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Solvation of the Tris(1,10-phenanthroline)iron(II) Cation as Measured by Solubility and Nuclear Magnetic Resonance Shifts[1]

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Abstract: A model for the solvation of the $[Fe(phen)_3]^{2+}$ cation is proposed based on the geometry of the complex. The solvation energy is considered to be the sum of two parts: that due to the ion-dipole interaction with the solvent and that due to the van der Waals interaction between the solvent and the aromatic ligands. The model was tested, and verified, by measuring the solubilities of $Fe(phen)_3(ClO_4)_2$ and naphthalene in ten pure solvents, and in mixtures of water with methanol, acetone, and *N,N*-dimethylformamide. The van der Waals interaction with the ligands was shown to parallel the interaction with naphthalene. The NMR chemical shifts of the 5,6 protons on $Fe(phen)_3{}^{2+}$ were measured in some of the solvent systems.

In attempting to understand the effect of solvent on the rates of racemization and dissociation of the complex $[Fe(phen)_3]^{2+}$ cation,[2] it became apparent that it would be necessary to investigate by independent methods the extent of the solvation of this ion. The large size of the ion, its nonspherical shape, and the aromatic character of the ligands cause this ion to have some unusual features in its interaction with solvents. Although a wide variety of experiments provide some hints about the interaction, there has been no attempt made to measure the solvation energy. This paper reports such an attempt.

We began with the view that the solvation of $[Fe(phen)_3{}^{2+}]$ is governed by two factors: one is the ion-dipole solvation energy, and the other is the solvation of the ligands by solvent molecules via an interaction of the van der Waals type. The solvation of the ligands by the latter interaction would then be similar to the solvation of an aromatic hydrocarbon by the solvent. If this view is correct it should be possible to relate the solubility of $Fe(phen)_3(ClO_4)_2$ to: (1) the solvent dielectric constant, and (2) the solubility of an aromatic compound whose solvent-solute interactions approximate those of the coordinated phenanthroline ligands. Naphthalene was chosen as the test solute for the comparison.

Experimental Section

Chemicals. The compound tris(1,10-phenanthroline)iron(II) perchlorate was prepared several times in the same manner. Typically 1.00 g of $FeCl_2 \cdot 4H_2O$ was dissolved in 25 ml of water and 3.00 g of 1,10-phenanthroline hydrate in 25 ml of methanol was added to it. The mixture was heated on a steam bath and 7.0 g of $NaClO_4 \cdot H_2O$ in 100 ml of water was slowly added. The resulting fine crystals of $Fe(phen)_3(ClO_4)_2$ were collected on a medium fritted glass filter, washed with cold water, and dried in a vacuum desiccator. With care nearly 100% yield could be achieved. If, however, the sodium perchlorate is rapidly added to a cold solution of $Fe(phen)_3{}^{2+}$ in water, a very fine precipitate is produced which is difficult to filter.

Methanol (Baker Chemical Co. "Defined Purity" grade) was dried by refluxing with and then distilling from magnesium methoxide.[3] Acetone (Baker "Analyzed" Reagent) was dried by treating with Drierite, filtering, and distilling. *N,N*-Dimethylformamide obtained from Matheson Coleman and Bell was treated with Drierite, filtered, distilled under vacuum, and stored in a glass stoppered bottle in a desiccator ($n^{24.7}\mathrm{D}$ 1.4303; lit. $n^{25}\mathrm{D}$ 1.4294[4]). Fisher Scientific Co. Certified Reagent dimethylformamide was used in preparing the dimethylformamide-water mixtures.

Formamide (Fisher Reagent Grade) was purified by vacuum distillation, the initial and final 20% being discarded. The remainder was fractionally frozen to a melting point of 2.50°C (lit.[5] 2.55°C, $K_f = 3.50$). It was stored in standard taper glass stoppered flasks under nitrogen and in the dark. Dimethyl sulfoxide (Fisher Certified Reagent) was treated with Linde 4A molecular sieve, and fractionally frozen twice. The melting point was 18.55°C (lit.[6] 18.55°C).

Glycerol (reagent, minimum purity 95%) was purified by distillation at reduced pressure, discarding the initial 30% and the final 20%. ($n^{25}\mathrm{D}$ (obsd) 1.4736; lit.[7] 1.4735). Ethylene glycol (Eastman Chemical Co.) was found to contain 0.2% water and was used as received. Acetonitrile (Matheson Coleman and Bell Spectro-quality Reagent) was used without further purification ($n^{30}\mathrm{D}$ (obsd) 1.3411; lit.[8] 1.3393; density (obsd) 0.7738 at 27°C; lit.[8] 0.7745 at 27°C).

Naphthalene was recrystallized from methanol. The melting point was 80.0°C (lit. 80.22°C, $K_f = 68$). Anhydrous sodium perchlorate was dried by heating to 120°C under vacuum before each use. Reagent grade acetic acid, minimum 99.7% AcOH, was used without further purification. Mixed solvents were prepared and stored in glass stoppered volumetric flasks. The components were either weighed in the flasks or transferred into the flasks from burets. Both methods allowed a precision of 0.001 in the mole fraction of the solvent components. All solvents were kept in tightly capped glass containers, and protected from direct exposure to the sunlight. In all cases solvents which had been stored for extended periods or opened repeatedly were discarded in favor of fresh solvents. Aqueous mixtures containing formamide, or *N,N*-dimethylformamide, were prepared immediately before use to prevent any errors due to decomposition of the amide. Solvents containing $NaClO_4$ were prepared immediately before use.

Solubility of $Fe(phen)_3(ClO_4)_2$. The determinations of solubility, in a variety of solvents and solvent mixtures, were made as follows. A saturated solution of $Fe(phen)_3(ClO_4)_2$ was prepared by adding the complex salt to 5 ml of the solvent in a 10-ml ampoule at about 40°C until no more complex would dissolve. The ampoules were capped with rubber septum caps, suspended in an aquarium bath held at 25.0 ± 0.1°C, and agitated continuously. The arrangement shook the ampoules vigorously enough to maintain the crystals of complex in suspension in the solutions.

Aliquots were withdrawn daily, and the concentration of $Fe(phen)_3(ClO_4)_2$ was measured as follows. The shaking was stopped, and the suspended crystals were allowed to settle. About 0.5 ml of the liquid phase was withdrawn from each ampoule with a capillary pipet and used to fill a lambda pipet. The same lambda pipet was used for all measurements and was calibrated to contain 0.250 ml. Care had to be taken not to include any of the crystals of complex in the dark solutions withdrawn from the ampoules. The contents of the pipet were discharged and washed into appropriately sized volumetric flasks. The flasks were filled with distilled water and samples withdrawn for analysis. The absorbance of each solution was measured at 510 mμ on a Cary Model 14 spectrophotometer in 1.00-cm silica cells.

The solutions in glycerol and ethylene glycol had to be filtered before diluting for analysis since small crystals would not settle out of the viscous solvents. The samples were filtered through a small pipet with a medium fritted glass filter in the end before filling the 0.250-ml pipet.

After three consecutive determinations of solubility in a solvent gave essentially the same value, the last three values were averaged.

Solvent of Crystallization. In order for the solubility studies to be meaningful, the nature of the solid in equilibrium with the solutions must be known. The complex perchlorate, as obtained from several solvents, was investigated to see if solvent was included in a stoichiometric way in the crystal.

The amount of water in material, which had been recrystallized from water and air-dried, was determined by weight loss on heating, Karl Fischer titration, and x ray unit cell size comparison with experimental density. Three 0.2-g samples of the solid were heated to 190°C for 20 hr in a drying pistol at 0.005 mmHg pressure in the presence of anhydrous magnesium perchlorate. The weight losses corresponded to 0.08, 0.09, and 0.09 mol of H_2O per mole of complex.

Crystal water was also determined by titration with Karl Fischer reagent. Fisher Scientific Co. SO-K-3 stabilized Karl Fischer reagent and SO-K-5 diluent were used. End points were detected electrically by a method[9] which depends on the depolarization of platinum electrodes by free iodine. The titrant and methanol solvent were protected from atmospheric moisture by Drierite traps, and the titration cell was arranged so that samples could be dissolved and titrated without exposure to atmospheric moisture. The strength of the titrant was determined by titration of a reference solution containing 10.08 mg of H_2O/ml. Two 0.1-g samples of $Fe(phen)_3(ClO_4)_2$ were dissolved in dried methanol and titrated. The water found in the two samples corresponded to 0.36 and 0.38 mol of H_2O per mole of complex.

A preliminary x-ray structure investigation of a crystal of $Fe(phen)_3(ClO_4)_2$, grown from aqueous solution, was made using a Picker full-circle automatic diffractometer. The space groups and unit cell dimensions were determined from $h00$, $0k0$, and $00l$ reflections. The unit cell parameters are $a = 35.743$ Å, $b = 15.918$ Å, $c = 11.642$ Å, and $\beta = 102.32°$. The space group is either *Cc* or *C*2/*c*. The calculated unit cell volume is 6782.8 Å^3. With eight formula units per unit cell the calculated densities are: $Fe(phen)_3(ClO_4)_2$, 1.558 g/cm^3; $Fe(phen)_3(ClO_4)_2 \cdot H_2O$, 1.593 g/cm^3; and $Fe(phen)_3(ClO_4)_2 \cdot 2H_2O$, 1.628 g/cm^3. The actual density, as measured on several crystals by the flotation method in CCl_4-$CHCl_3$ at 25°C, is 1.569 g/cm^3. This strongly suggests that the anhydrous formulation is correct.

Infrared spectra were recorded of the solids which crystallized in the solubility measurements using the solvents acetone, acetonitrile, formamide, and *N,N*-dimethylformamide. The crystals were dried of solvent adhering to the surface by tumbling on filter paper in a drybox, and KBr pellets were made from 2-mg samples of each solid and 100 ml of KBr. The infrared spectra were run on a Perkin-Elmer Model 237B spectrometer. In the specimen from acetonitrile no band was observed in the region 2210–2260 cm^{-1}, and in the specimens from acetone, formamide, and dimethylformamide only weak carbonyl absorptions were observed in the 1650–1720-cm^{-1} region. It is concluded that the solid in equilibrium with each solvent was $Fe(phen)_3(ClO_4)_2$.

Solubility of Naphthalene. The method of solubility determination was similar to that described for the solubility of $Fe(phen)_3(ClO_4)_2$. Two maxima from the reported ultraviolet spectrum of naphthalene at 283 and 286 mμ were selected for concentration measurement. A reference solution of 0.256 mg/ml of naphthalene in 95% ethanol was scanned in 0.100-cm matched silica cells on the Cary 14 spectrophotometer. The maximum at 283 mμ had an average absorbance of 0.748 and the maximum at 286 mμ had an average absorbance of 0.758.

Saturated solutions of naphthalene were prepared and thermostated in the same way as for $Fe(phen)_3(ClO_4)_2$. A 0.100-ml lambda pipet was used to measure aliquots of the saturated solutions. The aliquots were diluted with 95% ethanol, and absorbance was measured in 0.100-cm matched silica cells. For water, the sol-

Table I. Solubility of Naphthalene at 25.0°C

Pure solvents	Solubility (mol/l.)	Density (g/ml)	Solubility (mole fraction)	δ^a
Water	0.000234	0.9971	4.23×10^{-6}	23.4
Glycerol	0.01052	1.2528	0.000774	16.5
Formamide	0.0539	1.1320	0.00215	19.2
Ethylene glycol	0.0896	1.1040	0.00506	14.6
Methanol	0.579	0.8080	0.0247	14.5
Acetic acid	0.882	1.0376	0.0542	10.1
Acetonitrile	1.715	0.8368	0.102	11.9
Dimethyl sulfoxide	2.02	1.0750	0.162	–
Acetone	2.75	0.8776	0.233	9.9
N,N-Dimethylformamide	3.12	0.9828	0.281	12.1
Aqueous mixtures^b				
0.200 Acetone	0.0890	0.9240		
0.400 Acetone	0.648	0.8804		
0.600 Acetone	1.47	0.8656		
0.800 Acetone	2.19	0.8648		
0.200 DMF	0.0445	0.9908		
0.400 DMF	0.560	0.9800		
0.600 DMF	1.30	0.9752		
0.800 DMF	2.34	0.9748		
0.200 Methanol	0.00207	–		
0.400 Methanol	0.0203	–		
0.597 Methanol	0.0900	–		
0.796 Methanol	0.264	–		

^{a}Values from J. Brandrup and E. H. Immergut, "Polymer Handbook", Interscience, New York, N.Y., 1966. ^{b}Solvent composition in mole fraction of the organic component.

ubility of naphthalene proved to be too small to measure in this way. A 100-ml volumetric flask of distilled water and 1.0 g of naphthalene flakes were thermostated with the other samples. Quantities of this solution were filtered, and the absorbance of naphthalene was measured in 5.00-cm matched silica cells without dilution.

Three solubility measurements were made in each solvent.

Proton NMR of Fe(phen)$_3$(ClO$_4$)$_2$. The chemical shifts of the protons in the 5,6-positions of the phenanthroline ligands were measured in several pure solvents, and in mixtures of water with acetone and *N,N*-dimethylformamide. The dependence of the chemical shift on perchlorate ion concentration was measured in acetone. Spectra were run at 60 MHz on a Varian A-60D spectrometer, in combination with a Varian C-1024 time averaging computer. All spectra were recorded at the ambient temperature of the sample holder (36°C). The concentration of Fe(phen)$_3$(ClO$_4$)$_2$ generally was 4.0 mg/ml. In water it was limited to 0.6 mg/ml by the solubility. In acetone the concentration was varied between 0.75 and 6.00 mg/ml. Complex concentrations of 4.0 mg/ml could be scanned directly on the spectrometer. Lower concentrations required 4–20 scans with the C-1024 computer to give a measurable signal.

A reference signal was provided by including a sealed capillary of benzene in the sample tube. The same reference capillary was used in all measurements. This external reference system eliminates the solvent effect on the reference signal position and the reference compound's effect on the properties of the solvent which would exist with an internal reference. All chemical shifts are reported relative to the benzene signal, and could be reproduced to within 0.3 Hz.

Results

Solubility of Naphthalene. In Table I are given the measured values for the solubility of naphthalene in the various solvent media and the measured densities of the saturated solutions. The solubilities in pure solvents have been converted to mole fraction units to facilitate comparison with solubility values in the literature. Agreement is very good for acetone, methanol, and acetic acid,[10] and moderately good for water.[11] Solutions of naphthalene in nonpolar solvents have long served as good examples of "regular solutions".[12] Although the solvents used in this work are highly polar, it is interesting to examine the trend in solubility with the solubility parameter, δ. It will be noted (Table I) that the general trend is an increase in solubility as δ of the solvent decreases (the value of δ for naphthalene is 9.9), although there are several exceptions in the order.

Composition of the Solid. The weight loss on heating and the Karl Fischer moisture determinations on Fe(phen)$_3$(ClO$_4$)$_2$ give, respectively, 0.09 and 0.37 mol of H_2O per mole of Fe(phen)$_3$(ClO$_4$)$_2$. Thus, this salt is best formulated as an anhydrous salt and not as the dihydrate as suggested by Pfeiffer and Werdelmann.[13] The water which was found probably came from inclusions in the crystals or was adsorbed on the surface of the crystals. Heating under vacuum might not break open all of the inclusions but would remove the water adsorbed on the surface. The Karl Fischer titration would indicate both the surface water and that which was trapped in inclusions. The infrared spectra of crystals of Fe(phen)$_3$(ClO$_4$)$_2$ grown in other solvents do not show significant bands due to the solvent. It is concluded, therefore, that the solid in equilibrium with the saturated solutions in the solubility studies is best described as containing no solvent of crystallization. It should be noted that the solid used in the solubility studies was thoroughly dried while the solid used in the moisture determinations was not dried under nearly as drastic conditions.

Solubility of the Complex Perchlorate. The solubilities of Fe(phen)$_3$(ClO$_4$)$_2$ in the various solvent media are given in Table II. The value listed for acetic acid is not an accurate one. The solubility in this solvent varied from measurement to measurement in a random way, measured values differing by as much as factor of five. No reason for this is known, although the presence of small amounts of water in the acetic acid increased the solubility sharply. The value given is an estimate undoubtedly near the true value, but the error may be much larger than for the other solvents.

In each of the three systems containing water mixed with an organic solvent, the maximum solubility occurs in a mixture rather than in a pure solvent.

NMR Measurements. The chemical shifts of the protons in the 5,6 ring positions of the phenanthroline ligands in Fe(phen)$_3$(ClO$_4$)$_2$ were measured relative to an external benzene standard. These protons appear as a singlet in the NMR spectrum.[14] Measurements were made in pure solvents and some aqueous mixtures (Table III).

NMR measurements were also made on solutions in acetone containing excess ClO_4^-. The variation of chemical shift with total perchlorate concentration in acetone is given in Table IV.

Discussion

Structures of [Fe(phen)$_3$]$^{2+}$ and [Fe(phen)$_3$](ClO$_4$)$_2$. The detailed structure of the [Fe(phen)$_3$]$^{2+}$ complex cation has been reported[15] as a result of the x-ray structure determination of the compound [*l*-Fe(phen)$_3$][(*d*-$C_4H_2O_6$)$_2$Sb$_2$]. Rather than appearing spherical, the cation resembles a three-bladed propeller, the blades being the planar phenanthroline ligands. The maximum distance from the center of the complex to the edge of the ligands is about 7 Å.

The effect of the geometric characteristics of the complex on its reactions in aqueous solution has been discussed before.[16] There are three large V-shaped pockets between the phenanthroline ligands, each large enough to hold two small molecules (such as water) or anions. When in these positions, the molecules are essentially above six of the faces of the octahedron defined by the nitrogen atoms bound to the metal. There are two smaller pockets corresponding to the two remaining octahedral faces (the two faces perpendicular to the threefold axis of the complex). Approach toward the metal atom at each of these sites is hindered by the

Table II. Solubility of $Fe(phen)_3(ClO_4)_2$ at 25.0°C

Pure solvents	Solubility (mol/l.)	Density (g/ml)	D	K_{IP}	K_{SP}	ΔG_{ligand} (kcal/mol)	ΔG_{cation} (kcal/mol)
Water	0.000871	0.9972	78.39[a]	5.73	2.59×10^{-9}	−4.63	−163.58
Glycerol	0.00289	1.2532	42.5[a]	48.04	6.26×10^{-8}	−9.51	−166.72
Formamide	0.1897	1.1648	111.3[b]	2.72	9.16×10^{-3}	−11.83	−171.38
Ethylene glycol	0.00716	1.1064	37.7[a]	86.77	4.34×10^{-7}	−11.84	−168.57
Methanol	0.00286	0.7868	32.70[a]	193.18	3.00×10^{-8}	−12.80	−168.88
Acetic acid	0.0002	1.0436	6.195[c]	–	–	–	–
Acetonitrile	0.1044	0.8556	34.58[c]	139.15	7.80×10^{-5}	−15.54	−171.88
Dimethyl sulfoxide	0.303	1.1626	46.68[a]	31.70	2.87×10^{-3}	−15.57	−173.12
Acetone	0.00861	0.7848	20.70[a]	6389	1.16×10^{-8}	−16.14	−169.36
N,N-Dimethylformamide	0.3105	1.0500	36.71[a]	99.92	9.64×10^{-4}	−16.39	−173.00
Aqueous mixtures[d]							
0.200 Acetone	0.0459	0.9424	52.9[e]	19.28	8.81×10^{-5}	−12.26	−170.22
0.400 Acetone	0.1060	0.9084	38.7	75.79	1.47×10^{-4}	−14.67	−171.51
0.600 Acetone	0.0952	0.8676	29.8	347.6	2.61×10^{-5}	−16.04	−171.64
0.800 Acetone	0.0516	0.8284	24.7	1364	1.95×10^{-6}	−16.34	−170.82
0.100 DMF	0.01114	–	71.7[f]	7.25	4.20×10^{-6}	−9.16	−167.91
0.200 DMF	0.0480	1.0052	64.8	9.72	1.58×10^{-4}	−11.49	−170.01
0.500 DMF	0.1894	–	49.3	25.32	1.38×10^{-3}	−14.73	−172.46
0.600 DMF	0.228	–	46.2	33.12	1.55×10^{-3}	−15.16	−172.68
0.700 DMF	0.298	–	43.6	42.73	2.07×10^{-3}	−15.64	−172.95
0.800 DMF	0.322	1.0482	41.2	55.62	1.86×10^{-3}	−15.96	−173.05
0.900 DMF	0.335	–	38.9	73.83	1.52×10^{-3}	−16.21	−173.07
0.200 Methanol	0.00334	–	65.2[g]	9.54	1.32×10^{-7}	−7.51	−166.04
0.400 Methanol	0.00809	–	53.0	19.14	1.32×10^{-6}	−10.11	−168.07
0.597 Methanol	0.00902	–	43.8	41.85	1.20×10^{-6}	−11.59	−168.91
0.796 Methanol	0.00600	–	37.2	93.09	2.75×10^{-7}	−12.42	−169.09

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Table III. Chemical Shifts of the 5,6 Protons of $Fe(phen)_3(ClO_4)_2$ in Various Solvents and Mixtures[a]

Solvent composition (mole fraction)	F_{IP}	Chemical shift[b]
1.00 Dimethyl sulfoxide	0.22	107.9
1.00 Acetonitrile	0.51	84.3
1.00 Methanol	0.43	85.5
1.00 Water	0.008	109.9
0.80 Water–0.20 acetone	0.15	95.5
0.60 Water–0.40 acetone	0.38	88.0
0.40 Water–0.60 acetone	0.69	82.4
0.20 Water–0.80 acetone	0.88	79.0
1.00 Acetone	0.97	76.4
0.80 Water–0.20 *N,N*-dimethylformamide	0.09	102.6
0.60 Water–0.40 *N,N*-dimethylformamide	0.15	100.1
0.40 Water–0.60 *N,N*-dimethylformamide	0.23	97.8
0.20 Water–0.80 *N,N*-dimethylformamide	0.32	96.1
1.00 *N,N*-Dimethylformamide	0.44	96.2

[a] Concentration of complex = $5 \times 10^{-3}\,M$ except for water and methanol which are 7.5×10^{-4} and $2.5 \times 10^{-3}\,M$, respectively. [b] Chemical shifts in Hz (cycles per second).

Table IV. Dependence of the Chemical Shift of the 5,6 Protons of $Fe(phen)_3(ClO_4)_2$ in Acetone on Concentration and Added $NaClO_4$

$[Fe(phen)_3^{2+}]$	Molarity, $NaClO_4$	$[ClO_4^-]$	F_{IP}[a]	Chemical shift (Hz)
0.00094	0	0.00188	0.871	78.6
0.00189	0	0.00378	0.928	78.0
0.00377	0	0.00754	0.962	77.6
0.00754	0	0.0151	0.980	75.3
0.00377	0.00866	0.0162	0.988	75.4
0.00377	0.0203	0.0278	0.994	75.6
0.00377	0.0523	0.0598	0.997	75.4

[a] Calculated assuming K_{IP} = 6389.

three hydrogens in the 2-positions of the three ligands. In the crystal containing the $[(C_4H_2O_6)_2Sb_2]^{2-}$ anion, the latter is large and one side of it fits into one of the large pockets of the complex cation.

The crystal structure of $[Cu(phen)_3](ClO_4)_2$ has been reported recently.[17] The space group is the same, and the lattice parameters almost identical with those we have measured for the $[Fe(phen)_3](ClO_4)_2$ crystal. The $[Cu(phen)_3]^{2+}$ cation has the distorted octahedral arrangement often found with Cu(II); no such distortion would be expected with the Fe(II) complex. This difference probably accounts for the small difference in the cell parameters. Because of the similarities in the two structures, certain features of the $[Cu(phen)_3](ClO_4)_2$ structure are worth noting. In this structure, and presumably in the $[Fe(phen)_3](ClO_4)_2$ structure, there are eight ClO_4^- anions at relatively close distance to the central metal. The ClO_4^- ions show rotational disorder in the crystal, so that only the Cu–Cl distances are established. Six of the Cu–Cl distances are in the range 5.68–7.52 Å, and the two others are 8.65 Å.

A variety of values have been used in the literature for the "radius" of the ClO_4^- ion. The most carefully considered values appear to be 2.36 Å for the "thermochemical radius" and 2.90 Å for the "radius of the circumscribed sphere".[18] The latter value is consistent with the fact that in the $[Cu(phen)_3](ClO_4)_2$ crystal, in which the ClO_4^- ions show rotational disorder, Cl–Cl distances of 6.13 Å are observed. The conclusion to be drawn is that small molecules in the large pockets of the complex might approach at least as close as 3 Å to the central metal atom.

Thermodynamics of Solvation. The previous considerations indicate that, in solution, the phenanthroline ligands will be exposed to solvent molecules to a considerable extent. It seemed worthwhile to pursue the idea that the attractive interactions between the solvent and the complex consisted of two parts: (1) the electrostatic interaction of the polar solvent with the positively charged complex, and (2) the interaction of the solvent with the aromatic system of the ligands. To obtain quantitative information about these interactions the solubility of the complex perchlorate was measured in various solvents. The lattice energy of the complex perchlorate and the solvation energy of the perchlorate ion are other factors that affect the solubility, and they must be evaluated.

For purposes of evaluating the contributing energy terms,[19] the dissolution process is conceptually broken down into three steps:

$$\begin{array}{ll}
MX_2(\text{solid}) \rightarrow M^{2+}(\text{gas}) + 2X^-(\text{gas}) & \Delta G_{\text{lattice}} \\
M^{2+}(\text{gas}) + \text{solvent} \rightarrow M^{2+}(\text{solution}) & \Delta G_{\text{cation}} \\
2X^-(\text{gas}) + \text{solvent} \rightarrow 2X^-(\text{solution}) & \Delta G_{\text{anion}} \\
\hline
MX_2(\text{solid}) + \text{solvent} \rightarrow & \\
\quad M^{2+}(\text{solution}) + 2X^-(\text{solution}) & \Delta G_1
\end{array}$$

It is assumed that the electrostatic contributions to the free-energy changes in steps 2 and 3 will be given by expressions having the form of the Born equation. It is further assumed that there is an additional contribution, ΔG_{ligand}, to the free-energy change in step 2, resulting from the interaction of the solvent with the aromatic system of the phenanthroline ligands. Thus,

$$\Delta G_{\text{anion}} = -a\left(1 - \frac{1}{D}\right) \quad (1)$$

$$\Delta G_{\text{cation}} = -c\left(1 - \frac{1}{D}\right) + \Delta G_{\text{ligand}} \quad (2)$$

The free-energy change for the net dissolution reaction is

$$\Delta G_1 = \Delta G_{\text{lattice}} + \Delta G_{\text{cation}} + \Delta G_{\text{anion}} \quad (3)$$

and is related to the solubility product, K_{SP}, by the relation

$$\Delta G_1 = -RT \ln K_{SP} \quad (4)$$

It seemed reasonable that information about relative values of ΔG_{ligand} in the various solvents could be obtained by measuring the solubility of a model aromatic compound in the solvents. Naphthalene was chosen as the model compound; its solubility is given in Table I. The dissolution of naphthalene can be visualized as occurring in two steps:

$$\begin{array}{ll}
\text{naphthalene(solid)} \rightarrow \text{naphthalene(gas)} & \Delta G_{\text{subl}} \\
\text{naphthalene(gas)} + \text{solvent} \rightarrow & \\
\quad \text{naphthalene(solution)} & \Delta G_{\text{naphth}} \\
\hline
\text{naphthalene(solid)} + \text{solvent} \rightarrow & \\
\quad \text{naphthalene(solution)} & \Delta G_2
\end{array}$$

The free-energy change for the net dissolution reaction is

$$\Delta G_2 = \Delta G_{\text{subl}} + \Delta G_{\text{naphth}} \quad (5)$$

and, assuming ideality,

$$\Delta G_2 = -RT \ln S_{\text{naphth}} \quad (6)$$

where S_{naphth} is the solubility of naphthalene. ΔG_{subl} is calculated, from the vapor pressure[20] of naphthalene at 25°C, to be 7.306 kcal. Thus, data are available to calculate numerical values of ΔG_2 for the various solvents.

At this point we make the assumption that the solvation of naphthalene and the ligands is so similar, that their solvation energies are related by a proportionality constant which is independent of the solvent;

$$\Delta G_{\text{ligand}} = r\Delta G_{\text{naphth}} \quad (7)$$

Appropriate combination of equations then leads to the relation

$$\left(\frac{D}{D-1}\right)(\Delta G_{\text{lattice}} - \Delta G_1) = (a + c) - r\left(\frac{D}{D-1}\right)\Delta G_{\text{naphth}} \quad (8)$$

Ion-Pair Formation. Before calculating values of K_{SP} from the solubility data it is necessary to consider the extent to which $Fe(phen)_3(ClO_4)_2$ exists in these solvents as highly ion-paired species. The effect of added ClO_4^- on the racemization rate[2] and on the NMR spectrum provides evidence on this point. With respect to racemization, added ClO_4^- has a large effect on the rate in acetone, a significant effect on the rate in acetonitrile, and little effect on the rate in methanol and *N,N*-dimethylformamide. In acetone a significant shift in the NMR position of the 5,6 protons was observed on addition of $NaClO_4$.

These results clearly indicate that ion pairing is extensive in acetone. The question of whether or not the complex was completely associated and therefore neutral was investigated by ion migration experiments. The red complex migrated toward the cathode even in the presence of excess perchlorate. Saturated $NaClO_4$ in acetone, however, did arrest the motion of the complex ions.

Since ion-pair formation is significant in these systems, it is necessary to make some estimate of its extent. Two theoretical models are available for this purpose; that due to Bjerrum[21] and that due to Fuoss.[22] We have chosen the latter, since it appears to give the better values in the few cases where qualitative evidence provides a basis of choice. In the simplest form of the Fuoss model, the equilibrium constant for ion-pair formation is given by

$$K_{IP} = \left(\frac{4\pi Na^3}{3000}\right)e^b \quad (9)$$

where

$$b = \frac{|z_+z_-|e^2}{aDkT} \quad (10)$$

where a is the closest distance of approach of the two ions of charge z_+ and z_- and D is the dielectric constant. In calculating numerical values of K_{IP}, the value for a was taken as 5.68 Å, the shortest metal-Cl distance observed in the $Cu(phen)_3(ClO_4)_2$ crystal. From the values of K_{IP} so calculated and the measured solubilities, the concentrations of the free ions and the values of K_{SP} were calculated. Values of K_{IP} and K_{SP} are included in Table II.

Test of Proposed Model. A plot of $[(D/(D - 1))(\Delta G_{\text{lattice}} - \Delta G_1)]$ vs. $[(D/(D - 1))\Delta G_{\text{naphth}}]$ should give a straight line if the value of $\Delta G_{\text{lattice}}$ is chosen correctly. Examination of a few trial plots, where $\Delta G_{\text{lattice}}$ was allowed to range from 200 to 350 kcal, indicated that: (1) 21 of the 25 data points gave reasonable linearity, with the best fit occurring for values of $\Delta G_{\text{lattice}}$ about 300 kcal (this was true both when ion pairing was estimated as indicated and when it was regarded as negligible); (2) the behavior in acetic acid was drastically out of line; and (3) the three data points for solutions containing more than 0.5 mol fraction methanol were always significantly out of line.

The 21 data points were treated by linear regression, and best fit was obtained with $\Delta G_{\text{lattice}} = 314$ kcal, $(a + c) = 301.71$ kcal, and $r = 2.053$. Figure 1 shows the test plot and straight line corresponding to these values. The value of r is just the kind of value that might be expected from the model proposed. It implies that the exposure of the three phenanthroline ligands to the solvent molecules is equivalent, energywise, to the exposure of about two naphthalene molecules. The value of r, which is the slope of the line, is

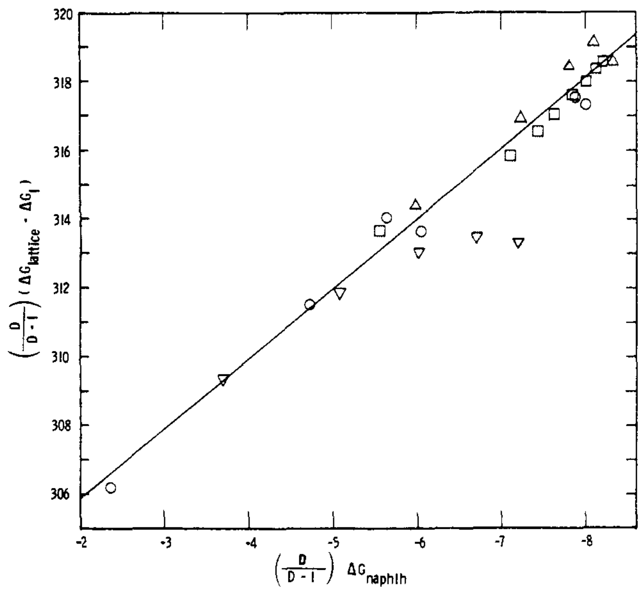

Figure 1. Correlation (for $\Delta G_{\text{lattice}}$ = 314 kcal) between solvation of complex and solvation of naphthalene in various solvent media: those containing acetone, △; *N,N*-dimethylformamide, □; methanol, ▽; other pure solvents, ○.

not greatly sensitive to the value chosen for $\Delta G_{\text{lattice}}$. Values of r obtained for $\Delta G_{\text{lattice}}$ assumed to be 250, 300, and 350 kcal are 1.84, 2.02, and 2.19, respectively. Overall, the results provide strong support for the model proposed.

Values of ΔG_{ligand} were calculated both from the expression

$$\Delta G_{\text{ligand}} = \Delta G_{\text{l}} - [\Delta G_{\text{lattice}} - (a + c)] - \frac{a + c}{D} \quad (11)$$

and from

$$\Delta G_{\text{ligand}} = r\Delta G_{\text{naphth}} \quad (12)$$

and the average of the two is listed for each solvent in Table II. Although the absolute values listed may be questioned because of the numerous assumptions inherent in the procedure, the relative values for the different solvents should be quite reliable. The results of the racemization study[2] support this view.

To this point no interpretation has been placed on a and c individually, other than that they are the proportionality constants defined by equations given earlier. If one assumes that they are related to the "radii" of the ions it is possible to calculate the effective radius of $[\text{Fe(phen)}_3]^{2+}$. The result is dependent on the value chosen for the radius of the ClO_4^- ion. If a value of 2.36 Å is assumed for this radius, then a = 140.71 kcal and c = 161.00 kcal. The latter value corresponds to an "effective radius" of 4.13 Å for the $[\text{Fe(phen)}_3]^{2+}$ ion. Values of ΔG_{cation}, calculated on this basis using eq 2, are included in Table II. Comparison of the values of ΔG_{ligand} and ΔG_{cation} shows that, although the former is only a small fraction of the latter, it is large enough to play a major part in determining the order of the solvents according to ΔG_{cation}.

The calculated "effective radius" of 4.13 Å for the cation is not unreasonable.

In the solid state, $[\text{Fe(phen)}_3](\text{ClO}_4)_2$ has a molar volume of 0.51 l. The "apparent molar volume" in solution can be calculated with reasonable accuracy for some of the solutions in Table II. The results are: formamide, 0.50–0.58; dimethyl sulfoxide, 0.49–0.56; *N,N*-dimethylformamide, 0.44–0.53. Thus it appears that, in these solvents at least, solvent molecules can occupy the space between the phenanthroline ligands in much the same way that ClO_4^- ions do in the solid. On the basis of proton NMR line width measurements, LaMar and van Hecke[23] concluded that, in aqueous solutions of the complex $[\text{Cr(phen)}_3]^{2+}$, water molecules penetrate about 2 Å into the pockets between the ligands, a behavior consistent with the model proposed for $[\text{Fe(phen)}_3]^{2+}$. They also concluded that methanol did not penetrate into the $[\text{Cr(phen)}_3]^{2+}$ complex to the same extent as water. Our results do not positively suggest, but would be consistent with, such a behavior of methanol with $[\text{Fe(phen)}_3]^{2+}$. That is, one could hold the view that the three points for methanol-rich solutions falling below the line on Figure 1 do so because of a larger effective radius for the cation. However, the points could be low for other reasons.

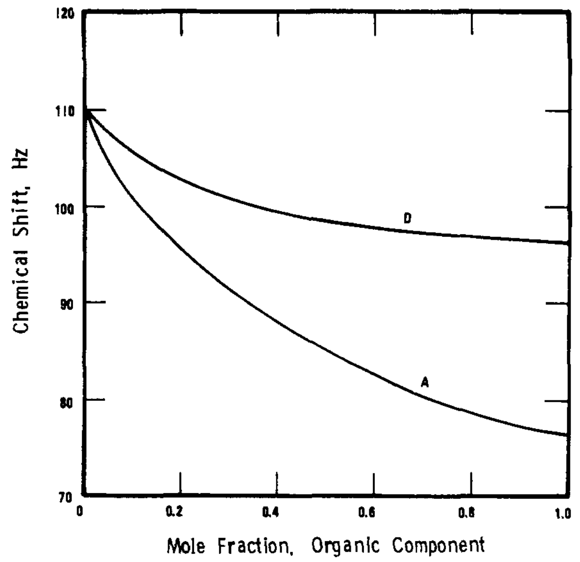

Figure 2. Chemical shift of 5,6 protons as a function of solvent composition: curve A, acetone–water; curve D, *N,N*-dimethylformamide–water.

NMR Measurements. It was hoped that the measurements of the chemical shifts of the protons in the 5,6 ring positions in mixed solvents would provide information about preferential solvation in mixed solvents. The NMR data of Figure 2, which show the variation in chemical shift with solvent composition for the mixed solvents, can be interpreted as indicating preferential solvation of the $\text{Fe(phen)}_3{}^{2+}$ ion by the organic component of the solvent. If the chemical shift is linearly related to the mole fraction composition of the solvation sphere, a negative deviation from a straight line between pure solvents indicates preferential solvation[24] by the solvent with the lower chemical shift, i.e., the organic solvent.

On the other hand, ion-pair formation is undoubtedly extensive in these solutions. Each of the tables of NMR data includes the value of F_{IP}, the fraction of $[\text{Fe(phen)}_3]^{2+}$ present as ion pairs, calculated from the values of K_{IP} given in Table II. It appears that ion-pair formation prevents drawing any conclusion about preferential solvation from the NMR data.

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The Rates of Racemization and Dissociation of the Tris(1,10-phenanthroline)iron(II) Cation in Various Solvents[1,2]

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Abstract: Rates of racemization and dissociation of $[Fe(phen)_3]^{2+}$ were measured in water, methanol, acetone, formamide, *N,N*-dimethylformamide, acetonitrile, and acetic acid, and in mixtures of water with methanol, acetone, formamide, and *N,N*-dimethylformamide. The rate of racemization was also measured in mixtures of water with glycerol and ethylene glycol. In all cases the dissociation rate was much slower than the racemization rate, indicating that racemization is predominantly intramolecular in all these solvents. Ion association (with ClO_4^-), when it occurs, has a retarding effect on the rate of racemization. The effect of a solvent on the racemization rate appears to be due to solvation of the aromatic phenanthroline ligands in the transition state, and to the viscous resistance to reorganization of the solvent in the vicinity of the complex ion when the latter undergoes inversion. Supporting this view is the fact that the rate constants can be empirically represented by the equation $\log k = c - (0.26\Delta G_{\text{ligand}}/2.303RT) - 0.48 \log (\eta V_{\text{m}})$, where ΔG_{ligand} is the free energy of solvation of the aromatic ligands, η is the coefficient of viscosity of the solvent, and V_{m} is the molar volume of the solvent. The effect of solvent on the dissociation rate appears to be due to solvation of the ligands in the transition state, and the solvent's ability to act as a replacing ligand.

The role of solvent in bimolecular reactions, or in unimolecular reactions that involve a formal separation of charge, has been extensively investigated.[3] By comparison, relatively little attention has been paid to solvent effects in unimolecular reactions involving no formal separation of charge. The racemization reaction of certain complex ions, particularly those occurring by an intramolecular mechanism, should provide interesting examples of such unimolecular reactions.

Investigations of solvent effects on racemization reactions are reported in the literature for several complex ions: the trisphenanthroline and tris(bipyridine) complexes of Ni(II),[4,5] the tris(oxalato)chromate(III) ion,[6] and the trisphenanthroline and tris(bipyridine) complexes of Fe(II).[5,7]

Davies and Dwyer[5] suggested that the racemization of $[Ni(bpy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ occurred by an intramolecular process, but later measurements[8,9] of both racemization and dissociation rates showed the two rates to be experimentally the same, indicating racemization by dissociation.

The racemization rates have been measured[6] for $[Cr(ox)_3]^{3-}$ in mixtures of water with methanol, ethanol, isopropyl alcohol, dioxane, acetone, and glycerol. The rates all decrease with increasing organic component in the solvent. The mechanism is thought to be dissociative.

Seiden, Basolo, and Neumann[7] measured the rates of racemization and dissociation of $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in methanol–water mixtures and found racemization rates to be appreciably faster than dissociation. This evidence suggests that the Fe(II) complexes favor intramolecular racemization in organic solvents. Accurate determination of the rate was difficult because of the rapidity of reaction in these solutions and the large absorbancies at the wavelengths normally used for polarimetry.

The acid dependence of the rate of racemization of $[Fe(bpy)_3]^{2+}$ suggests that a partial dissociation mechanism may be operative here.[10] In this mechanism only one end of the bipyridine ligand comes loose from the iron atom, the other nitrogen atom remaining bonded to it. Since rearrangement may occur before the free nitrogen atom becomes reattached, racemization may occur. In the $[Fe(phen)_3]^{2+}$ system, each ligand is constrained by the steric rigidity of the ring system, and both nitrogen atoms must be coordinated at the same time. Racemization of $[Fe(phen)_3]^{2+}$ in water is acid independent, which supports this view. The rate of racemization of $[Fe(phen)_3]^{2+}$ is strongly dependent on the solvent composition; there is almost a hundredfold increase in the rate on going from water to methanol.[7] The racemization in water at 25 °C was found to be 89% intramolecular, and the percentage increased as the methanol content of the solvent increased.[7] For these several reasons it was decided that the $[Fe(phen)_3]^{2+}$ system would provide a good model for investigating solvent effects.