4^-}$ [a]	11.08	464

[a] Values are from refs. 8, 15 and 18 or are calculated according to Walden's rule [16].

The values calculated according to eqn. (3) are approximately 280 dm^3 mol^{-1} for DCE and 7.5 dm^3 mol^{-1} for DMF using the fitted distance parameters. With the Bjerrum distances the values 304 and 8.3 dm^3 mol^{-1} are calculated. Whereas the values calculated for DMF are in the order of magnitude of the experimental values (in fact they agree fairly well for such a simplified electrostatic model) the DCE values are significantly smaller. This might be interpreted on the bases of a coordination of the anion towards the free positions perpendicular to the tmen–β-biketone plane which exceeds the only electrostatic ion-pair formation. As expected, this coordination is less pronounced for the $\mathrm{BPh_4^-}$ ion. However, the results suggest that even the weakly coordinating $\mathrm{ClO_4^-}$ and $\mathrm{BPh_4^-}$ ions show a significant tendency to coordinate towards at least one of the free positions of the square-planar complexes. In the case where these coordination sites are occupied by strong donor ligands, the ion-pair formation seems to be due mainly to electrostatic interactions.

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