The four methylene protons of I in the adduct undergo rapid site exchange. A single, effective T_1^{-1} is found which is dominated by the relaxation rate of the proton nearest Gd.

Acknowledgment. We thank the University of Kansas Computation Center for a generous allocation of computer time. The Bruker WP-80 spectrometer was purchased in part with an instrumentation grant from the National Science Foundation.

Registry No. I, 13878-48-3; Gd(fod)$_3$, 17631-67-3; La(fod)$_3$, 19106-89-9; Eu(fod)$_3$, 17631-68-4.

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Gallium-71 NMR Studies of Anionic Gallium Halide Species in Nonaqueous Solution

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^{71}Ga NMR spectra of the four-coordinate anions $GaX_nY_{4-n}^-$ and GaX_2YZ^- (X, Y, Z = Cl, Br, or I) are reported. Halide exchange between GaX_4^- and GaY_4^- in dichloromethane solution is slow, and the equilibrium proportions of the mixed-halide species GaX_3Y^-, $GaX_2Y_2^-$, and $GaXY_3^-$ do not correspond to a statistical redistribution of ligands. No resonance was detected from solutions of salts of $Ga_2X_6^{2-}$ (X = Cl or Br), which have a staggered ethane-type structure.

Introduction

Gallium is known to form tetrahalogeno complexes of the formulas GaX_4^- (X = Cl, Br, I) and $GaX_nY_{4-n}^-$, and partial or complete vibrational spectra have been reported for both series of anions.[1-5] Recent papers from this laboratory have reported the preparation and spectroscopic investigation of the analogous $InX_nY_{4-n}^-$ species,[6] and the use of ^{115}In NMR spectroscopy[7] in the study of the solution chemistry of these and related anions.

The tetrahedral GaX_4^- ions have been studied by ^{71}Ga NMR spectroscopy, both in aqueous solution and in melts.[8] In general, the quadrupole of the ^{71}Ga nucleus ($I = {}^3/_2$) means that resonance can only be observed in structures of high symmetry[9] such as octahedral or tetrahedral complexes or in species in which the Ga^{3+} ion is bonded to chemically similar ligands and especially halides. ^{71}Ga inversion–recovery spectra from a solution of $GaBr_3$ and $NbCl_5$ in acetonitrile have been studied[10,11] and the five experimental peaks assigned to the series $GaCl_4^-$–$GaCl_nBr_{4-n}^-$–$GaBr_4^-$.

We have now carried out ^{71}Ga NMR studies of the anionic four-coordinate gallium(III) chloride, bromide, and iodide mixed-halide complexes in dichloromethane solution and have obtained chemical shifts and other data for all the possible four-coordinate species $GaX_nY_{4-n}^-$ and GaX_2YZ^- (where X, Y, Z = Cl, Br, or I). Complex ions of the type MX_2YZ^- have not been previously reported for gallium. A particularly interesting aspect of the results is that the ligand-exchange reactions between GaX_4^- and GaY_4^- are found to be slow, so that ^{71}Ga NMR spectroscopy is a convenient technique for following the progress of the formation of the mixed-halide complexes. The behavior of gallium complexes is in contrast to that of the corresponding four-coordinate indium species[7] under similar conditions, since the formation of the InX_3Y^- and $InX_2Y_2^-$ anions (X ≠ Y = Cl, Br, or I) is complete within the time of mixing, yielding the mixed-halide complexes in proportions corresponding approximately to the statistical redistribution of the ligands.

Table I. ^{71}Ga Resonances for $GaX_4Y_{4-n}^-$ and GaX_2YZ^- Anions in Dichloromethane

no.	anion	$-\delta$ (±1%)	$w_{1/2}$(±5%), Hz
1	$GaCl_4^-$	0	180
2	$GaCl_3Br^-$	40	200
3	$GaCl_2Br_2^-$	84	215
4	$GaClBr_3^-$	133	210
5	$GaBr_4^-$	187	185
6	$GaBr_3I^-$	300	205
7	$GaBr_2I_2^-$	425	220
8	$GaBrI_3^-$	561	210
9	GaI_4^-	706	185
10	$GaCl_3I^-$	128	220
11	$GaCl_2I_2^-$	291	320
12	$GaClI_3^-$	486	290
13	$GaCl_2BrI^-$	181	255
14	$GaClBr_2I^-$	238	290
15	$GaClBrI_2^-$	356	340

Experimental Section

Materials. The previously reported[12] gallium salts $(n\text{-}C_4H_9)_4NGaX_4$ were prepared by dissolving gallium metal in an aqueous solution of the acid HX, prepared by mixing the concentrated reagent with an equal volume of water. The solution was boiled to ensure oxidation of Ga(II) intermediates to Ga(III) before adding a slight excess of tetra-*n*-butylammonium halide. The precipitated $(n\text{-}C_4H_9)_4NGaX_4$ was collected, dried, and recrystallized from dichloromethane; addition of diethyl ether resulted in the product being recovered in the form of small crystals. The identity of the products was confirmed by infrared and Raman spectroscopy.

The gallium(II) salts $[(n\text{-}C_4H_9)_4N]_2[Ga_2X_6]$ (X = Cl, Br) were prepared by methods previously reported.[13]

Dichloromethane was dried and stored over molecular sieves.

NMR Spectroscopy. ^{71}Ga NMR spectra were obtained with a Bruker CXP-100 variable-frequency FT spectrometer operating at 27.45 MHz, with a magnetic field of 2.114 T. The instrument was

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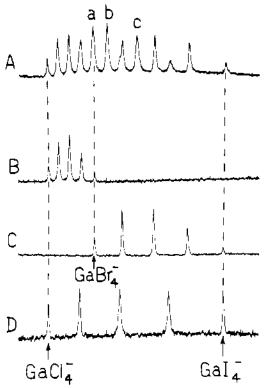

Figure 1. ^{71}Ga NMR spectra of mixed-halide systems (0.4 M solutions in dichloromethane). a, b, and c denote resonances of $GaCl_2BrI^-$, $GaClBr_2I^-$, and $GaClBrI_2^-$, respectively.

externally locked on to the deuterium resonance of D_2O. All samples were run as solutions (approximately V = 3 cm^3) in 1 cm (o.d.) tubes, at a temperature of 27 °C. A total of 300 pulses, at the rate of 5/s, served to obtain good quality spectra.

Results and Discussion

Mixed Tetrahalogenogallate(III) Anions. The single resonance peaks of dichloromethane solutions of GaX_4^- salts (X = Cl, Br, or I) were measured at concentrations of 0.1 and 0.4 M, with the use of the resonance of $[Ga(H_2O)_6]^{3+}$ in an aqueous solution of gallium(III) nitrate ([Ga] = 0.1 M, $[HNO_3] \approx 6$ M) as a standard. The resonance frequencies shifted by less than 1 ppm on change of concentration, and the experimental values agreed with the previous results[8,9] for these complexes in aqueous solutions of the corresponding hydrogen halide (6 M HCl, 5 M HBr, 3 M HI).

The resonance frequencies of GaX_3Y^- and $GaX_2Y_2^-$ anions were obtained from the spectra of solutions prepared by mixing equal volumes of 0.4 M solutions of GaX_4^- and GaY_4^- salts in dichloromethane. The eventual spectra (Figure 1) consisted in each case of five lines whose extremities corresponded to the ^{71}Ga resonance frequencies of $GaCl_4^-$, $GaBr_4^-$, or GaI_4^-, respectively, as indicated in the diagram, and the intermediate lines are therefore assigned to the appropriate GaX_3Y^-, $GaX_2Y_2^-$, and $GaXY_3^-$ resonances. Only in the $GaCl_4^-$/$GaBr_4^-$ series did the relative proportions come close to the 1:4:6:4:1 ratio required for statistical redistribution of halide ligands; we return to this point below. Confirmation of these assignments given in Table I for the $GaCl_4^-$/$GaBr_4^-$ series was obtained from previous work on $GaBr_3$/$NbCl_5$, for which the chemical shifts relative to $GaCl_4^-$ were reported[10,11] as −40 ppm for $GaCl_3Br^-$, −84 ppm for $GaCl_2Br_2^-$, −133 ppm for $GaClBr_3^-$, and −184 ppm for $GaBr_4^-$. Table I shows the chemical shifts of all the mixed-halogeno species, together with the appropriate line widths. The resonance line widths of the species of lower symmetry, GaX_3Y^- (C_{3v}) and $GaX_2Y_2^-$ (C_{2v}), are somewhat greater than those of the tetrahedral complexes, as previously observed in the case of mixed-halogeno complexes of aluminum[14] and indium.[7] There is also an effect related to the particular halide involved, in that the peak due to $GaCl_2I_2^-$, for example, is broader than either of those from $GaCl_2Br_2^-$ or $GaBr_2I_2^-$.

In previous work[7] on the InX_4^-/InY_4^- series, it was observed that the resonance frequency of the metal, which inter alia is a function of the electron density at the nucleus, has a nonlinear dependence on the total ligand electronegativity. Figure 2 shows the result of a similar treatment of the present results; the sum of χ_{halogen} (using Aldred–Rochow values for the electronegativities) is plotted against the chemical shift of the ^{71}Ga resonance. The results fall on a series of curves, one for each of the GaX_4^-–GaY_4^- series, generally very similar to those for the InX_4^-–InY_4^- series, although the range of chemical shifts is smaller in the gallium case.

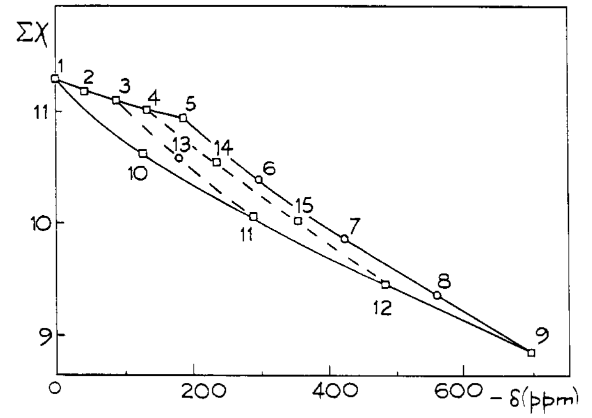

Figure 2. ^{71}Ga chemical shifts (δ) as a function of total ligand electronegativity ($\sum\chi$) for $GaX_nY_{4-n}^-$ and GaX_2YZ^- anions. Key numbers refer to entries in Table I.

We have also recorded the spectrum which is obtained when solutions containing equimolar amounts of $GaCl_4^-$, $GaBr_4^-$, and GaI_4^- are combined (see Figure 1). As would be expected from the values in Table I, there is an overlapping of the peaks of MCl_3I^- and $MClBr_3^-$ and also of $MCl_2I_2^-$ and MBr_3I^-; similar coincidences were observed in the series of mixed-halogeno complexes of indium.[7] In addition, three new resonances are identified (denoted by a–c in spectrum A in Figure 1) and attributed to the GaX_2YZ^- anions. That assigned to $GaCl_2BrI^-$, at −181 ppm, carries the $GaBr_4^-$ signal at −187 ppm as a weak shoulder, but the peaks of $GaClBr_2I^-$ at −238 ppm and $GaClBrI_2^-$ at −356 ppm are well removed from any other absorptions. These results for the GaX_2YZ^- anions show a similar dependence on electronegativity to that noted for the $GaX_nY_{4-n}^-$ species, and the set $GaClBr_3^-$–$GaClBr_2I^-$–$GaClBrI_2^-$–$GaClI_3^-$ again lies on a smooth curve, indicating that factors over and above ligand electronegativity are involved in determining the value of δ (cf. ref 7 for a similar conclusion for indium(III) species).

One notable feature of the spectrum of mixed $GaCl_4^-$, $GaBr_4^-$, and GaI_4^- (Figure 1A) is that $GaCl_3I^-$, $GaCl_2I_2^-$, and $GaClI_3^-$ appear as components of only minor intensity. This is in keeping with the results in Figure 1D, which shows that these species are not readily formed in $GaCl_4^-$/GaI_4^- mixtures.

Rate of Exchange in GaX_4^-/GaY_4^- Systems. The results for the four-coordinate gallium(III) anions are quantitatively similar to those for the aluminum[14] and indium[7] analogues in terms of dependence of resonance frequency on ligand. There are marked differences in the equilibrium distributions and in the rate at which equilibrium is reached, and we now turn to these matters.

The spectra of dichloromethane containing GaX_4^- and GaY_4^- anions, obtained within 1 min of mixing, were dominated by the peaks of these species, with only very weak signals due to GaX_3Y^- species and an even weaker one from $GaX_2Y_2^-$. Figure 3 shows the spectra of a $GaCl_4^-$–$GaBr_4^-$ mixture; the other system behaves similarly, except that the exchange of halide ligands occurs even more slowly in these cases. By way of quantifying these findings, Figure 4 shows the growth of the combined resonances due to the mixed-halide species GaX_3^-, $GaX_2Y_2^-$, and $GaXY_3^-$ as a function of time for each of the three systems. It is clear that exchange processes involving iodo species are the slowest under the experimental conditions used.

We thus have the following situation for MX_4^-/MY_4^- equilibration with Group 3A elements. For boron,[15] rapid

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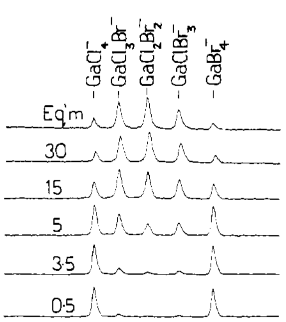


Figure 3. ^{71}Ga NMR spectra of mixture of $(n\text{-}C_4H_9)_4NGaCl_4$ and $(n\text{-}C_4H_9)_4NGaBr_4$ solutions as a function of time (minutes after mixing) (salts in dichloromethane, concentration 0.4 M).

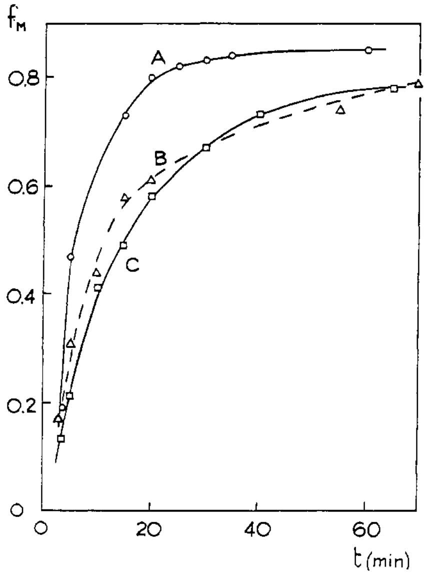


Figure 4. Fractional formation (f_M) of mixed-halide complexes GaX_3Y^- and $GaX_2Y_2^-$ as a function of time: A, $GaCl_4^-$–$GaBr_4^-$; B, $GaCl_4^-$–GaI_4^-; C, $GaBr_4^-$–GaI_4^-.

exchange is observed between BF_4^- and BI_4^- in dichloromethane, but the remaining systems equilibrate slowly, to the point at which heating to 60 °C for ca. 20 min is necessary for BF_4^-/BCl_4^-. No rates are reported for the corresponding aluminum systems,[7] and it seems reasonable to assume that equilibration was reached within the time required for mixing, and this result was established experimentally in the indium work[14] (and in the isoelectronic SnX_4/SnY_4 systems[16]). It should be emphasized that the complete elimination of possible catalytic species (and especially water) from such systems is extremely difficult to prove, and this brief survey should be read in that light. For gallium, on the basis of the present work, exchange is slow relative to that for aluminum and indium.

An explanation of the slow exchange between gallium(III) anions may be found in the known coordination chemistry of these complexes. A variety of investigations, including Raman[3-5] and gallium NMR[8] spectroscopy of solutions containing large excess of halide, have established that gallium(III) does not exceed a coordination number of four in its chloride, bromide, or iodide complexes, in contrast to indium, which does so for all halides except iodide.[17] On this basis we propose that a precondition for halogen exchange in the gallium systems is the dissociation

$$GaX_4^- \rightleftharpoons GaX_3 + X^-$$

This process will be unfavorable in the nonpolar solvent dichloromethane, since it involves the separation of a halide ion. Dissociation to GaX_3 can be followed by attachment of either Y^- directly or of GaY_4^- via a bridging halogen atom to form a complex $[X_3GaYGaY_3]^-$, whose dissociation may yield GaX_3Y^-. Complex ions involving a single bridging halogen with the structure $[Cl_3GaClGaCl_3]^-$ are known for gallium[18-20] and hence lend some plausibility to the latter argument.

The experimental results do not allow the kinetics of the halide-exchange reactions to be fully analyzed. If the reasonable assumption is made that the reaction is first order (i.e., provided that the rate-determining step is the ionization of GaX_4^-, as suggested) the half-time for the conversion of GaX_4^- into the mixed-halide species can be estimated. The initial concentrations of GaX_4^- or GaY_4^- are each 0.4 M, so that, when each concentration has dropped to 0.2 M, that of the mixed halides will total 0.4 M, and the fraction of $GaX_3Y^- + GaX_2Y_2^- + GaXY_3^-$ in the mixture will be 0.5. On this basis the appropriate half-times from Figure 4 are as follows: $GaCl_4^-$–$GaBr_4^-$ system, $t_{1/2} = 6$ min; $GaCl_4^-$–GaI_4^- system, $t_{1/2} = 12$ min; $GaBr_4^-$–GaI_4^- system, $t_{1/2} = 15$ min. Exchange is thus most rapid where $GaCl_4^-$ is involved, which may be rationalized by assuming that ionization (eq 1) occurs more readily for $GaCl_4^-$ than for $GaBr_4^-$ or GaI_4^-.

In summary, the experimental results are in keeping with the mechanism in eq 1–4. This mechanism is consistent with

$$GaX_4^- \rightleftharpoons GaX_3 + X^- \qquad (1)$$

$$GaX_3 + GaY_4^- \rightarrow [X_3GaYGaY_3]^- \qquad (2)$$

$$[X_3GaYGaY_3]^- \rightarrow GaX_3Y^- + GaY_3 \qquad (3)$$

$$GaY_3 + X^- \rightarrow GaXY_3^- \qquad (4)$$

the observed slow rate in a nonpolar solvent in which eq 1 will be energetically unfavorable. It is also consistent with the observation that GaX_3Y^- (and $GaXY_3^-$) resonances appear before those of $GaX_2Y_2^-$, whose formation will require further ionization and association steps such as eq 5–7.

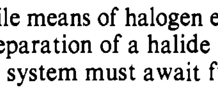
$$GaX_3Y^- \rightleftharpoons GaX_2Y + X^- \qquad (5)$$

$$GaX_2Y + GaY_4^- \rightarrow [X_2YGaYGaY_3]^- \qquad (6)$$

$$[X_2YGaYGaY_3]^- \rightarrow GaX_2Y_2 + GaY_3 \qquad (7)$$

A similar dissociative mechanism was proposed by Hartman and Schrobingen[15] to account for their results on BX_4^-/BY_4^- exchange. On the other hand, Lincoln, Sandercock, and Stranks[21] have argued that the rate of chloride exchange in concentrated aqueous media requires an associative mechanism. Their argument is based in part on the comparison of the experimental ΔS^* value with that predicted from the Born equation, which involves the dielectric constant as an important contribution, and this conclusion need not therefore necessarily be valid for the solution conditions of the present work.

We should also note that the ability of indium to expand its coordination sphere should permit the ready formation of intermediates such as



thus providing a facile means of halogen exchange without the need for the prior separation of a halide ion. Any discussion of the AlX_4^-/AlY_4^- system must await further experimental results.

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Inorg. Chem. **1981**, *20*, 2013-2016 **2013**

Table II. Statistical and Observed Proportions in Equilibrium Mixtures of GaX_{4-n}^- Anions in Dichloromethane

	GaX_4^-	GaX_3Y^-	$GaX_2Y_2^-$	$GaXY_3^-$	GaY_4^-
statistical ratio	1	4	6	4	1
proportions	0.062	0.250	0.375	0.250	0.062
X = Cl, Y = Br	0.09	0.29	0.37	0.20	0.05
X = Br, Y = I	0.11	0.30	0.34	0.20	0.05
X = Cl, Y = I	0.12	0.21	0.29	0.23	0.15

Equilibrium Ratios. The relative proportions of the various gallium halide complexes present at equilibrium, as represented by the resonance signals in Figure 1B–D, require some comment. The amounts of each species, at a total gallium concentration of 0.4 M, were computed from integral traces and confirmed by measuring the areas under the peaks to give the results in Table II. The proportions deviate from the figures for statistical redistribution of the halide ligands, particularly for $GaBr_4^-/GaI_4^-$ and $GaCl_4^-/GaI_4^-$ mixtures. This result suggests that the GaI_4^- complex is kinetically the most stable of the tetrahalogenogallium anions under the conditions of these experiments, and as with the other results reported, the greater covalent contribution to bonding in the case of Ga–I bonds provides a probable explanation.

Hexahalogenogallate(II) Anions. The $Ga_2X_6^{2-}$ anions (X = Cl, Br, or I) have been prepared, as salts of various cations, and shown by vibrational spectroscopy and X-ray crystallography to have a staggered ethane-like configuration in the solid state and in solution.[13,22] We attempted to observe the ^{71}Ga spectra of concentrated solutions of $[(n\text{-}C_4H_9)_4N]_2[Ga_2X_6]$ (X = Cl, Br) in dichloromethane. No resonance was detected in the case of bromide, despite the fact that the presence of $Ga_2Br_6^{2-}$ ion in solution was confirmed by Raman spectroscopy. A solution of the analogous $Ga_2Cl_6^{2-}$ salt containing (identified) additional $GaCl_4^-$ gave only a strong single resonance due to this latter ion. No other signals could be observed even after collecting more than 100 times as many pulses as were necessary to detect $GaCl_4^-$ and even though the concentration of $Ga_2Cl_6^{2-}$ was approximately 5 times that of $GaCl_4^-$.

We conclude that the gallium resonance is broadened beyond the limit of detection by the electric field gradient which results from the unsymmetrical environment of the ^{71}Ga nucleus when the atom is bonded to another gallium (either ^{71}Ga or ^{69}Ga, both of which have spin $I = {}^3/_2$) as well as to halogen atoms. Equally, we find no evidence for the disproportionation

$$M_2X_6^{2-} \rightleftharpoons MX_2^- + MX_4^-$$

which was observed with $In_2X_6^{2-}$ anions.[7]

Acknowledgment. This work was supported in part by Operating Grants (to B.R.M. and D.G.T.) from the Natural Sciences and Engineering Research Council of Canada. M.J.T. thanks the University of Auckland, Aukland, New Zealand, for the award of a sabbatical leave.

Registry No. $GaCl_4^-$, 15201-06-6; $GaCl_3Br^-$, 44006-78-2; $GaCl_2Br_2^-$, 57300-64-8; $GaClBr_3^-$, 44006-76-0; $GaBr_4^-$, 17611-23-3; $GaBr_3I^-$, 44006-77-1; $GaBr_2I_2^-$, 62938-85-6; $GaBrI_3^-$, 44006-79-3; GaI_4^-, 19468-10-1; $GaCl_3I^-$, 44007-68-3; $GaCl_2I_2^-$, 62883-26-5; $GaClI_3^-$, 44007-69-4; $GaCl_2BrI^-$, 77320-92-4; $GaClBr_2I^-$, 77320-93-5; $GaClBrI_2^-$, 77320-94-6.

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Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada K1A 0R9

Hydrogen Fluoride Containing Isostructural Hydrates of Hexafluorophosphoric, Hexafluoroarsenic, and Hexafluoroantimonic Acids[1]

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Received July 31, 1980

The similar X-ray diffraction patterns of the solid "hexahydrates" of HPF_6, $HAsF_6$, and $HSbF_6$ indicate that these hydrates are probably isostructural, with the same cubic *Im*3*m* space group. The ^{19}F NMR spectra clearly show the presence of one molecule of HF for each hexafluoride anion. These solids appear to form a class of clathrate-like hydrates in which the disordered MF_6^- ions occupy tetradecahedral cages in a fully hydrogen-bonded host lattice consisting of H_2O, H_3O^+, and HF molecules, randomly distributed on the sites forming the cages.

It is generally assumed that the common crystal hydrates formed by HPF_6, $HAsF_6$, and $HSbF_6$ are hexahydrates.[2a] By an X-ray study Bode and Teufer[2b] found that the HPF_6 hydrate crystallizes in the cubic space group *Im*3*m* with the O atoms occupying the apices of a four-coordinated network forming the space-filling truncated octahedra of Fedorov. The PF_6^- anions occupy these 14-sided voids. This structure for $HPF_6{\cdot}6H_2O$ failed to fit the extra proton into a fully four-coordinated hydrogen-bonding scheme for the water molecules. It was observed by Davidson and Garg,[3] on the basis of ^1H and ^{19}F wide-line NMR and chemical composition studies, that the hydrate formed by addition of water to the commercial 65% HPF_6 solution is really $HPF_6{\cdot}HF{\cdot}5H_2O$. The presence of one HF molecule for each H_3O^+ ion in the lattice matches the number of H atoms to the number of hydrogen bonds and makes full hydrogen bonding possible. We now confirm this result and show that the "hexahydrates" of $HAsF_6$ and $HSbF_6$ appear to have the same clathrate structure and to incorporate HF in the lattice in the same way as the HPF_6 hydrate.

Experimental Methods

The HPF_6 hydrate crystals were prepared by the addition of water to commercial 65% HPF_6 as before.[3] The $HAsF_6$ hydrate used consisted of colorless crystals of Ozark-Mahoning "$HAsF_6{\cdot}6H_2O$".

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[1] Issued as NRCC No. 18823.

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