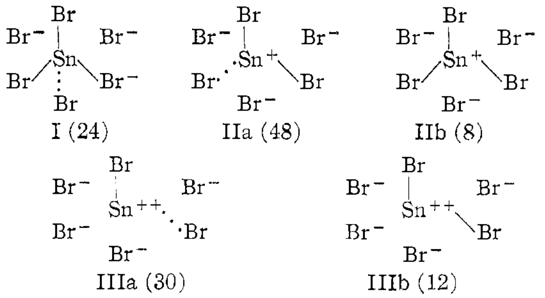
I (24) IIa (48) IIb (8) IIIa (30) IIIb (12)

Here, full lines and broken lines indicate bonds involving the p orbital and the s orbital, respectively. There are 24 equivalent structures for type I, while the II and III types have 56 and 42 structures, respectively. The predominance of types II and III over I is contrasted with the case of hexabromoplatinates(IV), in which structures having a vanishing charge on the platinum atom are the most important, as has been discussed already.[4] The increase in the positive charge on the central atom implies increase in the ionic character or decrease in the covalent character of metal–ligand bonds.

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Association Constants of Silver(I) and Cyanide Ions in Molten Equimolar Sodium Nitrate–Potassium Nitrate Mixtures

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Electromotive force measurements were used to evaluate the association constants K_1, K_2, and $K_{1,2}$ for the formation of AgCN, $Ag(CN)_2^-$, and Ag_2CN^+, respectively, in dilute solutions of Ag^+ and CN^- in molten equimolar $NaNO_3$–KNO_3 mixtures at 246, 286, and 326°. The very strong associations necessitated measurements at extremely low concentrations in order to evaluate the association constants. Values of K_1, K_2, and $K_{1,2}$ in mole fraction units are 230,000, 140,000, and 80,000 at 246°; 220,000, 105,000, and 60,000 at 286°; and 190,000, (50,000), and (36,000) at 326°. The entropies of association of the ion pair involving the diatomic CN^- (and the polyatomic SO_4^{-2} previously measured) are much more positive than for the association of Ag^+ with the monatomic ions Cl^- and Br^- and are larger than the "configurational" contribution to the entropy of association calculated from the quasi-lattice model.

Introduction

In previous papers[2] it has been shown that the temperature coefficients of some of the association constants for the monatomic ions Ag^+ with Cl^-, or Br^-, in molten nitrates are correctly predicted by the quasi-lattice theory.[3] It is of interest to test the theory for associations involving polyatomic ions to see what influence changes of the internal (including rotational) degrees of freedom of ions involved in the association process will have on the temperature coefficients of the association constants. In this report measurements are presented on solutions of Ag^+ and CN^- ions in molten equimolar mixtures of $NaNO_3$ and KNO_3. The only prior measurements in molten salts involving a polyatomic ligand were for the association of Ag^+ and SO_4^{-2} in molten KNO_3.[4] It also may be noted that values of K_1 do not appear to have been measured in water for the association of Ag^+ and CN^-.

Electromotive force measurements in the cell

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgNO_3}\\ \mathrm{NaCN}\\ \mathrm{NaNO_3\text{–}KNO_3}\\ (50\text{–}50)\\ \text{mole }\%\end{array}\right\|\left.\begin{array}{c}\mathrm{AgNO_3}\\ \mathrm{NaCN}\\ \mathrm{NaNO_3\text{–}KNO_3}\\ (50\text{–}50)\\ \text{mole }\%\end{array}\right|\mathrm{Ag}$$

were made and used to calculate the association constants K_1, K_2, and $K_{1,2}$ for the formation of AgCN, $Ag(CN)_2^-$, and Ag_2CN^+, respectively. The association constants are very high and measurements at extremely low concentrations of Ag^+ and CN^- were required to evaluate them.

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[2] See, for example, M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959); J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960); A. Alvarez-Funes, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962).

[3] M. Blander, *J. Chem. Phys.*, **34**, 432 (1961); M. Blander, *J. Phys. Chem.*, **63**, 1262 (1959).

[4] W. J. Watt and M. Blander, *ibid.*, **64**, 729 (1960).

Experimental

The apparatus, chemicals, and general technique were essentially the same as previously described.[2] Measurements were made on the change of e.m.f. of the cell, (ΔE) with incremental additions of NaCN to the right hand half-cell at several fixed concentrations of $AgNO_3$. The left hand or reference half-cell also contained fixed concentrations of solutes. Because of the extremely low concentrations (of the order of 10^{-6} mole fraction) needed for the evaluation of the association constants, important details of the technique had to be modified. Since the quantities of $AgNO_3$ and of NaCN which were required as solutes were too small to be weighed directly, an indirect dilution method was used. Reagent grade $AgNO_3$ and reagent grade NaCN, which had been vacuum dried at 150°, were weighed and dissolved in water to form a solution of known concentration. Aliquot portions of these solutions were withdrawn with a micropipet, placed on 0.5-oz. No. 18 cover glasses, and the water was evaporated using a heat lamp. These disks, containing a known quantity of the solute on the surface, then were dropped into the molten salt mixture as required. At very low concentrations (below 1.5×10^{-6}) it was found that the e.m.f. of the cell drifted appreciably and contained some electrode noise. The drift was in a direction which was consistent with the slow oxidation and dissolution of silver from the electrode by the solvent. This also was confirmed by polarographic measurements and estimated to be approximately 0.1 mg./hr. at 326°. Consequently, it was necessary to substitute a Brown recording potentiometer for the potentiometer while making some of the e.m.f. measurements. The recorder had a sensitivity of about 5 mv./in. and was connected in such a way as to record the ΔE after each addition of NaCN to the cell. The effect of noise, which was not large, could be minimized by averaging the e.m.f. over several minutes by drawing a line through the recorded e.m.f. at each fixed concentration of CN^-. The drift was minimized by conducting the measurements in as short a span of time as possible and extrapolating two successive recorded measurements of the e.m.f. to the same time. At the very lowest concentrations the total drift of the e.m.f. during a series of measurements was estimated to be less than 10 mv. and at concentrations above 1.5×10^{-6} mole fraction the total drift was less than 5 mv. The drift between two successive measurements is only a small fraction of the total drift. The drift and noise were negligibly small at concentrations above approximately 5×10^{-6} mole fraction of silver.

The concentrations and values of the e.m.f. at concentrations below 10^{-6} mole ratio are less certain than those at higher concentrations because of the drift and noise. They are consistent, however, with the measurements at higher concentrations.

Results

The results of measurements at 246, 286, and 326° at several concentrations of $AgNO_3$ and NaCN are listed in Table I. The activity coefficients of$AgNO_3$ could be calculated from the relation $\Delta E = (2.303\ RT/\mathfrak{F}) \log \gamma_{\mathrm{AgNO_3}}$. Because of the very strong association of Ag^+ and CN^-, graphical methods were considered to be more reliable and were used to evaluate K_1, K_2, and $K_{1,2}$.[5]

K_1 was evaluated by making large scale plots of $-\log \gamma_{\mathrm{AgNO_3}}$ *vs.* the mole ratio of $CN^-(R_{\mathrm{NaCN}})$ at each fixed concentration of Ag^+. The limiting slopes of these plots (S) at each of the three temperatures are plotted in Fig. 1 as a function of the mole ratio of Ag^+ ($R_{\mathrm{AgNO_3}}$). Since

$$\left(\frac{\partial \log \gamma_{\mathrm{AgNO_3}}}{\partial R_{\mathrm{NaCN}}}\right)_{\substack{R_{\mathrm{NaCN}} = 0 \\ R_{\mathrm{AgNO_3}} = 0}} = (-K_1/2.303)$$

the limits of the plots in Fig. 1 at $R_{\mathrm{AgNO_3}} = 0$ are equal to $(-K_1/2.303)$. Values of K_1 are listed in Table II.

The limiting slopes of the plots in Fig. 1 are equal to $(2K_1K_{1,2} - K_1^2/2.303$ and were used to evaluate the values of $K_{1,2}$ listed in Table II.

At 246 and 286° K_2 was evaluated by plotting the function $(-\log \gamma_{\mathrm{AgNO_3}} - SR_{\mathrm{NaCN}})$ *vs.* R^2_{NaCN}. The slopes of the plots at $R^2_{\mathrm{NaCN}} = 0$ were evaluated graphically and were plotted at several concentrations of $AgNO_3$. Since

$$-2.303 \log \gamma_{\mathrm{AgNO_3}} = K_1(1 + 2(K_{1,2} - K_1)R_{\mathrm{AgNO_3}} + \ldots)R_{\mathrm{NaCN}} + (K_1K_2 - (^1/_2)K_1^2)R^2_{\mathrm{NaCN}} + \ldots\ldots \quad (1)$$

then the limit of the plot of these slopes at $R_{\mathrm{AgNO_3}} = 0$ is equal to $(K_1K_2 - (^1/_2)K_1^2)/2.303$, from which K_2 could be evaluated.[5] Although at 246 and 286° there was a fairly large uncertainty in these slopes, K_2 did not differ very greatly from $K_1/2$, and a relatively large error in the limiting value of the slopes plotted led to a relatively small error in K_2. At 326°, K_2 was appreciably smaller than $K_1/2$, so that an alternate method was necessary to evaluate K_2. If Henry's law is valid for all solute species then it can be shown[5] from the mass balance equations that

$$\frac{1}{\gamma_{\mathrm{AgNO_3}}} = 1 + K_1(1 + (2K_{1,2} - K_1)R_{\mathrm{AgNO_3}})R_{\mathrm{NaCN}} + K_1K_2R^2_{\mathrm{NaCN}} + \ldots. \quad (2)$$

Consequently, the limiting slope of the plot of $(1/\gamma_{\mathrm{AgNO_3}}, - 1 - SR_{\mathrm{NaCN}}$ *vs.* R^2_{NaCN} was evaluated and was plotted as a function of $R_{\mathrm{AgNO_3}}$. The limit of these slopes at $R_{\mathrm{AgNO_3}} = 0$ is equal to K_1K_2 and was used to evaluate K_2. The value of K_2 at 326°, obtained by this alternate method, is listed in Table II.

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(5) J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

TABLE I

ACTIVITY COEFFICIENTS OF $AgNO_3$ IN SOLUTIONS OF Ag^+ AND CN^- IN EQUIMOLAR $NaNO_3$–KNO_3

Temperature 246°

$R_{AgNO_3} = 0.585 \times 10^{-6}$		$R_{AgNO_3} = 1.52 \times 10^{-6}$		$R_{AgNO_3} = 2.48 \times 10^{-6}$		$R_{AgNO_3} = 3.62 \times 10^{-6}$	
$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.184	0.0116	0.922	0.0835	0.830	0.0776	0.922	0.0718
.370	.0282	1.85	.167	1.76	.155	1.85	0.132
.555	.0455	2.77	.252	2.64	.217	2.77	0.202
.740	.0655	3.69	.330	3.52	.274	3.69	0.226
.924	.0775	4.61	.427	4.41	.359	4.61	0.338
1.11	.0970	5.53	.497	5.28	.448	5.53	0.410
1.29	.116	6.44	.594	6.16	.537	6.44	0.494
1.48	.136	7.39	.663	9.14	.873	7.39	0.585
1.66	.161	11.9	1.160	14.1	1.58		
1.85	.176			19.2	1.98		
2.03	.196			24.1	2.29		
2.21	.212			30.8	2.54		
				43.2	2.84		

$R_{AgNO_3} = 5.97 \times 10^{-6}$		$R_{AgNO_3} = 10.3 \times 10^{-6}$		$R_{AgNO_3} = 13.6 \times 10^{-6}$		$R_{AgNO_3} = 14.7 \times 10^{-6}$	
$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
4.16	0.231	2.50	0.090	4.16	0.060	2.50	0.068
8.33	0.503	5.00	0.191	8.33	.188	5.00	.137
12.4	0.885	7.50	0.270	12.4	.330	7.50	.196
16.6	1.33	10.0	0.367	16.6	.502	10.0	.226
20.8	1.82	15.0	0.600	20.8	.666	12.5	.337
25.0	2.19	17.5	0.755	25.0	.934	15.0	.416
29.1	2.47	22.5	0.922	29.1	1.29	17.5	.515
37.4	2.87	25.0	1.17	33.3	1.74	20.0	.620
41.6	3.01	30.0	1.76	37.4	1.99	22.5	.716
45.7	3.14	32.5	2.00	41.6	2.25	25.0	.868
50.0	3.21	35.0	2.18	45.0	2.47	27.5	1.00
54.0	3.32	40.0	2.51	49.0	2.65	30.0	1.17
62.4	3.48	45.0	2.76	53.0	2.97		
70.6	3.62	47.5	2.84	61.5	3.15		
83.0	3.88	50.0	2.90	70.0	3.39		
				74.0	3.48		
				78.3	3.55		
				82.5	3.60		

Temperature 286°

$R_{AgNO_3} = 1.17 \times 10^{-6}$		$R_{AgNO_3} = 2.11 \times 10^{-6}$		$R_{AgNO_3} = 3.28 \times 10^{-6}$	
$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.922	0.0775	0.833	0.063	0.832	0.055
1.85	.160	1.67	.137	1.67	.107
2.77	.234	2.50	.207	2.50	.158
3.69	.300	3.33	.269	3.30	.210
4.61	.363	4.16	.328	4.17	.258
5.55	.430	5.00	.390	5.00	.316
6.44	.495	5.83	.451	5.85	.355
7.39	.558	6.65	.513	6.66	.404
8.27	.630	7.46	.574	9.15	.563
9.21	.697	8.32	.640	11.6	.723
10.1	.748	10.8	.840	14.2	.872
11.0	.810	13.3	1.02	16.7	1.02
15.7	1.10	18.3	1.32	19.2	1.16
20.3	1.34	20.8	1.44	21.7	1.28
24.8	1.57	25.0	1.62	24.2	1.40
		29.1	1.76	26.6	1.50
		33.3	1.88	30.9	1.66
		37.4	1.97	35.0	1.81
		41.6	2.05	43.3	2.05

TABLE I (*continued*)

$R_{AgNO_3} = 6.55 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.036
1.67	.065
2.50	.084
3.33	.113
4.17	.144
6.66	.253
9.15	.370
11.6	.491
14.1	.628
16.7	.767
19.1	.915
21.6	1.05
24.1	1.20
26.6	1.32
29.2	1.44
33.3	1.58
37.5	1.73
41.6	1.87
45.7	2.00
50.0	2.10

$R_{AgNO_3} = 10.6 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.0263
1.67	.0450
2.50	.0648
3.33	.0828
4.17	.101
6.66	.182
9.15	.255
11.6	.338
14.1	.420
16.7	.515
19.1	.614
21.6	.720
24.1	.831
26.6	.950
29.2	1.08
33.3	1.30
37.5	1.50
41.6	1.68
45.7	1.73
50.0	1.90

$R_{AgNO_3} = 17.2 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.0153
3.33	.0622
4.21	.144
8.37	.234
12.5	.316
16.7	.431
20.8	.544
25.0	.675
29.2	.817
33.3	1.00
37.5	1.19
41.6	1.38
45.8	1.53
50.0	1.69
53.4	1.82
58.5	1.92
62.4	2.04
66.5	2.16
70.6	2.25
75.0	2.34

Temperature 326°

$R_{AgNO_3} = 0.585 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.184	0.0130
.370	.0286
.555	.0445
.740	.0662
.924	.0776
1.11	.0933
1.29	.108
1.48	.120
1.66	.134
1.85	.141
2.77	.195
3.70	.234
5.03	.274
5.55	.310
7.38	.384
9.21	.446

$R_{AgNO_3} = 1.40 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.922	0.0665
1.85	.128
2.77	.159
3.69	.206
4.61	.246
7.38	.372
10.1	.464
12.9	.555
15.7	.632
18.4	.718
23.0	.834

$R_{AgNO_3} = 3.16 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.0546
1.66	.100
2.49	.139
3.32	.168
4.16	.200
6.65	.304
9.15	.403
11.6	.500
14.1	.589
16.7	.681
25.0	.950

$R_{AgNO_3} = 6.31 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.0336
1.66	.042
2.49	.071
3.32	.101
4.16	.129
6.65	.219
9.15	.302
11.6	.390
14.1	.485
16.7	.575
20.8	.737
25.0	0.873
29.1	1.00
33.3	1.11
37.5	1.19
41.5	1.27
45.6	1.35

$R_{AgNO_3} = 6.80 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.922	0.0328
1.85	.0630
2.77	.095
3.69	.123
4.61	.152
7.38	.235
10.1	.315
12.5	.398
15.7	.483
18.4	.566
23.0	.706
27.6	.840
32.3	.975
36.9	1.09
50.5	1.40
64.5	1.65

$R_{AgNO_3} = 10.8 \times 10^{-6}$

$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
0.833	0.0193
1.66	.0462
4.16	.108
6.65	.170
9.15	.232
13.3	.338
17.5	.445
21.6	.568
25.8	.696
30.0	.820
34.0	.933
38.2	1.05
42.4	1.18
50.5	1.36

TABLE I (*continued*)

$R_{AgNO_3} = 17.1 \times 10^{-6}$		$R_{AgNO_3} = 0.585 \times 10^{-6}$		$R_{AgNO_3} = 1.54 \times 10^{-6}$	
$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$	$R_{NaCN} \times 10^6$	$-\log \gamma_{AgNO_3}$
2.50	0.0437	0.184	0.0155	0.833	0.052
5.00	.0890	.370	.0286	1.67	.107
7.50	.129	.555	.0420	2.50	.143
10.0	.163	.740	.0555	3.33	.176
12.5	.209	.924	.0656	4.16	.218
16.2	.290	1.11	.0815	5.00	.232
21.2	.376	1.29	.0960	5.83	.287
25.0	.460	1.48	.106	6.65	.321
29.2	.545	1.66	.119	7.46	.355
33.3	.631	2.03	.141	8.32	.382
37.5	.724	2.21	.153	10.8	.474
41.7	.827	3.13	.193	15.8	.596
45.7	.920	4.06	.234	20.8	.745
50.0	1.04	4.97	.272	25.0	.856
53.2	1.16	5.80	.313	29.1	.950
58.4	1.26	7.75	.374	33.3	1.04
62.5	1.34	9.60	.445	37.4	1.12
66.6	1.44				
70.5	1.52				

Discussion

The values of K_1, K_2, and $K_{1,2}$ in Table II were used to evaluate the "specific bond free energies," ΔA_1, as defined in the quasi-lattice theory[3] using the relations

$$
\begin{aligned}
K_1 &= Z(\beta_1 - 1) \\
K_1K_2 &= (Z(Z-1)/2)(\beta_1\beta_2 - 2\beta_1 + 1) \\
K_1K_{1,2} &= (Z(Z-1)/2)(\beta_1\beta_{1,2} - 2\beta_1 + 1)
\end{aligned}
$$

where $\beta_i = \exp(-\Delta A_i/RT)$ and Z is the quasi-lattice coördination number. The values of ΔA_1, ΔA_2, and $\Delta A_{1,2}$ listed in Table II were calculated for values of $Z = 4$, 5, and 6, which should cover the range of possible values of Z. The values of ΔA_1 become more negative with increasing temperature, indicating a positive value for the specific entropy for bond formation, ΔS_1, where $\Delta S_1 = -\mathrm{d}\Delta A_1/\mathrm{d}T$. This means that the standard entropy of association, ΔS_1^0 $(= -\mathrm{d}\Delta F_1^0/\mathrm{d}T = \mathrm{d}(RT \ln K_1)/\mathrm{d}T)$, is more positive for the association of Ag^+ with CN^- than with Cl^- or Br^-. This also is true for the association of Ag^+ with SO_4^{-2}. The experimental precision for the higher associations of Ag^+ with CN^- is not good enough to demonstrate this for ΔS_2 or $\Delta S_{1,2}$. It is not simple to rationalize a *positive* value of ΔS_1. It does seem that positive values of ΔS_1 are related to internal (including rotational) degrees of freedom of the ligand and it may be necessary to include changes in the configuration of ions, which includes the central cation, the ligand anion, and also the environmental solvent ions, in order to explain this. Although it is tempting to adduce rationalizations of this behavior, such rationalizations are too spectulative at the present time and will be re-

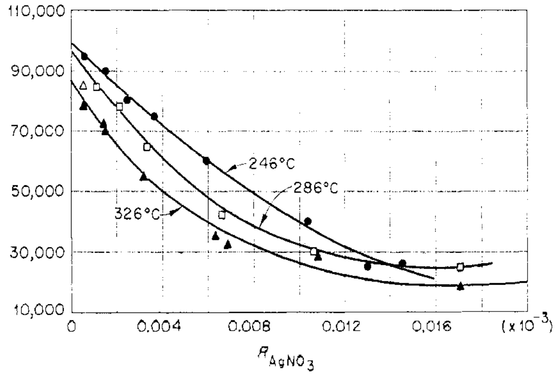

Fig. 1.—Plot of $-(\partial \log \gamma_{AgNO_3}/\partial R_{NaCN})_{R_{NaCN}=0}$ *vs.* R_{AgNO_3}.

TABLE II[a]

		T, °C		
		246	286	326
K_1		230,000	220,000	190,000
K_2		140,000	105,000	(50,000)
$K_{1,2}$		80,000	60,000	(36,000)
$Z = 4$	$-\Delta A_1$	11.3	12.1	12.8
	$-\Delta A_2$	11.8	12.4	(12.4)
	$-\Delta A_{1,2}$	11.2	11.8	(12.0)
$Z = 5$	$-\Delta A_1$	11.1	11.9	12.6
	$-\Delta A_2$	11.5	12.1	(12.1)
	$-\Delta A_{1,2}$	10.9	11.5	(11.7)
$Z = 6$	$-\Delta A_1$	10.9	11.7	12.3
	$-\Delta A_2$	11.3	11.8	(11.8)
	$-\Delta A_{1,2}$	10.7	11.2	(11.4)
Estimated error	K_1	±7%	±7%	±7%
	K_2	±20%	±35%	±50%
	$K_{1,2}$	±15%	±20%	±50%

[a] K_i in mole fraction units, ΔA_i in kcal./mole.

served for the future. It should be noted that the associations of Ag^+ and CN^- are the strongest which have been measured in molten salt solutions. Values of $-\Delta A_1$ for associations of Ag^+ with various ions in molten nitrates are in the order $CN^- > I^- > Br^- > Cl^- > SO_4^{-2}$.

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Studies on Nickel(II) Complexes. III.[1,2]
Bis-(N-arylsalicylaldimine) Complexes

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It has been found that upon alteration of the R substituent in bis-(R-N-salicylaldimine)-nickel(II) complexes from methyl or *n*-alkyl to certain aryl groups, large increases in the solution paramagnetism in inert solvents are produced. The factors affecting this surprising behavior were investigated in an extensive study of the R = aryl complexes. By variation of substituents and their positions on the aryl portion of the molecules, it was found that the spectral and magnetic properties and the extent of molecular association could be consistently controlled. On the basis of this behavior the complexes fall into three categories: (1) those with *o*-substituted aryl groups, which are diamagnetic and monomeric; (2) those with phenyl and *p*-substituted aryl complexes, which are strongly paramagnetic in solution ($\mu_{eff} \geqslant 2.8$ B.M.), associated ($1.5 < \bar{n} < 2.0$), and are either diamagnetic or paramagnetic solids; (3) those with *m*-substituted aryl groups, which have in solution $\mu_{eff} \geqslant 3.2$ B.M., $2 < \bar{n} < 3$, and are always paramagnetic solids. For complexes of the second category the magnetic and molecular weight data at 37° were interpreted in terms of a diamagnetic monomer–paramagnetic dimer equilibrium. The results present further substantiation of the relation between solution paramagnetism and molecular association of apparently quadricoördinate Ni(II) complexes. The nature of the associated forms in no case could be deduced with certainty from the data; however, the presence of axially perturbed *trans*-planar coördination units appears likely.

Introduction

Considerable evidence has been accumulated recently which demonstrates that certain paramagnetic nickel complexes, apparently four-coördinate on the basis of simplest formulation, are in fact additionally coördinated in a fashion such that the triplet state of the metal ion becomes substantially stabilized. The best characterized example of this effect at present is Ni(II) acetylacetonate, which has been shown to contain octahedrally coördinated nickel ions in the discrete trimers[3] present in the fully paramagnetic solid[4] and to be trimeric in benzene,[5] in which it is likewise fully paramagnetic.[4] Only at relatively high temperatures is the association appreciably broken down in inert solvents and spectral evidence indicates that diamagnetic monomers are formed.[6] Further, molecular association of more sterically encumbered β-diketone complexes has been shown to be less complete and the spectral and magnetic features of these complexes in inert media have been successfully though not uniquely interpreted in terms of monomer–trimer equilibria.[4,6] In a preceding part[2] of this series it was demonstrated that the anomalous partial paramagnetism of bis-(N-methylsalicylaldimine)-nickel(II) in solution has its origin in molecular association and a model of the associated species was suggested. All of these results tend to emphasize the relation between paramagnetic behavior and molecular association in both the solid and solution phases.

Previously it had been found that variation of the nature of the group appended to the imine nitrogen in bis-(salicylaldimine)-nickel(II) complexes from *n*-alkyl to certain aryl functions produced in solution a change from essentially complete occupation of a singlet state to predominant

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[1] Part I, R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).

[2] Part II, R. H. Holm, *ibid.*, **83**, 4683 (1961).

[3] G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

[4] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

[5] D. P. Graddon and E. C. Watton, *Nature*, **190**, 906 (1961).

[6] J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).