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Reactions of Bis(pentafluoroselenium) Peroxide. Synthesis of Pentafluoroselenium Fluorosulfate and of Bis(pentafluoroselenium) Oxide

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When SeF_5OOSeF_5 is produced by the reaction of fluorine with selenium dioxide, a substantial proportion of SeF_5OSeF_5 is also formed. Bis(pentafluoroselenium) oxide is relatively stable and resists hydrolysis. The new compound pentafluoroselenium fluorosulfate (SeF_5OSO_2F) is produced by the reaction of SeF_5OOSeF_5 with peroxydisulfuryl difluoride ($S_2O_6F_2$).

Even though bis(pentafluoroselenium) peroxide (SeF_5-$OOSeF_5$) has been known for several years,[1] there is little information about its properties. The purpose of the present study was to supply some of the missing information and, hopefully, to obtain new compounds containing the SeF_5 group. In the course of the work it was found that SeF_5OOSeF_5 was caused to decompose by ultraviolet radiation or by heating to 85° and above. The compound reacted with $S_2O_6F_2$ to give the new substance SeF_5OSO_2F. Other possible reactants which were tested were CF_3OOCF_3, NO_2, N_2F_4, SO_2, Cl_2, and Br_2. None of these yielded new substances containing the SeF_5 group. It appeared that SeF_5OOSeF_5 simply decomposed in the presence of the added reagents.

During the course of his work on the synthesis of SeF_5OOSeF_5, Mitra[1] found evidence for the formation of SeF_5OSeF_5 as a by-product. The oxide was not clearly identified, however, so this part of the work was not published. At a later date Smith and Cady[2] reported evidence for SeF_5OSeF_5. Their sample of the material was so small that they too did not clearly establish the identity of the substance. In the present work bis(pentafluoroselenium) peroxide was produced by the reaction of fluorine with selenium dioxide (one of the methods of Mitra and Cady[1]). Distillation of the product gave a substantial amount of bis(pentafluoroselenium) oxide as a by-product which was then identified beyond doubt.

Experimental Section

Materials. Bis(pentafluoroselenium) Peroxide. A portion of selenium dioxide weighing several grams was added to a nickel boat having dimensions about 1 × 1 × 12 cm. This was then placed within a reactor made from nickel tubing 2.5 cm in diameter having a length of 45 cm. Streams of fluorine and nitrogen, each at 3 l./hr, were mixed, and the gas was passed over the selenium dioxide. The gases then passed (within the reactor) over a mass of copper gauze coated with silver fluoride(s), which had been formed by plating the gauze with silver and then treating the metal with fluorine. During the period of operation, the temperature at the center of the reactor was held at about 110°. The stream of gas from the reactor passed through a glass trap at −183°. Up to this point the procedure was like one described by Mitra and Cady.[1] In the present work the product usually was separated by fractional codistillation. The last substance to distil was SeF_5OOSeF_5 in a substantially pure condition. This product was used for studies of its properties.

Bis(pentafluoroselenium) Oxide. During the codistillation just mentioned, the graphical record indicated the presence of a substance somewhat more volatile than SeF_5OOSeF_5. To obtain enough of the by-product to allow it to be identified, a mixture was produced by fluorination of SeO_2. A simple trap-to-trap distillation then gave about 2.5 ml of a liquid which boiled above room temperature. This was subjected to conventional fractional distillation in a small glass still having a hold-up of liquid of only about 1 ml. The first constant-boiling fraction to come over was bis(pentafluoroselenium) oxide. A codistillation made on part of the product indicated only one substance to be present. The proportion of any contaminant must have been small.

Pentafluoroselenium Fluorosulfate. A liquid mixture having a volume of about 3.5 ml was produced by the reaction of SeF_5OOSeF_5 with an excess of $S_2O_6F_2$ (see below). When this was refined by fractional distillation, a constant-boiling cut was obtained which was substantially pure SeF_5OSO_2F.

Peroxydisulfuryl Difluoride. The substance, $S_2O_6F_2$, was prepared from SO_3 and F_2 by the usual method.[3]

Bis(trifluoromethyl) Peroxide. CF_3OOCF_3 was produced by holding a mixture of fluorine and carbonyl fluoride in contact with silver difluoride in a nickel vessel at about 100° for a few hours. The resulting products were separated by fractional codistillation.[4] The peroxide was produced in high yield and was the highest boiling substance in the mixture.

Physical Methods. Infrared spectra over the range 400–4000 cm^{-1} were taken using a Beckman IR-10 spectrometer. The cell was 11 cm in length and was equipped with silver chloride windows attached to the glass cell by halocarbon wax. **Molecular weights** were determined by vapor density using a glass bulb of known volume. Pressures were measured with a mercury manometer and with the help of a cathetometer. **Mass spectra** were taken using an AEI MS-9 mass spectrometer. **Nmr spectra** were taken using a Varian Associates Model V-4311 spectrometer with an oscillator at 56.4 Mc for fluorine. Samples were sealed into 5-mm glass tubing. Trichlorofluoromethane in a glass capillary was used as an external standard. **Vapor pressures** were measured by boiling a liquid substance under a known and measured pressure. The vapor was totally condensed and returned to the boiler. The temperature for equilibrium between vapor and refluxing liquid was measured with a thermocouple shielded by glass tubing. The heat of vaporization and Trouton constants were calculated with the aid of the Clausius–Clapeyron equation.

Properties of SeF_5OOSeF_5. Infrared Spectrum. The following absorption bands (in cm^{-1}) were observed: 839 (w), 763 (s), 738 (s), 579 (m), and 409 (w, br). See Figure 1. Mitra and Cady[1] had reported strong bands at 762 and 737 cm^{-1} which must have been caused by SeF_5OOSeF_5, but they had also reported strong absorptions at 842, 775, and 722 which must have been caused by the impurity SeF_5OSeF_5. This compound absorbs strongly at 842, 779, and 722 cm^{-1}.[2]

Nmr Spectrum. The ^{19}F nmr spectrum for SeF_5OOSeF_5 (Figure 2) was much like that for the corresponding sulfur compound.[5] The spectrum had characteristics indicating that the spin–spin coupling constant for the two types of fluorine atoms (apical and basal for a square pyramid) was much larger than the difference in chemical shift. The chemical shift for the most intense part of the spectrum was −55.1 ppm with respect to external $CFCl_3$. This is somewhat less negative than the usual shift for compounds containing the SeF_5 group (normal, about −70 to −76 ppm) and is like the situation for SF_5OOSF_5 among compounds containing the SF_5 group.[5] The value found for the spin–spin coupling constant for ^{77}Se with ^{19}F was 1474 Hz.

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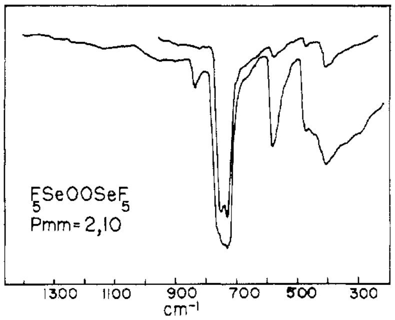

Figure 1. Infrared spectrum of SeF_5OOSeF_5.

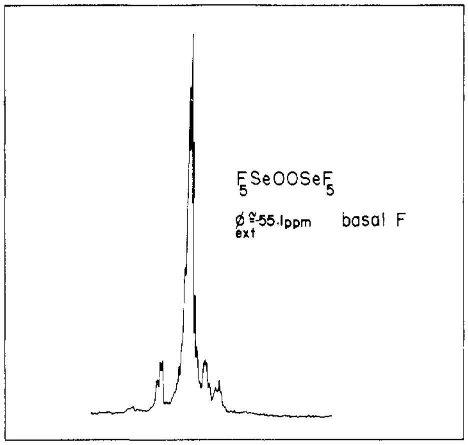

Figure 2. ^{19}F nmr spectrum of SeF_5OOSeF_5.

Decomposition by Ultraviolet Irradiation. A 1.03-mmol sample of SeF_5OOSeF_5 was placed in a 2-l. glass flask equipped with an internal quartz glass finger containing a water-cooled Hanau 350-W mercury arc lamp. The lamp was operated for 3 hr while the flask was held at room temperature. Separation of the gaseous products by fractional codistillation gave 0.18 mmol of SeF_5OOSeF_5, 0.19 mmol of SeF_6, 0.14 mmol of SiF_4, and some O_2. Substances of lower volatility than these were present in the flask but were not identified.

Thermal Decomposition. A 1.56-mmol sample of SeF_5OOSeF_5 was placed in a 100-ml Pyrex glass bulb equipped with a mercury manometer. As the temperature of the bulb was increased, the pressure of gas rose in proportion to the absolute temperature up to about 85°. Above this temperature the pressure increased abnormally indicating decomposition. In another experiment a 0.90-mmol sample of SeF_5OOSeF_5 was held in a nickel bomb at 140° for 18 hr. Separation of the products which were volatile at −78° gave oxygen and 0.88 mmol of SeF_6. The remaining less volatile product probably was SeF_4 but due to an experimental difficulty the compound was not identified.

Reaction with Peroxydisulfuryl Difluoride. One-half millimole of SeF_5OOSeF_5 and 1 mmol of peroxydisulfuryl difluoride ($S_2O_6F_2$) were transferred into a 500-ml flask equipped with an internal Pyrex-glass finger containing a water-cooled 350-W mercury arc lamp manufactured by Hanau. The sample was irradiated for 1.5 hr, with the flask at about 23°. The material was then cooled to −183° and subjected to pumping to remove oxygen. The remaining product was fractionally codistilled. This process gave as products SeF_6, SiF_4, $S_2O_6F_2$, and the new substance pentafluoroselenium fluorosulfate (SeF_5OSO_2F).

In another experiment 1.5 mmol of SeF_5OOSeF_5 was mixed with 2.49 mmol of $S_2O_6F_2$ in a 15-ml glass vessel and allowed to remain at about 23° for 15 days. Fractional codistillation then gave back the original materials. When the same mixture was then held at 83° for 9 hr, a reaction occurred. Fractional codistillation of the product gave peroxydisulfuryl difluoride together with about 3 mmol of pentafluoroselenium fluorosulfate.

Reaction with Bis(trifluoromethyl) Peroxide. A mixture of SeF_5OOSeF_5, 0.44 mmol, with CF_3OOCF_3, 1.33 mmol, was held at about 23° in a 500-ml glass flask and irradiated for 2 hr through Pyrex glass by the water-cooled mercury arc lamp. Fractional codistillation showed substances remaining in the flask to be CF_3OOCF_3, SeF_6, SiF_4, SeF_5OOSeF_5 (trace), and SeF_5OSeF_5 (trace). Oxygen was also present. Apparently no substance containing both carbon and selenium was formed.

Reaction with SO_2. SO_2, 0.90 mmol, was mixed with SeF_5OOSeF_5, 0.51 mmol, in a glass flask and held at 80–85° for 5 hr. The identified products were SO_2, SeF_5OSeF_5 (trace), SeF_5OOSeF_5, SeF_6, and SiF_4. The latter could very well have been produced by attack upon glass by SeF_4. Apparently SeF_5OOSeF_5 decomposed thermally without reacting with SO_2.

Reaction with Tetrafluorohydrazine. A mixture of N_2F_4, 0.4 mmol, with SeF_5OOSeF_5, 1.33 mmol, was held at about 23° and irradiated for 1.5 hr through Pyrex glass by the water-cooled mercury arc lamp. One product was a gas (probably O_2) which did not condense at −183° when under a pressure less than 1 atm. Fractional codistillation of the volatile products gave N_2F_4, SiF_4, SeF_5OOSeF_5, and NF_3. A nonvolatile white solid was present on the wall of the reactor.

A mixture of N_2F_4, 8.84 mmol, with SeF_5OOSeF_5, 1.63 mmol, was held at 80–83° in a glass flask for 50 min. A white solid appeared on the wall of the glass reactor after about 15 min. Fractional codistillation of the gaseous product gave N_2F_4, SeF_5OOSeF_5, SeF_5OSeF_5, and SiF_4. Analysis of the white solid showed it to contain Se, 0.50 mmol, and F, 2.55 mmol. The 5:1 ratio of F to Se suggests that SeF_5 groups probably were present in the solid and that other fluorine-containing groups, such as NF_2, probably were absent. The solid was not identified.

Reaction with Nitrogen Dioxide. A mixture of SeF_5OOSeF_5 with nitrogen dioxide was held at low pressure in a glass flask at about 23° and was irradiated for 2.25 hr by the water-cooled mercury arc lamp held in a quartz glass finger. Separation of the materials gave O_2, SeF_6, SiF_4, SeF_5OOSeF_5, and nitrogen dioxide. Apparently the reaction was simply the photochemical decomposition of SeF_5OOSeF_5 accompanied by attack of glass, probably by SeF_4.

Reaction with Chlorine or Bromine. A mixture of SeF_5OOSeF_5, 0.44 mmol, with Cl_2, 1.77 mmol, was held in a 0.5-l. glass flask at about 23° and irradiated through quartz glass with the water-cooled mercury arc lamp for 2 hr. The remaining material was found to contain Cl_2, O_2, SeF_6, SiF_4, and a small amount of an unidentified substance. Irradiation of a mixture of Br_2 with SeF_5OOSeF_5 through Pyrex glass for 1.8 hr gave a mixture containing Br_2, SeF_6, SiF_4, SeF_5OSeF_5, and SeF_5OOSeF_5. In both cases the primary change appeared to be the photochemical decomposition of SeF_5OOSeF_5. Neither chlorine nor bromine was observed to react.

Properties of SeF_5OSO_2F. Values obtained for the **molecular weight** by vapor density were 269, 270, 275, and 269 (theory 273). As the temperature of a solid sample was allowed to increase, the material appeared to be half liquid at −113° and to become completely liquid at −112°. This indicates the **melting point** for the pure substance to be −111°. It was easy to cause the liquid to supercool. Duplicate **elemental analyses** were performed. *Anal.* Calcd: Se, 28.9; S, 11.7; F, 41.8. Found: Se, 28.1, 28.1; S, 12.2, 12.05; F, 42.1, 42.4.

In the region from about 200 to 700 mm the **vapor pressure** came close to that of the equation

$$\log P_{\text{mm}} = -\frac{1633}{T} + 7.8950$$

which corresponds to a normal boiling point of 52.6°, a heat of vaporization of 7480 cal mol^{-1}, and a Trouton constant of 23.0. A few experimental values for vapor pressures in mm follow: −6.7°, 56.4; 0.1°, 78.8; 7.4°, 117.2; 14.3°, 161.8; 18.9°, 199.8; 25.9°, 272.8; 33.7°, 377.4; 39.6°, 472.8; 44.4°, 574.8; 47.3°, 628.0; 50.0°, 724.0.

The **infrared spectrum**, shown in Figure 3, had absorption bands at 1483 and 1242 cm^{-1} (due to S-O stretch) at 765 cm^{-1} (assigned to Se-F stretch) and at 421 cm^{-1} for F-Se-F bend. There were also bands at 842, 740, 641, 589, and 544 cm^{-1}.

Hydrolysis. A small sample of liquid SeF_5OSO_2F was stored in contact with water at about 22°. At first two liquid phases could be seen, but after 2.5 months only one liquid phase was present. The reaction with water was slow.

Nmr Spectrum. The ^{19}F nmr spectrum in Figure 4 had an AB_4 type pattern for the square-pyramidal SeF_5 group. The four basal fluorine atoms had a chemical shift of −72.5 ppm relative to external $CFCl_3$ while the apical fluorine atom had a shift of −56.2 ppm and the fluorine of the SO_3F group a shift of −44.9 ppm. The spin-spin coupling constant $J_{SO_3F\text{-}SeF_4}$ was 5.1 Hz while $J_{SeF\text{-}SeF_4}$ was 209 Hz. Within the resolution of the spec-

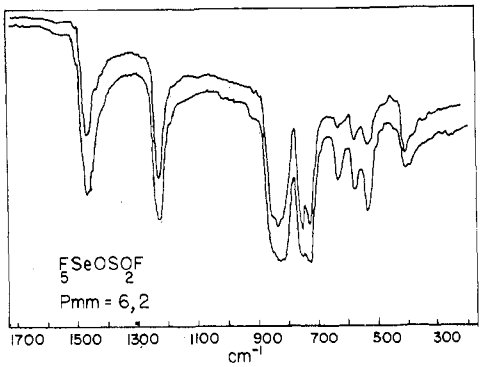

Figure 3. Infrared spectrum of SeF_5OSO_2F.

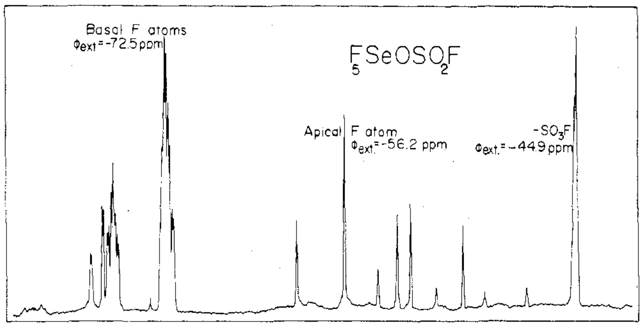

Figure 4. ^{19}F nmr spectrum of SeF_5SO_3F.

trometer, no evidence was found for coupling between the fluorine of SO_3F and the apical fluorine atom of the SeF_5 group. The spin-spin coupling constant for ^{77}Se with the four basal fluorine atoms was 1390 Hz.

Properties of SeF_5OSeF_5. Analysis. A weighed sample was condensed upon potassium in a glass vessel cooled by liquid nitrogen. The vessel was later heated to cause complete reaction of the sample with the metal. (*Caution!* One of the tubes exploded as it warmed toward room temperature.) *Anal.* Calcd: Se, 43.4; F, 52.2. Found: Se, 42.4; F, 53.1. Smith and Cady[2] obtained experimental values for the molecular weight of 368 and 373 (theory for SeF_5OSeF_6 366).

Behavior toward Water. A 1.5-mmol sample of bis(pentafluoroselenium) oxide was stored in contact with 49 mmol of water at about 22° for 9 months. Apparently no reaction occurred. Two liquid phases were continually present and there seemed to be no change in the relative amounts.

A sample of the compound was frozen and then allowed to warm slowly. It appeared to be one-third melted at $-83.2°$, to be two-thirds melted at $-82.8°$, and to be completely liquid about $-82.5°$. These data indicate the **melting point** to be close to $-82.1°$.

The **vapor pressure** of the liquid between 200 and 700 mm followed the equation

$$\log P_{\mathrm{mm}} = -\frac{1615}{T} + 7.8017$$

This corresponds to a heat of vaporization of 7390 cal mol^{-1}, a normal boiling point of 55.2°, and a Trouton constant of 22.5. Some of the experimentally observed vapor pressures (in mm) follow: $-12.9°$, 37.8; $-4.6°$, 58.8; 2.2°, 83.3; 10.2°, 119.6; 15.6°, 157.6; 21.4°, 206.4; 24.9°, 240.2; 31.9°, 321.8; 39.3°, 425.8; 45.1°, 518.0; 48.4°, 598.8; 51.1°, 658.4; 53.4°, 722.2.

The **^{19}F nmr spectrum** in Figure 5 showed the SeF_5 group to have the AB_4 pattern characteristic of a square-pyramidal structure. Chemical shift for the four basal fluorine atoms with respect to external $CFCl_3$ was -76.0 ppm while the shift for the **apical fluorine** was -62.8 ppm. The spin-spin coupling constant between the two kinds of fluorine atoms was 223 Hz. In establishing these constants, use was made of the procedure of Merrill, *et al.*,[5] for the SF_5 group.

The **infrared spectrum** for the compound as reported by Smith and Cady[2] was confirmed in the present research.

Thermal Stability. When a 0.60-mmol sample of the gas was heated in a glass vessel attached to a mercury manometer, the pressure increased substantially in proportion to the absolute temperature up to 160° at which point the heating was discontinued. Fractional codistillation showed the gas still to be SeF_5OSeF_5.

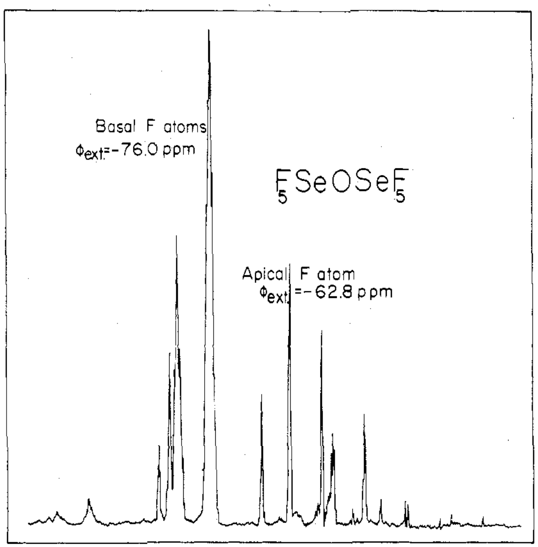

Figure 5. ^{19}F nmr spectrum of SeF_5OSeF_5.

Test of Possible Behavior of SeF_5OSeF_5 as a Donor Molecule. Since the compound may be regarded as analogous to an ether, there appears to be a chance that SeF_5OSeF_5 can form a donor-acceptor complex with BF_3, etc. To test this hypothesis a 5.7-mmol portion of bis(pentafluoroselenium) oxide was allowed to stand in contact with 9.3 mmol of BF_3 in a 100-ml glass flask. When the flask was held at $-78°$ for 10 min, no visible formation of a solid adduct occurred. The flask was then held at room temperature and shaken for 5 min after which it was quenched at $-78°$. Material volatile at this temperature was removed by pumping for 10 min. All of the BF_3 was removed. Apparently no adduct was formed.

Discussion

SeF_5OOSeF_5 starts to decompose at a much lower temperature (85°) than that for SF_5OOSF_5 (200°).[6] Perhaps this fact together with relatively low stability of other molecules containing the SeF_5O group is responsible for the selenium compound being less interesting as a reagent than its sulfur analog.[6,7] For both sulfur and selenium it appears likely that the molecule first breaks into $EF_5O\cdot$ radicals. In the case of sulfur it is possible from the radical to obtain many products containing the SF_5O group. $SeF_5O\cdot$ does not show corresponding behavior; it goes to pieces, probably giving $SeF_5\cdot$. The formation of SeF_5OSeF_5 may very well result from the combination of $SeF_5\cdot$ with $SeF_5O\cdot$, and SeF_5OSO_2F may come from $SeF_5\cdot$ and $SO_3F\cdot$.

When this research was started, the authors anticipated that studies involving fluorine-containing compounds of selenium would be nearly as fruitful in revealing new compounds as had been studies of sulfur analogs. This expectation did not materialize. In addition to the work with SeF_5OOSeF_5, determined efforts were made to produce CF_3SeF_5 starting with CSe_2. This unsuccessful venture together with several others of a similar nature has been reported by Reichert.[8]

Registry No. Bis(pentafluoroselenium) peroxide, 37988-

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78-6; selenium dioxide, 7446-08-4; fluorine, 7782-41-4; bis(pentafluoroselenium) oxide, 27218-15-1; pentafluoroselenium fluorosulfate, 37988-80-0; peroxydisulfuryl difluoride, 13709-32-5; bis(trifluoromethyl) peroxide, 927-84-4; carbonyl fluoride, 353-50-4; SO_3, 7446-11-9.

Acknowledgment. This work was performed in part under contract with the Office of Naval Research. Nmr spectra were obtained with the assistance of B. J. Nist. Professor H. J. Emeleus suggested that the donor properties of SeF_5OSeF_5 should be tested.

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Isotropic Nuclear Magnetic Resonance Shifts in Ion-Paired Systems. A Study of Some Penta- and Hexanitratolanthanate (III) Complexes

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A series of complexes of the formulas $[R_4N]_2Ln(NO_3)_5$ and $[R_4N]_3Ln(NO_3)_6$ have been prepared and characterized. The proton nmr spectra of the organic cations in solution reveal shifts which can be ascribed to a dipolar mechanism. On the basis of these data an anion–cation distance of between 6 and 7 Å is calculated. Factors affecting the shape of the cation in solution in this as well as in other systems are discussed.

Introduction

Recent proton nmr studies of organic cations ion paired to paramagnetic anions in solvents of low dielectric constant have given rise to the possibility of ascertaining the nature and structure of ion aggregates in solution.[1-12] The basis of the method lies in the fact that protons on an organic ion in solution experience shifts from their normal resonance frequencies in diamagnetic solutions when the ion is in contact with a paramagnetic counterion.

In general, the isotropic nmr shift in solution, $\Delta\nu$, is a sum of two terms: the Fermi contact term, $\Delta\nu_f$, which depends for its magnitude on the presence of unpaired spin density at the nucleus,[13] and the dipolar term, $\Delta\nu_{dip}$, which occurs in complexes where the metal ion experiences fields of less than cubic symmetry. Thus

$$\Delta\nu = \Delta\nu_f + \Delta\nu_{dip} \qquad (1)$$

The dipolar shift is of interest to the solution chemist because of its dependence on bond distances and angles. In general we have[13,14]

$$\Delta\nu_{dip} = \nu[F_1G_1(R,\theta) + F_2G_2(R,\theta,\Omega)] \qquad (2)$$

where F_1 and F_2 are functions of the principal susceptibilities of the metal complex. In axial symmetry, $F_2 = 0$ and we are left with an expression containing the first term only, for which

$$G_1(R,\theta) = \frac{3\cos^2\theta - 1}{R^3} \qquad (3)$$

where R is the distance between the proton and the unpaired electron, assumed to be at the center of the metal atom, while θ is the angle between vector R and the major susceptibility axis ($\chi_\parallel = \chi_z$) of the molecule.

It is therefore possible, provided no Fermi contact shift is present, to use the observed shifts to obtain anion–cation distances and to obtain information on the structure of the cation in the ion pair.

In this paper, we report the results of a study on ion pairing between tetraalkylammonium cations and hexanitrato- and pentanitratolanthanate(III) anions. These complexes have the advantage of being soluble to a marked degree in a wide variety of solvents, making the study of ion association possible under a considerable range of conditions. Most important, the nitrato complexes, unlike the previously studied hexachloro complexes,[11] will be shown to give shifts which are less complicated by either the rhombic dipolar or Fermi contact effects. This frees us from the unwholesome burden of factoring the isotropic shift into its constituent parts, for which there is at present no simple or unambiguous method.

Experimental Section

Reagents. Rare earth oxides (99.9%) were obtained from American Potash and Chemical Co., West Chicago, Ill., and were converted to the nitrates with concentrated nitric acid. Tetrapropylammonium iodide and tetrabutylammonium iodide (Eastman) were used as received. All solvents used in this work, with the exception of pyridine, were dried at least 24 hr before use over BDH Type 3A molecular sieve. Dichloromethane (Anachemia, Toronto) was fractionally distilled, and the fraction boiling between 40 and 41° was collected and stored over molecular sieve.

Preparation of Complexes. The basic technique used follows closely that employed by Straub, Drago, and Donoghue[15] in preparing the nitrato complexes of the first transition series. Stoichiometric amounts of hydrated rare earth nitrate, finely powdered silver nitrate, and tetraalkylammonium iodide were allowed to react in refluxing acetonitrile for several hours, with complete exclusion of light. An excess of triethyl orthoformate was added during reflux to remove co-

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