Five ml of the resulting solution was then chromatographed on a 20-cm Cl^- Dowex AG 1-X8 column at 2°, after first swirling the solution with *ca.* 15 g of H^+ Dowex AG 50W-X8 (100–200 mesh) to remove excess cationic species. The elution was again made first with 0.001 F $HClO_4$ to remove the residual cationic and neutral species and then with 0.3 F HNO_3. The 0.3 F HNO_3 eluted two overlapping pink bands, the lower being of lighter color. The lower band (designated as complex Y) gave a visible absorption spectrum similar to that reported by Wolsey, *et al.*,[2] for their tetrachloro species but with higher molar absorptivities: λ_{max} 484 $\pm$ 2 and 384 $\pm$ 2 mμ (ϵ 99.6 and 78.2 M^{-1} cm^{-1}, $\epsilon_{384}/\epsilon_{484} = 0.78$) and λ_{min} 429 $\pm$ 2 mμ (ϵ 38.5 M^{-1} cm^{-1}).[10] The upper band (designated as complex Z) gave the same visible absorption spectrum, within experimental error, as complex X. The determination of Cl:Rh atom ratio of complexes Y and Z was not possible because excess chloride was present in the solutions; Fine[4] and Wolsey, *et al.*,[2] encountered the same difficulties in their work. Attempts to chromatograph the chloride-anation solution on a NO_3^- Dowex AG 1-X8 column were unsuccessful.

Since the chloroaquorhodate(III) anions aquate quite rapidly at room temperature, all solutions being eluted were kept in ice; and all visible absorption spectra were measured at about 5°, using a Beckman DB spectrophotometer.

Discussion

The procedure of Wolsey, *et al.*,[2] for the production of tetrachlorodiaquorhodate(III) anion was tried but without success. One wide, red band was eluted by 2 F HCl, as reported by Wolsey, but the visible absorption spectra of the different fractions of the effluent were not consistent. On the other hand, if the elution was made with more dilute acids, three overlapping bands of yellow and orange colors were eluted by 0.001 F $HClO_4$ and two overlapping pink bands were eluted by 0.3 F HNO_3. The yellow and orange bands must be neutral and cationic species, and the identification of these species will be reported in a later communication. The two pink bands appeared to be the two isomers of tetrachlorodiaquorhodate(III) anion because of their elution behavior.

It is quite obvious that, from the Cl:Rh atom ratio, complex X is a tetrachlorodiaquorhodate(III) anion. Since its visible absorption spectrum is different from that reported by Wolsey, *et al.*, for their tetrachloro species, complex X and their complex must be the two isomers of tetrachlorodiaquorhodate(III) anion. Furthermore, two complexes were eluted by 0.3 F HNO_3 in the chromatography of chloride-anation solution, and the visible absorption spectrum of one corresponds to the tetrachloro species reported by Wolsey while that of the other corresponds to complex X. The fact that these two complexes were both eluted by 0.3 F HNO_3 further suggests that they have the same charge and similar structure. This elution behavior is similar to the corresponding iridium(III) complexes.[8] From these considerations, it was concluded that complexes X and Z are the same and are the *cis* isomer, and complex Y is the *trans* isomer of tetrachlorodiaquorhodate(III) anion, the assignment of configuration being made based upon the order of elution from the ion-exchange column.

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(10) Wolsey, *et al.*, reported λ_{max} 488 and 385 mμ (ϵ 72.0 and 54.1 M^{-1} cm^{-1}, $\epsilon_{385}/\epsilon_{488} = 0.75$) and λ_{min} 430 mμ (ϵ 25.0 M^{-1} cm^{-1}) as interpolated from the spectrum in ref 2.

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High-Resolution Nuclear Magnetic Resonance Spectroscopy of Some Beryllium-Containing Compounds. Beryllium-9 and Fluorine-19 Spectra[1a]

BY JOHN C. KOTZ,[1b] RILEY SCHAEFFER, AND ARTHUR CLOUSE

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Although the literature contains reports on the ^{9}Be wide-line spectra of the solids beryl,[2a] chrysoberyl,[2b] and beryllium oxide,[3] the nmr signal of the ^{9}Be nucleus in solution apparently has not been reported. Therefore, owing to the recent interest in beryllium chemistry and the variety of structural problems encountered,[4] we have undertaken an investigation of high-resolution ^{9}Be nmr spectroscopy in order to determine its suitability for structural studies. This investigation has led also to a brief study of the ^{19}F spectra of ammonium tetrafluoroberyllate, $(NH_4)_2BeF_4$, solutions.

Results

^{9}Be Spectra.—Spectra of the following compounds were observed: $BeCl_2 \cdot 2[O(C_2H_5)_2]$ in diethyl ether; beryllium acetylacetonate in chloroform; beryllium(8-hydroxy)quinaldinate in chloroform; ammonium tetrafluoroberyllate, 1 M, in water; beryllium sulfate, 0.1 M, pH 2.8; beryllium sulfate, 1.1 M, pH 1.8; beryllium sulfate, 1.9 M, pH 1. All of the compounds showed a single resonance line; the width at half-height of the band was generally 5–10 cps. Within the limits of experimental error (*ca.* 6 cps) no chemical shifts from the basic beryllium acetate standard were observed, except for ammonium tetrafluoroberyllate

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(1) (a) Supported by a Public Health postdoctoral fellowship (to J. C. K.; 7-F2-CA-21, 198-02) from the National Cancer Institute; (b) Department of Chemistry, Kansas State University, Manhattan, Kansas 66502. To whom correspondence should be addressed.

(2) (a) J. Hatton, B. V. Rollin, and E. F. W. Seymour, *Phys. Rev.*, **83**, 672 (1951); (b) N. A. Schuster and G. A. Pake, *ibid.*, **81**, 886 (1951).

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which exhibited an upfield shift of 15–20 cps (*ca.* 2 ppm).

The tetrafluoroberyllate anion gave the expected five-line spectrum in both absorption and dispersion modes ($J_{^9\mathrm{Be}-^{19}\mathrm{F}} = 33 \pm 2$ cps). Resolution was improved by cooling the sample in ice and rapidly scanning the spectrum after insertion in the probe (Figure 1). Added fluoride (*vide infra,* ^{19}F spectrum) also apparently improved the resolution.

^{19}F Spectrum of $(NH_4)_2BeF_4$.—The ^{19}F spectrum of 1 *M* $(NH_4)_2BeF_4$ was run in order to measure more accurately the ^{9}Be–^{19}F coupling constant. At the normal probe temperature of 28° the multiplet shown in Figure 2 (C) was obtained. The temperature dependence of the spectrum indicates fluoride exchange between BeF_4^{2-} and another Be–F species in solution.

The ^{9}Be–^{19}F coupling constant obtained from the lowest temperature spectrum was 33.2 ± 1.2 cps. The chemical shifts of the two components at low temperature were +85.9 and +88.1 ppm. The spin-coupling constants for the two multiplets were identical.

According to the literature concerning Be–F systems, a likely contaminant of commercial ammonium tetrafluoroberyllate is ammonium trifluoroberyllate.[5] Fluoride exchange between these two species could result in the temperature-dependent spectrum discussed above. Evidence for an ion such as $H_2O \cdot BeF_3^-$ was obtained from an experiment in which ammonium fluoride was added to a solution of the tetrafluoroberyllate (fluorine ratio, $BeF_4^{2-}:F^- = 1:10$). A well-resolved quartet was obtained at room temperature ($\delta = +84.9$ ppm, $J_{\mathrm{Be-F}} = 33.2$ cps); apparently BeF_4^{2-} is now the only Be–F species in solution, and fluoride exchange with this ion, or intramolecular fluoride exchange, is either very slow or nonexistent. No evidence for another Be–F ion was found in the ^{9}Be spectrum of the tetrafluoroberyllate anion; this is probably due to the virtual absence of chemical shifts for beryllium-containing compounds.

Discussion

In order to be useful as a structural tool, the ^{9}Be signal should be sharp, give rise to observable chemical shifts, and show spin coupling with appropriate nuclei. The first of these criteria has been satisfied. Since all of the compounds investigated were tetrahedral, the electric field surrounding the ^{9}Be nucleus is relatively symmetrical. Therefore, quadrupolar coupling is minimized, and narrow lines could be observed.

The virtual absence of a chemical shift for the compounds investigated was disappointing. However, a plausible explanation for this observation can be developed by noting the relative position of the ^{19}F signal of the BeF_4^{2-} ion. Gutowsky and Hoffman[6] reported that the fluorine resonance line of an aqueous solution of BeF_2 was shifted 599.1 ppm upfield from gaseous fluorine, 50.9 ppm upfield from aqueous KF, and 25.9 ppm downfield from HF. (An upfield shift of 51.3 ppm for BeF_4^{2-} relative to NH_4F was found in this work.) The dominant cause of ^{19}F chemical shifts is a variation in the local paramagnetic term, a contribution which leads to a shift to lower fields.[7] The effect is greater the more covalent the F–M bond; it should theoretically be a minimum in the case of the spherically symmetric fluoride ion, and the ion should appear at highest field. However, in practice this is apparently not the case since the F^- resonance line lies at a considerably lower field than does the signal arising from hydrogen fluoride; this is evidently due to solvation of the fluoride ion. Therefore, hydrogen fluoride can be considered the practical point at which the paramagnetic contribution to the shift is at a minimum and diamagnetic shielding is of prime importance. Since the resonance lines of the beryllium–fluorine species do not lie at a field value much lower than that of hydrogen fluoride, it would appear that the partial ionic character of the Be–F bond is approaching that of the H–F bond; this argument is only valid, of course, if we interpret the chemical shifts solely on the basis of the results of diamagnetic shielding. However, Pauling's relation of partial ionic character to electronegativity difference would predict an even greater degree of ionic char-

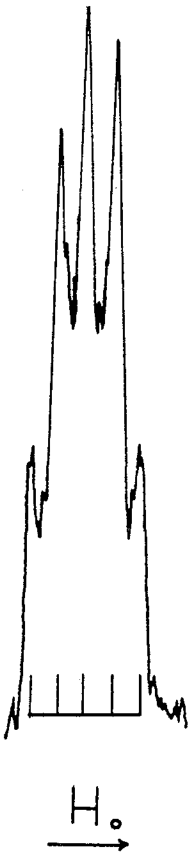

Figure 1.—^{9}Be nmr spectrum of aqueous ammonium tetrafluoroberyllate, $(NH_4)_2BeF_4$. $\delta \simeq 17$ cps or 2 ppm upfield from the standard, basic beryllium acetate $[Be_4O(C_2H_3O_2)_6]$; $J_{^9\mathrm{Be}-^{19}\mathrm{F}} = 33$ cps.

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[5] See ref 4, pp 38–49.

[6] H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

[7] (a) A. Saika and C. P. Slichter, *ibid.*, **22**, 26 (1954); (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 172, 173, 318, 319.

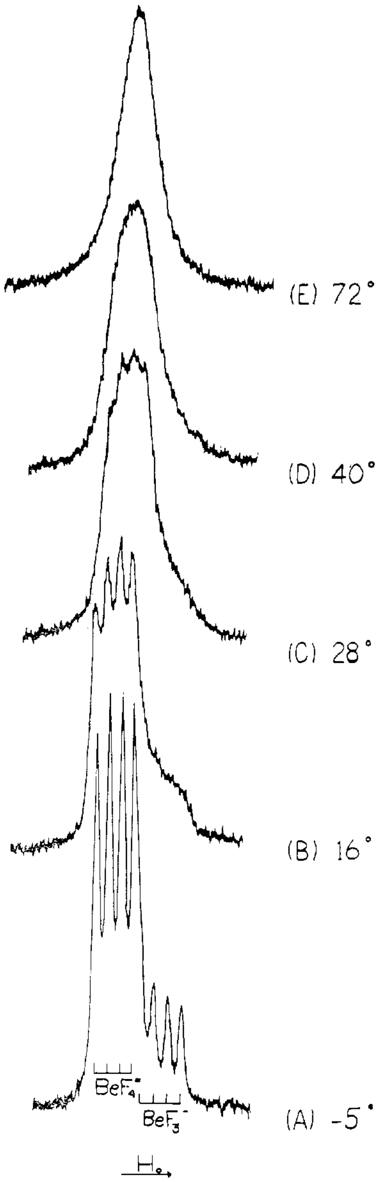

Figure 2.—Temperature dependence of the ^{19}F nmr spectrum of aqueous commercial ammonium tetrafluoroberyllate, $(NH_4)_2BeF_4$. Low-field multiplet assigned to BeF_4^{2-} ($\delta = +85.9$ ppm *vs.* external trifluoroacetic acid) and high-field multiplet assigned to an ion such as $H_2O \cdot BeF_3^-$ ($\delta = +88.1$ ppm).

acter for Be–F than for H–F; an argument based only on electron density and diamagnetic shielding would thus predict that BeF_4^{2-} would appear at higher fields than HF. It is evident that the shifts of beryllium compounds must be explained on the basis of diamagnetic shielding with a considerable contribution from paramagnetic effects.[8]

All of the beryllium compounds investigated were those in which the beryllium was bound to atoms having reasonably high electronegativities; therefore, the partial ionic character of all of these bonds must be considerable. This high degree of ionicity evidently leads to an insensitivity of the beryllium nucleus to its environment, since no chemical shifts are observed in the ^9Be spectra except the small shift in the case of BeF_4^{2-}. The fact that the ^9Be resonance line of BeF_4^{2-} was shifted to slightly higher fields than the standard, $Be_4O(C_2H_3O_2)_6$, appears to be another indication that paramagnetic effects are indeed important.

The third criterion—that of spin coupling with appropriate nuclei—was satisfied to some extent; well-defined ^9Be–^{19}F coupling was observed for the BeF_4^{2-} ion. Apparently no other examples of spin coupling with beryllium have been reported.[9]

Another feature of interest in the spectrum of BeF_4^{2-} is the relatively small value of the coupling constant; except for $J_{^{11}B-^{19}F}$ in BF_3 (18 cps)[10] and BF_4^- (1–5 cps),[11] it would appear to be one of the smallest constants observed for fluorine bonded to an element other than carbon. This small J value may be a reflection of the ionic character of the Be–F bond. On the other hand, it could be a consequence of the existence of coupling terms other than the Fermi contact term.[11]

Experimental Section

With the exception of those compounds noted below, most chemicals were used as received. Ammonium tetrafluoroberyllate (Alfa Inorganics) contained a water-insoluble impurity which was removed by filtration. Basic beryllium acetate ($Be_4O(C_2H_3O_2)_6$; E. H. Sargent) was purified by dissolution in chloroform and filtration from insoluble residues. Beryllium acetylacetonate (Alfa Inorganics) was recrystallized from benzene–hexane. The diethyl etherate of beryllium chloride (Alfa Inorganics) was prepared *in vacuo* by dissolution of the chloride in ether and filtration directly into the nmr tube. The 8-hydroxyquinaldine complex of beryllium was prepared by standard procedures.[12]

Owing to the relatively low magnetogyric ratio of ^9Be, a slightly different method for observing the high-resolution spectra was utilized.[13] The components of a Varian Model 4300B high-resolution spectrometer were employed (variable frequency radiofrequency transmitter, V-4210A; probe, V-4230B). The transmitter was crystal-controlled at 8.436 Mc/sec. Receiver output was further amplified by a Varian V-3521 integrator (modulation frequency 2054 cps).

The solutions of the beryllium compounds were contained in 15-mm tubes. Basic beryllium acetate was the standard for ^9Be chemical-shift measurements. Shifts were measured by inserting into the sample tube a 5-mm tube containing a concentrated chloroform solution of the standard.

The ^{19}F spectra of the tetrafluoroberyllate anion and other fluorides were obtained at 56.4 Mc/sec using standard Varian equipment. Chemical shifts were measured relative to external trifluoroacetic acid.

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