field of polyhalogen complexes. Tentative calculations have shown that this theory may also be successful in other fields, for instance that of the inert gas compounds.

Acknowledgments.—We wish to thank Dr. M. P. Bogaard for the nqr data he made available to us and Miss A. Migchelsen for permission to use the results of her calculations on some trihalide ions. E. H. W. is very much indebted to Professor C. A. Coulson for the hospitality he enjoyed in the Mathematical Institute in Oxford where our calculations were performed in a preliminary form.

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Raman Spectroscopic Study of Stepwise Bromide and Chloride Complexes of Indium(III) in Aqueous Solution[1]

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From measured Raman frequencies and intensities in aqueous indium bromide solutions, three complexes were detected. These were indicated to be $InBr^{2+}$, $InBr_2^+$, and $InBr_3$. That no anionic complexes were present was confirmed by the lack of anionic migration, which however was found for the corresponding chloride system. Three complexes were also detected in the chloride system, which were indicated to be $InCl^{2+}$, $InCl_2^+$, and $InCl_4^-$. However, the last of these is not the tetrahedral ion known to exist in ether and nonaqueous solvents. Raman experiments in methanol–water mixtures suggest that, in the presence of water, $InCl_4^-$ coordinates water molecules. This behavior accounts for both the Raman results and the relatively poor extractability of $InCl_4^-$ from water. In addition, absolute Raman intensities are given and discussed for $InCl_4^-$ and $InBr_4^-$ in nonaqueous solvents, and equilibrium quotients are determined for stepwise complex formation in water.

For Raman studies of the halide complexes in solution of various metal ions, indium occupies an interesting position. It lies intermediate between gallium which has been shown by Raman studies to form only the tetrachloro[2] and tetrabromo[3] complexes in aqueous solution and just above thallium which has been shown by Raman studies to form a stepwise series of complexes.[4] In attempting to understand the factors responsible for the different behavior of Ga and Tl, it seems worthwhile to conduct a similar study on the indium halides. An additional motivation for the work is the problem of the apparent uniqueness of indium(III) chlorides in extraction studies. It has been found that the distribution coefficients for indium are abnormally low both in anion exchange[5] and solvent extraction.[6,7] Woodward and Taylor[8] have observed from Raman spectra that $InCl_4^-$ is not present in aqueous solution and have postulated that it is likely that the solutions contain instead anionic chloro complexes containing more than four chlorides per indium. However, Maydan and Marcus[9] noted that anion-exchange results are adequately described without including the penta- or hexachloride complexes. Thus a more detailed Raman study seems in order—one which differs from the earlier study in that Raman intensities as a function of concentration are photoelectrically measured. In addition, from measured Raman intensities it is possible to draw inferences concerning the nature of chemical bonding in complex ions,[10] and in the present study the Raman intensities will be measured in both aqueous and nonaqueous solvents.

Experimental Section

Chemicals used in this study were of analytical reagent grade. The indium stock solutions were prepared by dissolving metallic indium in perchloric acid to which was added a piece of platinum foil to speed the dissolution. The indium concentration was determined gravimetrically by precipitation with 8-hydroxyquinoline.[11] Solutions of $InCl_4^-$ in diethyl ether were prepared by dissolving indium metal in concentrated HCl, saturating the resultant solution with HCl gas, and extracting with diethyl ether.[8]

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TABLE I

RAMAN DATA FOR AQUEOUS INDIUM(III) BROMIDE SOLUTIONS

$[In^{3+}]$, *M*	$[Br^-]$, *M*	Br^-/In^{3+} ratio	Rel peak heights 220 cm^{-1}	200 cm^{-1}	180 cm^{-1}	160 cm^{-1}
0.788	0.198	0.250	0.0676	0.0358	0	0
0.493	0.493	1.00	0.140	0.133	0.0491	0
0.394	0.592	1.50	0.085	0.220	0.088	0.034
0.328	0.658	2.00	0.079	0.211	0.093	0.041
0.282	0.704	2.50	0.063	0.193	0.093	0.041
0.246	0.740	3.00	0.0442	0.166	0.128	0.057
0.219	0.767	3.50	0.056	0.169	0.107	0.050
0.197	0.789	4.00	0.046	0.146	0.092	0.040
0.164	0.822	5.00	0.040	0.132	0.083	0.036
0.141	0.845	6.00	0.033	0.166	0.068	0.029
0.123	0.863	7.00	0.031	0.110	0.073	0.032

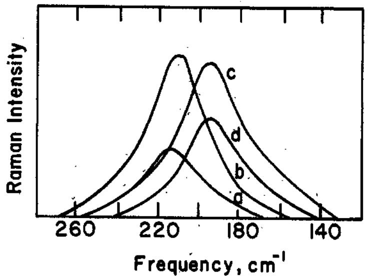

Figure 1.—Raman band for Job solutions with bromide-to-indium ratios of: a, 0.25; b, 1.00; c, 3.00; d, 6.00.

Spectra were recorded photoelectrically with a Cary 81 Raman spectrophotometer using the 4358-Å mercury line for excitation. All spectra were recorded at least six times alternating between the ν_1 line of perchlorate ion and the line of interest of the sample. In addition, a full spectrum of the sample from 0 to 1000 cm^{-1} was measured for each sample. Narrowing the slits from the nominal 10 cm^{-1} failed to produce sharper, better resolved bands. Sample tubes were surrounded by a Wratten 2-A filter and a Polaroid screen oriented such that the electric vector of the incident light was perpendicular to the sample tube axis (to eliminate the convergence error in intensity measurements). In the nonaqueous solutions the internal Raman intensity standards used were chloroform for the indium bromide solutions in methanol and diethyl ether itself in the ether extracts of indium chloride.

Results

For the bromide complexes of indium, a series of Raman experiments was run at various ratios of bromide to indium. In the entire series, only a single Raman line was observed at a frequency near 200 cm^{-1}. However, both the position of the band and its intensity changed with a change of the ratio of bromide to indium. The shape and changes of the band are shown in Figure 1. The changing contour indicates that more than one indium bromide species is present. In order to assess quantitatively the changes in terms of species in solution, the height of the envelope was measured at 20-cm^{-1} intervals. For a series of solutions prepared in the manner prescribed by Job,[12] which emphasizes change of species, the results of the contour height measurements are given in Table I. Plots of the data for 200 cm^{-1} or for 220 cm^{-1} show a distinct maximum at a bromide to indium ratio of 1.0, a shoulder at a ratio near 2.0, and a local maximum at 3.5. Plots of the 180- and 160-cm^{-1} contour heights show a maximum at a ratio of 3.0 and a distinct shoulder at 2.0.

As an aid to interpreting these Raman data, an electrophoresis experiment was performed with indium in a carrier electrolyte of 1.00 *M* NaBr to approximate the condition of the Raman experiments. The motion of the indium ion could be followed by spraying the filter paper at the end of a run with a dilute solution of 8-hydroxyquinoline which formed a bright yellow precipitate with indium. This experiment showed no observable transference of the indium species, indicating that, at the highest ratios of bromide to indium, the indium was present predominantly in an uncharged complex.

Raman spectra of the indium chloride solutions are similar to those for the indium bromide solutions. Again, only a single band is observed, this time centered near 300 cm^{-1}. Figure 2 shows that the peak is centered at 310 cm^{-1} for low chloride-to-indium ratios. The peak grows in intensity until the ratio reaches about 1.0; then with only slight changes in intensity, the peak maximum gradually migrates to about 295 cm^{-1} at a chloride-to-indium ratio of 4.0. At higher ratios, there is no further frequency change—only an intensity decrease due to the decreased In(III) concentration dictated by the Job method. The frequency shift of the peak maximum implies the existence of more than one species. In order to determine the nature of the species, again a Job study was performed and the results are given in Table

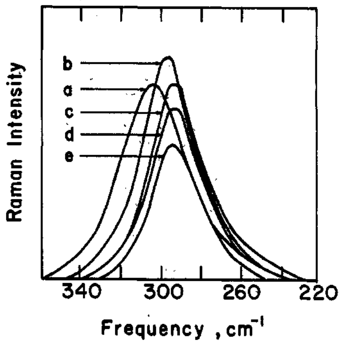

Figure 2.—Raman band for Job solutions with chloride-to-indium ratios of: a, 1.0; b, 2.0; c, 4.0; d, 5.0; e, 6.0.

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[12] P. Job, *Ann. Chim.* (Paris), [10] **9**, 113 (1928).

TABLE II

RAMAN DATA FOR AQUEOUS INDIUM(III) CHLORIDE SOLUTIONS

Cl^-/In^{3+} ratio	$[In^{3+}]$, M	$[Cl^-]$, M	Rel peak heights	
			320 cm^{-1}	280 cm^{-1}
0.167	2.01	0.335	0.062	
0.200	1.96	0.392	0.068	
0.250	1.88	0.470	0.071	
0.333	1.76	0.592	0.096	0.0431
0.500	1.58	0.790	0.116	0.068
1.00	1.18	1.18	0.177	0.122
1.50	0.94	1.41	0.118	0.168
2.00	0.78	1.56	0.104	0.185
2.50	0.67	1.68	0.085	0.203
3.00	0.59	1.77	0.078	0.184
3.50	0.523	1.83	0.054	0.188
4.00	0.472	1.89	0.056	0.189
5.00	0.393	1.97	0.036	0.155
6.00	0.395	2.01	0.034	0.149

II. The table includes the relative contour heights at 320 and 280 cm^{-1}. Plots of these heights *vs.* chloride-to-indium ratio show the following characteristics. At 320 cm^{-1} a strong maximum is observed at a ratio of 1.0 with a noticeable shoulder near 2.0 and another maximum at 4.0. For 280 cm^{-1} two maxima are observed—the first at a chloride-to-indium ratio of 2.5 and the second at 4.0. From this behavior of the intensities as a function of ratio, it is apparent that there are three different indium chloride complexes in solution. A plot of the intensity at 320 cm^{-1} divided by the total indium concentration increases in an almost linear fashion with total chloride concentration. Such behavior indicates a single species, with all of the chloride complexed. It seems reasonable to assume that this first species is the monochloro complex, as would be indicated even if not all of the chloride were complexed.

An electrophoresis experiment was performed in a carrier electrolyte of 2.00 *M* sodium chloride to approximate the conditions of the Raman experiments at a high chloride-to-indium ratio. This experiment showed anionic migration of indium at a rate approximately the same as dichromate ion which was run in parallel for comparison. In similar experiments with a carrier electrolyte of lower chloride concentration, the indium showed cationic migration.

In addition to the above measurements in aqueous solution, Raman spectra were measured in nonaqueous solutions. For indium bromide, methanol was used as solvent where it was found that the only species present is the tetrahedral $InBr_4^-$. This finding and the resulting spectrum is in agreement with an earlier study.[13]

A four-line Raman spectrum characteristic of a tetrahedral species was also observed for extracts from acidic indium chloride solutions into diethyl ether. For such solutions, the present measurements give Raman frequencies in close agreement with earlier work.[8] As was noted in both of the earlier studies, the spectra for the nonaqueous solutions differ significantly from those in aqueous solution indicating that different species are present in the different solvent systems. In addition to measuring the frequencies, the Raman intensities for the ν_1 (A_1) line of $InBr_4^-$ (197 cm^{-1}) and the ν_1 (A_1) line of $InCl_4^-$ (316 cm^{-1}) were determined. The molar intensity relative to carbon tetrachloride for $InBr_4^-$ was found to be 15.2 and for $InCl_4^-$ it was 7.80.

For the chloride solutions, experiments were run in methanol–water mixtures. For these experiments, three solutions were prepared all at the same indium ion concentration. Two of these solutions had chloride concentration 4 times that of indium; the third had a chloride concentration 10 times that of indium. In one of the solutions with a 4:1 ratio of chloride to indium, perchloric acid was added to 6 times the concentration of indium. The three solutions were then diluted to 10 times their volume with methanol and the Raman spectra were recorded. Figure 3 shows these spectra. Comparison of these results with Figure 2 shows that in a solution with only a 4:1 ratio of chloride to indium without $HClO_4$ there is little difference from the corresponding aqueous system. However, upon addition of either more Cl^- or perchloric acid, the Raman spectrum indicates formation of a new species with a spectrum which is that of the $InCl_4^-$ ion in diethyl ether (ν_1 316 cm^{-1}).

Discussion

Comparison of the Raman spectra of indium bromide solutions in methanol, where the species is clearly tetrahedral, with the spectra in aqueous solutions indicates that the tetrahedral $InBr_4^-$ ion is not formed in aqueous solution. From the frequency of the aqueous solution spectra (A_1 higher than that for the tetrahedral species) and from the greater width of the A_1 line, it has been postulated that the aqueous solutions contain a mixture of complexes containing less than four bromides.[13] The Job analyses made in the present studies are consistent with this finding. The facts that the contour height in the region 200–220 cm^{-1} peaks at a 1:1 ratio of bromide to indium and that

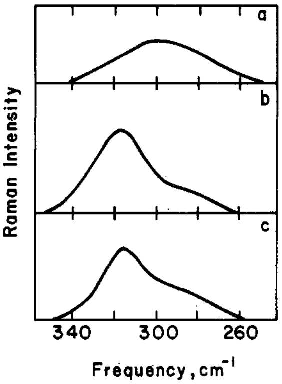

Figure 3.—Raman spectra of indium chloride solution in methanol–water: (a) 4 Cl^- per In(III); (b) 10 Cl^- per In(III); (c) 4 Cl^- and 10 $HClO_4$ per In(III).

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[13] L. A. Woodward and P. T. Bill, *J. Chem. Soc.*, 1699 (1955).

in the 160–180-cm^{-1} region it peaks at ratio of 3 with a definite shoulder at a ratio of 2 indicate that all three of the lower species are present in solution. That the highest of these three species is not a tetrabromo complex is indicated by the lack of anionic migration in the electrophoresis experiment. To further substantiate these conclusions, stepwise equilibrium constants for the formation of the three indium bromide complexes in aqueous solution were calculated. It was necessary to assume that at the lowest bromide to indium ratio, all of the bromide was in the form of the monobromide and at the highest ratio all the indium was in the form of the highest bromide to indium complex. The equilibrium constants so obtained were by far the most constant if the three species were assumed to be the mono-, the di-, and the tribromide complexes. The constants so obtained (and each was constant to ±50%) were 50, 5, and 5 for the three successive steps.

For the aqueous indium chloride solutions the situation seems more complicated than for bromide solutions. Although the Job analysis of the band contour again indicates three complex species, it further indicates that the highest of these may well be the tetrachloro complex. This is consistent with the electrophoresis experiment in which anionic migration was shown for the chloride as opposed to the bromide. The species does not seem to be $InCl_6^{3-}$, which has ν_1 at 277 cm^{-1} in the solid state.[14] A pentachloro complex is less easily eliminated since a Raman line at 294 cm^{-1} has been assigned to $InCl_5^{2-}$ in an anhydrous solid.[15] However, comparison of the spectra in water with those in ether indicates that if a tetrachloro complex is formed in water, it cannot be the same as the tetrahedral $InCl_4^-$ found in ether solution. Of particular significance are the experiments performed in methanol–water mixtures. These experiments indicate that at a 4:1 ratio of chloride to indium the predominant species is the same as for the purely aqueous solutions at high chloride concentration. If however the water activity in these solutions is lowered by adding either additional chloride or perchloric acid, there is the appearance of the tetrachloroindium complex as found in ether solution. It seems reasonable to conclude that there is present in the predominantly aqueous phases a tetrachloroindium species which contains additional waters of hydration as has been proposed by Tuck and Woodhouse.[16] This can account for the lowered Raman frequency, for the poor extractability into ether, and for the apparent equilibrium in the methanol–water mixtures which appears to shift as a function of water activity.

The question next arises as to the nature of the two additional indium chloride complexes in the aqueous phase. The one which forms at lowest chloride to indium ratio has an A_1 frequency near 280 cm^{-1}. As noted, experiments performed at low ratios of chloride to indium were consistent with this species being the monochloro complex. There is less evidence as to the nature of the species intermediate between this and the solvated tetrachloro complex. In an attempt to find whether it is the dichloro or trichloro complex, which is more probable, equilibrium constants were calculated using the same assumptions as for the bromide solutions. Assuming that the two lower species were the monochloro and the trichloro complexes did not give acceptably constant values. In particular, the values found for the first constant varied by some two orders of magnitude and that for the third constant varied by four orders of magnitude. If, however, the two species were assumed to be the monochloro and the dichloro complexes, reasonably constant values were obtained. The best average values for the first two stepwise association constants are 10 and 5. For the formation of the tetrachloro complex from the dichloro complex a constant of about 30 is indicated. It should be noted that the present work does not eliminate the possibility of the existence of a trichloro species, but if it does exist, it must be in much lower concentration than that of the other complexes or else have a much less intense Raman spectrum which seems unlikely.

From the intensities determined for the tetrahedral complexes $InCl_4^-$ and $InBr_4^-$ present in nonaqueous solutions, estimates can be made of the type of bonding present in the complexes. It is instructive to compare these values with corresponding ones for the gallium tetrahalides since the two metals seem to show relatively large differences in their behavior in aqueous solution. Whereas gallium forms only the tetrahalide complex in water, indium forms lower species and shows no tendency to form the simple tetrahedral halide complex with either chloride or bromide. For comparisons of Raman intensity, the useful quantity is $\partial\bar{\alpha}/\partial r$, the change of mean molecular polarizability with interatomic distance.[17] From the intensities found for indium tetrachloride and indium tetrabromide values can be calculated[18] for $\partial\bar{\alpha}/\partial r$ of 2.34 Å^2 for $InCl_4^-$ and 6.24 Å^2 for $InBr_4^-$. These can be compared with the corresponding values for $GaCl_4^-$ of 1.12 Å^2 (from a molar Raman intensity of 1.04 relative to 1 M CCl_4) and 3.08 Å^2 (from a molar Raman intensity of 2.96 relative to 1 M CCl_4) determined previously in our laboratory.[19] Although the values are both larger for indium than for the corresponding gallium species, the difference may be largely due to the increased bond length in the indium complex. Making correction for the size and electronegativity differences,[10] the covalent bond orders calculated for $InCl_4^-$ and $InBr_4^-$ are 0.44 and 1.0, respectively. These correspond to covalent bond orders for the gallium complexes of 0.26 for $GaCl_4^-$ and 0.64 for $GaBr_4^-$. Although the indium

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[15] I. Wharf and D. F. Shriver, *Chem. Commun.*, 526 (1968).

[16] D. G. Tuck and E. J. Woodhouse, *J. Chem. Soc.*, 6017 (1964).

[17] L. A. Woodward and D. A. Long, *Trans. Faraday Soc.*, **45**, 1131 (1949).

[18] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **32**, 319 (1960).

[19] Work performed by Gertrude Schuler Kudrak and James Nixon.

complexes thus seem to show increased covalency, it is not obvious that there is a sufficiently large difference to cause the marked difference in behavior between the two elements. Instead, the difference in the nature of the tetrahalo complexes in aqueous solution may lie in the fact that the smaller gallium ion does not exhibit a coordination number greater than 4 as would be called for by a mixed halide–water complex.

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Fluorine-19 Nuclear Magnetic Resonance Studies of Diamagnetic Fluoride Complexes of Nickel(IV), Palladium(IV), and Platinum(IV) in Anhydrous Hydrogen Fluoride Solutions[1]

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Received July 9, 1968

The ^{19}F nuclear magnetic resonance spectra of the complexes MF_6^{2-} [M represents Ni(IV), Pd(IV), and Pt(IV)], prepared by dissolving the K^+ or Rb^+ salts in anhydrous HF, have been studied over the temperature range -60 to $+15°$. These diamagnetic complexes, having M(IV) in the low-spin d^6 electronic configuration, exhibit extremely large diamagnetic ^{19}F shifts which are independent of the temperature: NiF_6^{2-}, +253 ppm; PdF_6^{2-}, +284 ppm; and PtF_6^{2-}, +297 ppm, with respect to the doublet signal of the external standard, $CFCl_2CF_2Cl$. The ^{19}F line widths of the PtF_6^{2-} and PdF_6^{2-} ions are narrow at all temperatures indicating that the ions are nonlabile. The line widths obtained for the solutions of K_2NiF_6 and Rb_2NiF_6 are large, but evidence is presented that these are due, not to the lability of NiF_6^{2-}, but to the presence of small amounts of a paramagnetic Ni(III) complex in the salts. The ^{195}Pt–^{19}F spin–spin coupling constant, 2082 Hz, was obtained from the spectra of PtF_6^{2-}.

Introduction

Nickel(IV),[3,4] palladium(IV),[5] and platinum(IV)[5] form diamagnetic fluoride complexes A_2MF_6 containing the octahedral MF_6^{2-} unit in which the central metal ion has the low-spin d^6 electronic configuration. Spectroscopic and magnetic data[3-5] have been obtained for the solids but little is known about the chemistry of these unusual species in solution. As part of a general program of study of the solution chemistry of fluoride complexes, particularly those of metal ions in unusual oxidation states, we have obtained the ^{19}F nmr spectra of solutions of the salts KMF_6. Because these tetravalent ions are reduced by water, we found it was necessary to employ another solvent. Anhydrous HF, which is an excellent solvent for electrolytes and which is extremely resistant to oxidation, proved to be satisfactory.

Experimental Section

1. Preparation of K_2MF_6.—The salts K_2MF_6 were prepared by fluorinating the appropriate divalent cyanide $K_2M(CN)_4$ or chloride K_2MCl_4 complexes. Both starting materials gave the same solid product after the treatment with fluorine. In several experiments, the salt Rb_2NiF_6 was employed. It was prepared by fluorinating $Rb_2Ni(CN)_4$.

In a representative preparation of the K_2MF_6 salt, several grams of $K_2M(CN)_4$ was charged to a sapphire boat which was then placed in a nickel reactor. An equimolar ratio of F_2 and He gases at 1 atm was then streamed through the reactor for several hours at 425°. Following this treatment, pure F_2 gas at 3 atm was admitted to the reactor which was held at 425° for 24 hr. After cooling the reactor to $\sim 25°$, the residual F_2 gas was displaced by helium.

The reactor was opened to an inert-atmosphere (helium) box, the sapphire boat was removed, and the product was ground in a mortar. The product was then recharged to the sapphire boat in the reactor and was refluorinated to ensure complete conversion to K_2MF_6.

The ^{19}F nmr spectra of concentrated HF solutions of the K_2MF_6 salts prepared from $K_2M(CN)_4$ are identical with those of K_2MF_6 prepared from K_2MCl_4. In each case, only the signals attributable to HF and the MF_6^{2-} ion could be distinguished. X-Ray powder patterns of the preparations were in excellent agreement with the data reported by Klemm and Huss for K_2NiF_6.[3]

2. Preparation of Solutions.—All solutions for the nmr measurements were prepared by weight under inert-atmosphere conditions. Cylindrical Kel-F tubes (inner diameter ~ 3 mm and outer diameter ~ 3.5 mm) were sealed at one end. These were fitted with nickel valves at the open end and attached to a fluorine-transfer line and treated with F_2 gas to remove adsorbed water and oxygen. After F_2 had been displaced from the tube with He gas, the tube was evacuated, detached, weighed, charged with 100–200 mg of K_2MF_6 in an inert-atmosphere box, again evacuated, and reweighed. The tube was then attached to an HF-transfer line and 0.5–0.8 ml of prepurified HF was distilled into the tube.[6] After the appropriate amount of HF had been

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[1] This work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Visiting Staff Member from The Pennsylvania State University.

[3] W. Klemm and E. Huss, *Z. Anorg. Chem.*, **258**, 221 (1949).

[4] M. J. Reisfeld, L. B. Asprey, and R. A. Penneman, *J. Mol. Spectry.*, **29**, 109 (1969).

[5] D. H. Brown, D. R. Russell, and D. W. A. Sharp, *J. Chem. Soc., A*, 18 (1966), and references therein.

[6] HF (Matheson) was purified by treatment with F_2 gas on a fluorine-transfer line. It was then distilled into a Kel-F storage bulb containing K_2NiF_6, an excellent scavenger for oxygen. In the preparation of the solutions it was distilled from the storage bulb.