in resolution that we obtain by dilution further corroborates this interpretation. Note that all these solutions have the same room-temperature spectrum. On the other hand, there must be other factors influencing the resolution. The spectrum is also broadened even with perchlorate present if the samples are kept at a temperature (200°K) at which the molecules can hardly diffuse. Possibly, the structure of the ice changes at these higher temperatures and this may affect the resolution.

Proton Magnetic Resonance and Raman Spectral Studies of the Complexes Tetrakis(dimethylformamide)beryllium(II) and Acetylacetonatobis(dimethylformamide)beryllium(II) in the Solvent N,N-Dimethylformamide. Direct Determination of Solvation Numbers and Kinetics of Solvent Exchange[1]

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Abstract: At temperatures below 0°, the proton nmr signals of N,N-dimethylformamide (DMF) in the first coordination sphere of the Be(II) ion in DMF solutions can be distinguished. From the relative intensities of these signals, a primary solvation number of four was calculated for Be(II). The complex ion, $Be(DMF)_4^{2+}$, reacts with bis(acetylacetonato)beryllium(II) ($Be(acac)_2$) in DMF solutions with the formation of the mixed complex, $(DMF)_2Be(acac)^+$, which exhibits well-resolved proton nmr signals at temperatures below +5°. From the temperature dependence of the proton relaxation rates, the solvent (DMF) exchange parameters k_1 (sec^{-1} at 25°), $\Delta H^{\ddagger}$ (kcal), and $\Delta S^{\ddagger}$ (eu) were calculated for $Be(DMF)_4^{2+}$ and $(DMF)_2Be(acac)^+$, respectively: 310, 14.6, 2.6; and 22, 13.9, −6. Both complexes exhibit an intense, highly polarized Raman line at 478 cm^{-1} which is assigned as a Be–O symmetric stretching vibration of the system, Be–acac. The results are discussed briefly in terms of ligand–ligand interactions within the primary coordination sphere of Be(II).

We have initiated a general study of the coordination chemistry of the diamagnetic cations of the d^0 and d^{10} series and have focused our attention upon two main points: (1) determining the stoichiometry, structure, and lability of the primary coordination spheres of the simple solvated ions in a variety of solvents; and (2) evaluating the effects of ligands in mixed complexes upon the nature of the remaining metal ion–solvent bonds. The elucidation of these properties of diamagnetic cations is not possible using conventional experimental techniques because the complexes generally are quite labile and the cations themselves lack a property which is sufficiently sensitive to the nature of the environment that the symmetry of the primary coordination sphere can be deduced. However, the nmr techniques are particularly well suited to the study of these complexes.

The application of the nmr techniques has been discussed elsewhere.[2–10] The complexes which have been studied include, for example, $Ga(OH_2)_6^{3+}$,[9,10] $Al(OH_2)_6^{3+}$,[5] and $Be(OH_2)_4^{2+}$ in water (using ^{17}O nmr), and $Al(DMSO)_6^{3+}$ in DMSO,[7] $Al(DMF)_6^{3+}$ in DMF,[8] $Mg(CH_3OH)_{6-n}(OH_2)_n^{2+}$ in aqueous methanol,[4] $Mg(OH_2)_6^{2+}$ in aqueous acetone,[11] $Mg(CH_3OH)_6^{2+}$ in anhydrous methanol[11,12] and methanolic acetone[11] (using ^1H nmr; DMSO represents dimethyl sulfoxide and DMF represents N,N-dimethylformamide).

Experimental Section

Reagents. Eastman White Label DMF was purified as described previously.[13] Acetylacetone (2,4-pentanedione) was obtained from Matheson Coleman and Bell and was distilled immediately before use, the middle fraction being retained. Hydrated beryllium perchlorate was prepared by dissolving beryllium metal (Fisher Reagent) in 4 *M* HCl and "fuming" the resulting solution with concentrated perchloric acid until a negative test for chloride ion in solution was obtained (with a concentrated aqueous solution of silver nitrate). Then the solution was concentrated slowly by distillation until fine needles of $Be(ClO_4)_2 \cdot 4H_2O$ were deposited.[14] After the resulting mixture had been allowed to cool to room temperature, the crystals of $Be(ClO_4)_2 \cdot 4H_2O$ were separated by filtration. $Be(NO_3)_2 \cdot 4H_2O$ was obtained from Alfa Inorganics, Inc., and was used without further purification.

Preparation of Complexes. Bis(2,4-pentanedionato)beryllium(II), $Be(acac)_2$, was prepared by the method of Arch and Young.[15] The solid obtained was recrystallized from benzene and dried *in vacuo* at 25°. The white crystals have mp 108° (lit.[15] 108.5°).

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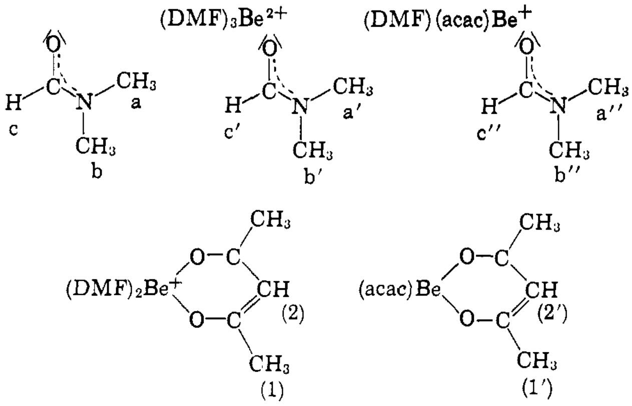

Figure 1. DMF and acac protons corresponding to the assignments in Tables I and II and Figure 3.

The complexes $Be(ClO_4)_2 \cdot 4DMF$, $Be(NO_3)_2 \cdot 4DMF$, and $Be(NO_3)_2 \cdot 2DMF$, which have not been described before, were prepared from the appropriate hydrated salts by the general method outlined by Drago, *et al.*[16] $Be(ClO_4)_2 \cdot 4DMF$ was recrystallized from a methylene chloride solution by the addition of anhydrous ether. In a similar fashion, $Be(NO_3)_2 \cdot 4DMF$ was recrystallized from a methylene chloride solution to which a slight amount of DMF has been added (less than 1 vol. %). Since the latter solid undergoes desolvation readily, it is crystallized in a pure form (free of $Be(NO_3)_2 \cdot 2DMF$) only with difficulty from H_2CCl_2 alone. $Be(NO_3)_2 \cdot 2DMF$ was prepared by the desolvation of $Be(NO_3)_2 \cdot 4DMF$ at 25° and a pressure maintained at 1 mm for 18 hr.

Anal. Calcd for $Be(ClO_4)_2 \cdot 4DMF$: Be, 1.80; ClO_4, 39.75; DMF, 58.4. Found: Be, 1.7; ClO_4, 39.6; DMF, 57.9. Calcd for $Be(NO_3)_2 \cdot 4DMF$: Be, 2.12; DMF, 68.7. Found: Be, 2.0; DMF, 68.1. Calcd for $Be(NO_3)_2 \cdot 2DMF$: Be, 3.23; DMF, 52.4. Found: Be, 3.3; DMF, 51.8.

Each of the solids was found to be free of water by titration with the Karl Fischer reagent.

Analyses. Perchlorate ion analyses were obtained using the method of Willard and Perkins.[17] Beryllium was determined spectrophotometrically as the complex $Be(acac)_2$.[18] The solids were analyzed for DMF using a proton nmr technique. Weighed quantities of methanol and the salt to be analyzed were dissolved in a known amount of water containing a trace of Mn(II) ion, and the proton nmr spectrum of the solution was recorded. The concentration of DMF was then obtained by comparing the area of the methyl proton signal of methanol with those of the N-methyl proton signals of DMF. The areas were obtained by planimetry and manual integration. The quantities of solid and methanol were adjusted, by trial and error, until the proton nmr signals (O-methyl and N-methyl) obtained were of approximately equal intensity. The analyses are reproducible and accurate to within 1%. The accuracy was checked by analyzing the pure liquid DMF.

Measurements. Raman spectra were recorded using a Cary Model 81 spectrometer. The mercury 4358-A line used as the exciting frequency was isolated with a Du Pont Rhodamine 5G DN-Extra filter solution and an Eastman Kodak Wratten 2a single-sheet filter. The wavenumber scale calibration, obtained using the known frequencies of CCl_4, CH_3Cl, $(CH_3)_2S$, and certain mercury lines, was provided by Professor T. V. Long, II, of this department.

Proton nmr spectra were obtained at 60 and 100 Mc using the Varian A-60 and HA-100 spectrometers. The spectrometers were equipped with variable-temperature probes and the Varian variable-temperature control system V-6057. The systems were calibrated and the measurements were obtained in the manner described previously.[7,13]

Electronic absorption spectra were obtained using a Cary Model 15 spectrometer and matched 1-cm cells equipped with standard-taper stoppers.

Results

1. Characterization of $Be(DMF)_4^{2+}$ by Proton Nmr. At temperatures below 0°, the 60-Mc proton nmr spectrum of a DMF solution of $Be(ClO_4)_2$ consists of six signals, three of which may be assigned to DMF in the primary coordination sphere of Be(II) and three to DMF in the bulk of the solution. The signals of DMF in each environment consist of a low-field one due to the formyl proton and two high-field ones due to the nonequivalent N-methyl groups (see Figure 1). The higher field N-methyl resonance for DMF in each environment is assigned to the methyl group *cis* to the oxygen atom.[8,18,19,20] Because the nonequivalence of the N-methyl groups is preserved in the primary coordination sphere of Be(II), it is assumed that the site of coordination is the oxygen, rather than the nitrogen, atom.[8,13]

In Table I are summarized the relative areas of the signals assigned to coordinated DMF. From the areas which were obtained at temperatures in the range 0 to −40° using the spectra obtained for two solutions of $Be(ClO_4)_2$ in DMF, the solvation number n of Be(II) in the complex, $Be(DMF)_n^{2+}$, was calculated. It is evident from the data in the table that the solvation number is 4 and independent of the temperature and the solution composition.

Table I. Solvation Number of the Be(II) Ion in DMF

Temp, $10^3/T$, °K^{-1}	Be(II) concn, m	Area rel to signal C			Calcd solvation no.		
		a′	b′	c′	a′	b′	c′
3.69	0.415	0.414	0.412	0.135	3.99	3.98	3.92
3.98	0.415	0.410	0.414	0.139	3.96	3.99	4.02
4.24	0.415	0.417	0.409	0.137	4.02	3.95	3.99
3.69	0.100	0.0910	0.0920	0.0320	4.03	4.07	4.23
4.24	0.100	0.0903	0.0901	0.0301	3.99	3.98	3.99

The chemical shifts observed for $Be(DMF)_4^{2+}$ are summarized in Table II. The temperature dependence of the line widths of the b′ proton of the complex is summarized in Figure 2, in which log ($\Delta\nu$) is plotted *vs.* $10^3/T$. Since the shifts are constant over the temperature range 0 to −60° (and for solutions which encompass a fourfold change of the $Be(ClO_4)_2$ concentration), the line width, $\Delta\nu$, for the protons of the complex should conform to the equation[21,22]

$$\pi\Delta\nu = \frac{1}{T_2^0} + \frac{1}{\tau} = \pi\Delta\nu^0 + k_1 \qquad (1)$$

where τ represents the mean lifetime of DMF in the primary coordination sphere of $Be(DMF)_4^{2+}$, k_1 represents the pseudo-first-order rate constant for the exchange of DMF between the free solvent and a coordinated solvent site, and $1/T_2^0$ and $\Delta\nu^0$ are respectively the transverse relaxation rate and the line width of a proton of $Be(DMF)_4^{2+}$ when the rate of solvent exchange is negligible. The variation of τ and $1/T_2^0$

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Table II. Proton Chemical Shifts of Be(II) Complexes in DMF at 60 Mc[a]

Solute in DMF	a	b	c	a′	b′	c′	c′′	1′	1	2′	2
			DMF protons[b]						acac protons[b]		
$Be(DMF)_4(ClO_4)_2$ (0.1–0.4 *M*)	..	−11	−315	−18	−27.5	−334	...	...	...	...	...
$Be(acac)_2$ (0.1–1.0 *M*)	..	−10	−315	...	...	...	...	+45	...	−179	...
$Be(DMF)_4(ClO_4)_2$ (0.1–0.8 *M*) + $Be(acac)_2$ (0.1–1.0 *M*)	..	−11	−315	−17	−28.5	−333	−326	+45	+45	−180	−183

[a] In cps, ±0.5. [b] Shifts relative to that for proton a. Assignments correspond to the sites defined in Figure 1.

with the temperature is given by the equations

$$\frac{1}{\tau} = k_1 = \frac{kT}{h} \exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}R) \qquad (2)$$

$$\frac{1}{T_2^0} \propto \exp(-E_a/RT) \qquad (3)$$

where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ represent the entropy and enthalpy of activation for the solvent exchange reaction and E_a can be viewed as an apparent Arrhenius activation energy associated with the transverse relaxation rate of the proton in $Be(DMF)_4{}^{2+}$.[23,24]

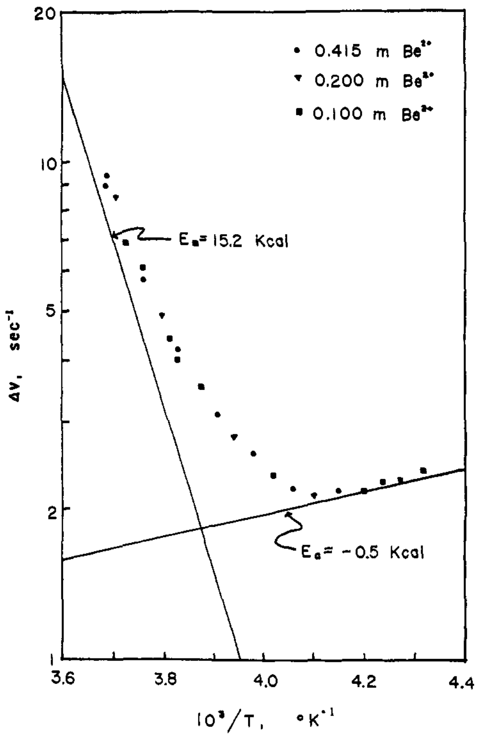

Figure 2. Temperature dependence of the line width of the N-methyl (b) proton of $Be(DMF)_4{}^{2+}$.

The two straight lines drawn in Figure 2 can be fitted to the line width data: (a) one line fits the data at the higher temperatures and, because of its large negative slope (E_a = 15.2 kcal), is associated with line broading due to the exchange of DMF; (b) the other line can be fitted independently to the low-temperature data ($10^3/T > 4.1$) and, because of its small positive slope (E_a = −0.5 kcal), is associated with relaxation of the protons within the primary coordination of Be(II). The chemical exchange parameters calculated from the data in Figure 2 are listed in Table III. The parameters calculated from the data obtained for the c′ proton at both 60 and 100 Mc are the same, within experimental error.

Table III. Parameters Calculated from Figures 2 and 4 for the Exchange of DMF from the First Coordination Sphere of Be(II)

	Complex	
Parameter	$Be(DMF)_4{}^{2+}$	$(DMF)_2Be(acac)^+$
k_1, sec⁻¹ (25°)	310	22
$\Delta H^{\ddagger}$, kcal mole⁻¹	14.6 ± 0.3	13.9 ± 0.8
$\Delta S^{\ddagger}$, eu	2.6 ± 1	−6 ± 2

2. Characterization of [$(DMF)_2Be(acac)$] by Proton Nmr. In Figure 3 is reproduced a proton nmr spectrum which is typical of those obtained at temperatures below 0° for solutions of $Be(ClO_4)_2$ in DMF containing $Be(acac)_2$. The assignments of the lines in the spectrum have been made in accordance with the proton sites defined in Figure 1, and the chemical shifts have been summarized in Table II. The assignments are based upon the following considerations.

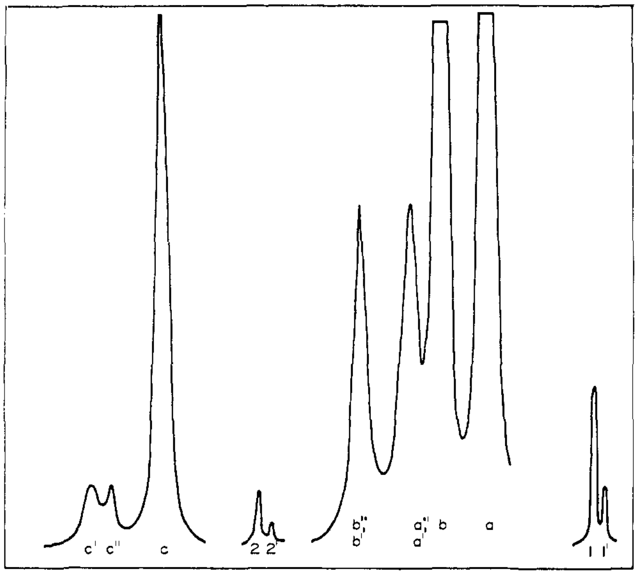

Figure 3. Proton nmr spectrum (60 Mc) of a DMF solution of $Be(ClO_4)_2$ (0.843 *m*) and $Be(acac)_2$ (0.478 *m*) at −5.0°.

(a) The methyl and vinyl proton resonances of the free ligand, acac⁻, in the form of either its sodium or ammonium salt, occur upfield of the 2′ and 1′ signals.

(b) For the concentration ratios, [acac⁻]:[Be(II)] > 2, the only signals that are distinguished in the nmr spec-

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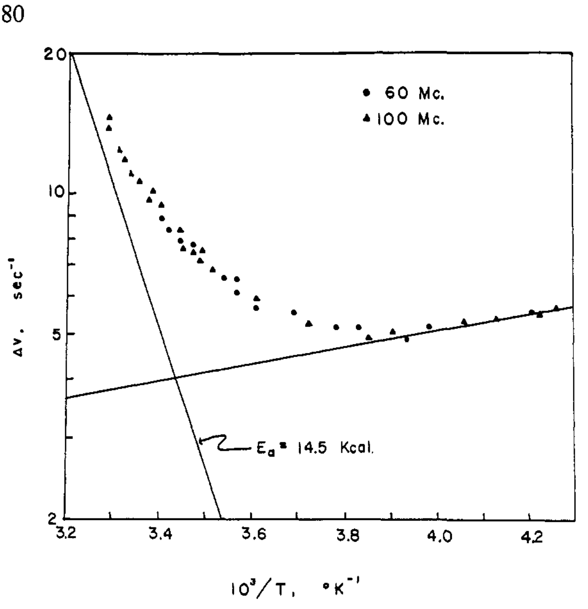

Figure 4. Temperature dependence of the line width of the formyl proton (c′′) of $(DMF)_2Be(acac)^+$ at 60 and 100 Mc.

tra over the temperature range, −70 to +120°, are those which can be assigned to the free ligand, to the bulk solvent DMF (signals a, b, and c), and to the complex $Be(acac)_2$ (signals 1′ and 2′).

(c) The signals a′, b′, and c′ can be assigned to the protons of $Be(DMF)_4^{2+}$ on the basis of the chemical shifts observed.

(d) Using the relative areas of the signals observed, it can be shown that for each 4 moles of DMF which "appear" at the c′′ site (assigned to the formyl protons of the complex $Be(acac)(DMF)_2^+$), 4 moles of DMF are "lost" to the c′ site. The signals expected for the N-methyl protons (a′′ and b′′) of the complex, (acac)-$Be(DMF)_2^+$, could not be distinguished even at the lowest temperatures studied. However, since it was observed that the a′ and b′ signals are asymmetric at the low-field side of the resonance line, it was concluded that the a′′ and b′′ signals overlap the a′ and b′ ones. The changes which occur in the relative areas of the appropriate resonance signals are consistent with this conclusion: for each 4 moles of DMF which are lost to the c′ site, none is lost to the a′ and b′ sites.

From the relative areas of the appropriate signals and the known solution compositions, the thermodynamic parameters for reaction 4 can be calculated. The

$$Be(DMF)_4^{2+} + Be(acac)_2 \rightleftharpoons 2(DMF)_2Be(acac)^+ \quad (4)$$

parameters (at 25°), $K = 10 \pm 2$, $\Delta H = 0 \pm 1$ kcal, and $\Delta S = +5 \pm 3$ eu, were obtained using the data for each of the sets of signals: c, c′, and c′′ (over the temperature range −50 to 0°); 2 and 2′ (13 to 92°); and 1 and 1′ (13 to 92°).

The temperature dependence of the relaxation rates of the formyl proton of $(DMF)_2Be(acac)^+$, derived from the widths of the c′′ signal at both 60 and 100 Mc, is summarized in Figure 4. The data were obtained using four independent solutions in which the composition was varied over the limits $0.1\ M \leq Be(DMF)_4^{2+} \leq 0.8\ M$ and $0.1\ M \leq Be(acac)_2 \leq 0.4\ M$. The chemical exchange parameters (for the rate of DMF exchange) calculated from the line fitted to the high-temperature data in Figure 4 are listed in Table III.

3. Raman Spectra of the Complexes $Be(DMF)_4^{2+}$, $(DMF)_2Be(acac)^+$, and $Be(acac)_2$. Studies of the Raman spectra of the complexes were undertaken to assess the effect of ligand–ligand interactions upon the Be–O stretching frequencies. Since each of the complexes is mildly fluorescent, recordings of the spectra could not be extended with confidence beyond 800 cm⁻¹. No Be–O vibrations could be distinguished for DMF solutions of $Be(ClO_4)_2$ and $Be(NO_3)_2$. However, the region, 350–450 cm⁻¹, where such vibrations might occur may be obscured by the three relatively weak Raman lines of DMF at 454, 409, and 359 cm⁻¹.[25]

Both of the complexes $Be(acac)_2$ and $(DMF)_2Be(acac)^+$ exhibit a number of relatively intense lines in the region, 100–800 cm⁻¹, which can be distinguished readily from the weak scattering of DMF. The frequencies observed are listed in Table IV. The assignments of the frequencies to the vibrations of the system Be–acac conform to those that have been made for other metal acetylacetonates.[27–30] The line observed at 478 cm⁻¹ for both complexes is strongly polarized and has been assigned to the symmetric Be–O stretch: the depolarization ratio measured for the $Be(acac)_2$

Table IV.[a] Raman Frequencies and Vibrational Modes for the Complexes $Be(acac)_2$ and $(DMF)_2Be(acac)^+$

$Be(acac)_2$[b]	$(DMF)_2Be(acac)_2^+$[c]	Assignment
441 (s), dp	441 (s), dp	δ(ring), in-plane
478 (s), sp	478 (s), sp	ν_s(Be–O)
565 (m), dp	565 (m), dp	C–C(–O)–C
661 (m), dp	661 (m), dp	Not assigned
700 (mw), p	. . .[d]	ν(Be–O) + δ(ring)
785 (m), p	. . .[d]	Not assigned[e]

[a] Relative band intensities in parentheses: medium (m), medium weak (mw), and strong (s); dp represents a depolarized line, p a polarized one, and sp a strongly polarized one; δ represents an "in-plane" deformation and ν_s a symmetric stretch. [b] For a solution of the complex in benzene. The positions of the bands are unaffected by changing the solvent to DMF. However, since DMF exhibits weak lines at 459, 409, and 359 cm⁻¹, it interferes with the measurement of an accurate depolarization ratio of the 478-cm⁻¹ line. [c] Complex present as the ClO_4^- or NO_3^- salt in DMF. The depolarization ratios could be measured only for the NO_3^- salt since the ClO_4^- ion has a weak Raman line at 460 cm⁻¹. [d] The complex fluoresces more strongly than $Be(acac)_2$ and the lines at 700 and 785 cm⁻¹ could not be distinguished from the background scattering. [e] The line in the Raman at 785 cm⁻¹ corresponds to an absorption in the infrared which we can distinguish at 783 cm⁻¹ (±2). The infrared band at this frequency (780 cm⁻¹) is assigned by Nakamoto[27] to the π(C–H) vibration. However, that mode under the operations of the point group appropriate to the full symmetry of the complex (D_{2d}) or to the local symmetry of the ligand (C_{2v}) should not be polarized in the Raman. Although the vibration is too weak to allow the measurement of an accurate depolarization ratio, it was found to be less than 0.4. The line may be associated with the C–(CH_3) A_1 vibration of the acac ring.[28]

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(25) However, no Raman lines attributable to the Be(II)–solvent stretch can be distinguished in solutions of $Be(ClO_4)_2$ and $Be(NO_3)_2$ in water and anhydrous methanol.[26]

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is 0.10 ± 0.03; that for $(DMF)_2Be(acac)^+$ is 0.16 ± 0.09.

4. Electronic Absorption Spectra. The ligand, acac, and the metal ion complexes derived from it exhibit an intense $\pi \rightarrow \pi^*$ transition in the ultraviolet region.[31] The spectral parameters for this electronic transition of $Be(acac)_2$ dissolved in chloroform or ethanol have been reported to be λ_{max} 294 mμ (ϵ_{max} 33,300) and 292 mμ (ϵ_{max} 33,200), respectively. The parameters obtained in this study for each of the complexes, $Be(acac)_2$ and $(DMF)_2Be(acac)^+$, dissolved in DMF are λ_{max} 292 mμ and ϵ_{max} 15,000. The molar absorptivities, ϵ_{max}, were calculated using the total formal concentration of acac.

Discussion

The proton nmr data obtained in this study demonstrate that the complexes $Be(DMF)_4^{2+}$ and $(DMF)_2Be(acac)^+$ are kinetically well-defined entities in the solvent DMF. The lability of $Be(DMF)_4^{2+}$ is greater than that of the corresponding Al(III) complex, $Al(DMF)_6^{3+}$, for which the following solvent exchange parameters have been reported:[8] k_1 (25°) = 4 sec^{-1}, $\Delta H^{\ddagger}$ = 17.7 kcal, and $\Delta S^{\ddagger}$ = 4.7 eu. The enhanced lability of the former complex is clearly due to an activation enthalpy rather than an entropy effect. If an SN1(lim) mechanism for the solvent exchange is accepted,[32] then the relative labilities cannot be accounted for solely in terms of a simple electrostatic model for the binding of DMF to the ions: the value of the charge to radius ratio for the Be(II) ion is ~6.5 and the ion is bonded to four DMF molecules, whereas that for the Al(III) ion is ~6.0, and it is bonded to six DMF molecules.

The inclusion of steric effects does not serve to simplify the problem if the SN1 mechanism is accepted. Using scaled molecular models, it can be shown that the Be(II) complex is sterically hindered to about the same extent as the Al(III) complex, but the entropy of activation for the solvent exchange of the former is somewhat *less* than that for the latter. Thus, although the effects of steric and electrostatic interactions in the primary coordination spheres of these ions undoubtedly are of importance in the solvent exchange reactions,[33] additional effects, such as the relative stabilization of these ions by ion pairing or solvation in the *second* coordination sphere, must be considered. The effects are being assessed *via* studies of the solvent exchange rates of these and similar complex ions in nonpolar solvents using proton nmr techniques.

The ion $(DMF)_2Be(acac)^+$ is *less* labile than $Be(DMF)_4^{2+}$ and the difference in labilities is due largely to the relative activation entropies. In terms of the SN1(lim) mechanism for solvent exchange, the result is unexpected but yet is *not* inconsistent with an electrostatic model for the bonding in these complexes if (a) the activation entropy for the DMF exchange reaction of $Be(DMF)_4^{2+}$ is "anomalously" large because of a steric effect (using scaled molecular models, it can be shown that $(DMF)_2Be(acac)^+$ is less hindered); and/or (b) two DMF molecules are as effective as the $acac^-$ ligand in transmitting charge to the Be(II) ion. At the present, it is not possible to assess these factors critically. It is interesting to note that Margerum and Rosen,[34] using temperature-jump techniques, have found that the effect of a ligand upon the rate of water exchange for mixed complexes of the Ni(II) ion in water depends more upon the nature of the ligand than upon its net charge. In addition, Pearson and Moore[35] have reported that the rates of replacement of acac by water in the complexes $Be(acac)_2(aq)$ and $Be(acac)^+(aq)$ are the same. In our studies over the temperature range −70 to +120°, we could not detect chemical exchange of acac for either $Be(acac)_2$ or $(DMF)_2Be(acac)^+$; the line widths of the acac protons are controlled by viscosity broadening effects over the complete range of temperatures.

If there are differences in the ligand–ligand interactions of the two DMF complexes of Be(II), they are too small to affect the ground-state properties which we studied. For example, considering the thermodynamic parameters obtained for the reaction depicted in eq 4 above, it is evident that the complex $(DMF)_2Be(acac)^+$ is neither strongly favored nor disfavored with respect to the more symmetrical ones. Indeed the "driving force" for the reaction is due to the entropy change, which can be accounted for solely on the basis of the differences between the symmetry numbers of the reactants and the product. From the "site" symmetries of $Be(DMF)_4^{2+}$ (Td), $(DMF)_2Be(acac)^+$ (C_{2v}), and $Be(acac)_2$ (D_2d), the value of ΔS associated with the symmetry number change is found to be ~+5 eu.[36] In any event the simplest electrostatic model (neglecting the solvation energies of the species) should lead one to expect that the ion $[(DMF)_2Be^{2+}(acac)^-]$ would be much more strongly favored with respect to the ion–dipole complex, $Be(DMF)_4^{2+}$, and the neutral complex, $[(acacBe^+)(acac^-)]$, than is observed.

That the symmetric Be–O stretching frequency, 478 cm^{-1}, of the system Be(acac) is the same for both acetylacetone complexes also suggests that the ligand–ligand interactions for the two species are negligible or the same. Similar results have been obtained from an infrared study of the Pt(II)–acac system.[30] It is interesting that the Be–O stretching frequency is larger than the symmetric M–O stretching frequencies of the complexes $M(acac)_3$, where M represents Al(III) (465 cm^{-1}), Ga(III) (460 cm^{-1}), and In(III) (444 cm^{-1}).[29] Hester and Plane[29] have suggested that, since the metal ion remains stationary during the vibration, the relative frequencies may be taken as an indication of the relative M–O bond strengths. Such a correlation may be valid for the isosymmetric species, $M(acac)_3$, but the inclusion of $Be(acac)_2$ in the series must be accepted with caution until it can be established unequivocally that the M–O vibrations are independent of the vibration of other bonds in the system.

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[33] The complex, $Mg(DMF)_6^{2+}$, is much more labile than that of Be(II): k_1 (25°) > 10^5 sec^{-1}, $\Delta H^{\ddagger}$ < 10 kcal.[26]

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