Table III. Kinetic Parameters for Aquation of N-Bonded Cr(III) Complexes at 25 °C[a]

	$10^6 k$, s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} K^{-1}	ref
$Cr(EtaH)_3(OH_2)_3^{3+}$	227	18.0	−15	*b*
	130	16.1	−23	4a
fac-$Cr(NH_3)_3(OH_2)_3^{3+}$	0.0017	27.2	−4	16
$Cr(EtaH)_2(OH_2)_4^{3+}$	16.8	21.3	−9	*b*
	81	16.0	−24	4a
cis-$Cr(NH_3)_2(OH_2)_4^{3+}$	0.0071	27.5	−4	6
$Cr(EtaH)(OH_2)_5^{3+}$	0.64	21.2	−16	*b*
	30	15.3	−25	4a
$Cr(NH_3)(OH_2)_5^{3+}$	0.0019	28.0	−4	6
$Cr(enH)(OH_2)_5^{3+}$	0.021	25.4	−11	17

[a] *k*'s extrapolated to 25 °C when necessary. [b] This work.

The stage III aquations of the monodentate N-bonded 2-aminoethanol complexes are seen to be much faster than those of the analogous ammine or monodentate 1,2-diaminoethane complexes (Table III) by factors as high as 10^5. Facial and cis configurations are assumed for the tri- and disubstituted complexes because they are so readily produced from the solid dimer with a facial arrangement of oxygens. The qualitative rate comparisons are not affected by this assumption. These data suggest a mechanism for labilization that involves a reduction of activation enthalpy. By analogy with the labilizations described above, perhaps pseudochelate formation without breaking the Cr–O bond reduces the energy required to break the Cr–N bond.

[We agree with the suggestion of a reviewer that, within experimental error, ΔH and ΔS for the second step of the amine aquation could be equal to the mean values for the first and third steps. This corresponds to uncertainties of 0.5 kcal mol^{-1} and 4 cal mol^{-1} K^{-1}, respectively.]

Acknowledgment is made to Liquid Carbonics Corp., Subsidiary of Houston Natural Gas, for support of this research.

Registry No. $Cr(Eta)_3$, 38819-71-5; $[Cr_2(Eta)_3(EtaH)_3]I_3$, 86852-61-1; $[Cr_2(Eta)_3(EtaH)_3](ClO_4)_3$, 86852-63-3; $[Cr(Eta)_2(EtaH)(OH_2)]Cl$, 22764-68-7; $[CrCl_2(OH_2)_4]Cl$, 13820-85-4; $Cr(Apr)_3$, 86834-54-0; $Cr(i\text{-}Pra)_3$, 86834-55-1; $[Cr(n\text{-}Pra)_2(n\text{-}PraH)(OH_2)]Cl$, 62768-52-9; $Cr(EtaH)_3^{3+}$, 52242-22-5; $Cr(EtaH)_3(OH_2)_3^{3+}$, 57385-74-7; $Cr(EtaH)_2(OH_2)_4^{3+}$, 86834-56-2; $Cr(EtaH)(OH_2)_5^{3+}$, 86834-57-3; $Cr[AprH]_3^{3+}$, 86834-58-4; $Cr_2[Apr]_3[AprH]_3^{3+}$, 86852-64-4.

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Coordinatively Saturated Complex Fluoro Cations. Synthesis and Characterization of $ClF_6^+AsF_6^-$ and $ClF_6^+SbF_6^-$

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The reaction of KrF_2 with ClF_5 and AsF_5 in either ClF_5 or anhydrous HF solution produces pure $ClF_6^+AsF_6^-$. The white, crystalline solid is stable up to 110 °C under a dynamic vacuum and decomposes at higher temperature to ClF_5, F_2, and AsF_5. X-ray powder diffraction patterns show that $ClF_6^+AsF_6^-$ (face-centered cubic; $a = 9.47$ Å) is isotypic with $IF_6^+AsF_6^-$. The reaction of KrF_2 with ClF_5 and SbF_5 produces $ClF_6^+SbF_6^-$; however, this salt could not be isolated in pure form. ^{19}F NMR and vibrational spectra were recorded for the ClF_6^+ salts, and an anharmonic general valence force field was computed for ClF_6^+ by using the observed frequencies and the ^{35}Cl–^{37}Cl isotopic shift of ν_3 (F_{1u}). General methods for the syntheses of coordinatively saturated complex fluoro cations are compared and discussed.

Introduction

The two kinetically most stable covalent inorganic fluorides are CF_4 and SF_6. Their exceptional stability is due to the energetically favorable sp^3 and sp^3d^2 hybridization, respectively, of the valence-electron orbitals of the central atoms and their coordinative saturation. Their isoelectronic complex fluoro cations are NF_4^+ and ClF_6^+, respectively. Recent studies in our and other laboratories have shown that the NF_4^+ cation possesses unusual kinetic stability[1] and forms a surprisingly large number of stable salts.[2] Consequently, a similar behavior might be predicted for ClF_6^+, which is isoelectronic with SF_6.

Although the ClF_6^+ cation has been known for a decade,[3-5] the only salt prepared to date is its PtF_6^- salt

$$2ClF_5 + 2PtF_6 \xrightarrow[\text{Pyrex filter}]{\text{UV}} ClF_6^+PtF_6^- + ClF_4^+PtF_6^- \quad (1)$$

$$6FClO_2 + 6PtF_6 \rightarrow 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2 \quad (2)$$

In both reactions the $ClF_6^+PtF_6^-$ product could not be separated from the other solid byproducts, and to our knowledge the preparation of a pure ClF_6^+ salt has previously not been achieved. Although claims for the syntheses of $ClF_6^+AuF_6^-$[6] and $ClF_6^+CuF_4^-$[7] have previously been made, either these claims have been withdrawn[8] or, for $ClF_6^+CuF_4^-$, the reported properties are incompatible with the presence of a ClF_6^+ salt.[42] Therefore, the purpose of this study was the preparation of pure ClF_6^+ salts, preferably containing counterions more accessible than the exotic PtF_6^-.

Experimental Section

Caution! The reaction of KrF_2 with AsF_5 can result in a spontaneous exothermic decomposition of KrF_2 accompanied by a bright flash and gas evolution.[9] Proper safety precautions should be used in working with this system.

Apparatus and Materials. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless-steel-Teflon FEP vacuum system. The reactions between KrF_2, ClF_5, and a Lewis acid were carried out in either a 10-mL stainless-steel cylinder (Hoke) or a 30 cm long, 0.5-in. o.d. sapphire tube that was connected to a stainless-steel valve with a Swagelok compression fitting using a Teflon

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front and a stainless-steel backup ferrule. A metal support frame was used to guard against slippage of the sapphire tube out of the compression seal at elevated pressure. To avoid the facile decomposition of KrF_2 during dead-end transfers, the reactors were designed to permit pump-through operation by means of a dip tube. Solid materials were handled in the dry-nitrogen atmosphere of a glovebox.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.[10,11] The reported frequencies and isotopic shifts are believed to be accurate to ±2 and ±0.3 cm^{-1}, respectively. Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Claassen filter[12] for the elimination of plasma lines. Sealed glass or quartz tubes were used as sample containers. The low-temperature spectra were recorded by using a previously described device.[13]

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer using heat-sealed Teflon FEP sample tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard with positive shifts being downfield from the standard.[14]

X-ray powder diffraction patterns were recorded on a General Electric XRD6 diffractometer using Ni-filtered Cu Kα radiation. The sample holder was machined out of a solid Teflon block, and the powdered sample was held in place and protected against atmospheric moisture by a 1 mil thick Teflon FEP sheet, which was sealed against the Teflon block with a plastic snap ring. Lines having θ values of less than 10° were difficult to measure by this technique due to interference by Teflon lines. The instrument was calibrated with NaCl and IF_6AsF_6 powder.

Chlorine pentafluoride[15] and KrF_2[16-18] were prepared by previously described methods. Hydrogen fluoride (Matheson) was dried by storage over BiF_5.[19] Arsenic pentafluoride (Ozark Mahoning) and BF_3 (Matheson) were purified by fractional condensation, and SbF_5 (Ozark Mahoning) was purified by distillation.

Synthesis of ClF_6AsF_6. In a typical experiment, KrF_2 (11.61 mmol) and AsF_5 (11.60 mmol) were combined at −196 °C in a 33-mL sapphire reactor. The mixture was allowed to warm slowly to −78 °C and then to ambient temperature for 10 min, resulting in the formation of solid $KrFAsF_6$. The sapphire tube was cooled to −142 °C, and the amount of Kr and F_2 (0.50 mmol) that had formed by decomposition of some KrF_2 during the $KrFAsF_6$ formation was measured. Chlorine pentafluoride (29.6 mmol) was added to the reactor at −142 °C, and the mixture was gently warmed to ambient temperature for 30 min, resulting in a clear colorless solution containing some white solid. Slow gas evolution was observed and measured by recooling the reactor to −142 °C. This process was repeated 10 times, and the reactor was finally kept at ambient temperature for 2 days and at 40 °C for 1 h. A total of about 21 mmol of gas (Kr and F_2), volatile at −142 °C, was removed in this manner, suggesting that the decomposition of KrF_2 was essentially complete. The unreacted ClF_5 and any ClF_4AsF_6 that has a dissociation pressure of about 1 atm at room temperature[20] were pumped off at 25 °C for 12 h. The white solid residue (428.4 mg = 1.27 mmol) was shown by ^{19}F NMR, infrared, and Raman spectroscopy to consist of pure ClF_6AsF_6 (11.15% yield based on $KrFAsF_6$).

The reaction between $KrFAsF_6$ and ClF_5 was carried out as described above, except for adding about 6 mL of liquid HF to the reactor after the KrF_2 addition and before the AsF_5 addition. The Kr and F_2 evolution at ambient temperature was faster than in the absence of HF; however the yield of ClF_6AsF_6 (based on $KrFAsF_6$) was only 3.33%.

When $Kr_2F_3^+AsF_6^-$ was reacted with an excess of ClF_5 in the absence of HF, the best yield of $ClF_6^+AsF_6^-$ obtained was 18.36%, based on AsF_5, and 9.18%, based on KrF_2, but on several runs, yields of only about 6% were obtained.

Synthesis of ClF_6SbF_6. In the drybox SbF_5 (1.67 mmol) was syringed into a passivated sapphire reactor, and KrF_2 (7.19 mmol) was added at −196 °C on the vacuum line. The mixture was carefully warmed to room temperature and then recooled to −78 °C. This temperature cycling was repeated several times and a small amount of Kr and F_2 (0.42 mmol) formed by decomposition of some KrF_2 was pumped off at −78 °C. Chlorine pentafluoride (15.94 mmol) was added to the reactor at −196 °C, and the resulting mixture was warmed for 30 min to 25 °C. At this temperature slow gas evolution was observed. The reactor was cooled to −196 °C and then to −142 °C at which temperatures F_2 (1.1 mmol) and Kr (1.2 mmol) were pumped off and measured. This procedure was repeated several times to avoid overpressurization of the reactor by the evolved F_2 and Kr. When the KrF_2 decomposition rate became very slow, the temperature was raised to 35 °C. After most of the KrF_2 had been decomposed and removed in this manner, the excess of ClF_5 was pumped off at 25 °C. The white solid residue (896 mg) was shown by infrared, Raman, and ^{19}F NMR spectroscopy to be a mixture of ClF_6SbF_6, ClF_4SbF_6, and $KrF_2{\cdot}nSbF_5$. Heating of the solid to 50 °C for 4 h under a dynamic vacuum resulted in decomposition and removal of all $(KrF_2)_n{\cdot}SbF_5$, leaving behind a mixture (~0.6 g) of ClF_6SbF_6, ClF_4SbF_6, and the corresponding polyantimonates, as shown by infrared and Raman spectroscopy.

Results and Discussion

Synthesis of Coordinatively Saturated Complex Fluoro Cations. At present, only three coordinatively saturated complex fluoro cations are known. They are NF_4^+, ClF_6^+, and BrF_6^+.[21,22] The principal difficulty with their syntheses stems from the fact that the corresponding parent molecules, NF_5, ClF_7, and BrF_7, do not exist.[1,5,21] Therefore, a simple transfer of a fluoride anion to a strong Lewis acid according to

$$ClF_7 + AsF_5 \rightarrow ClF_6^+AsF_6^- \tag{3}$$

is not possible. Addition of a fluorine cation F^+ to a lower fluoride according to

$$ClF_5 + F^+ \rightarrow ClF_6^+ \tag{4}$$

is preempted by the fact that fluorine is the most electronegative element, and F^+ can therefore not be generated by chemical means.

The following three methods are presently known for the synthesis of these coordinatively saturated complex fluoro cations.

(i) Reaction of a Lower Fluoride with F_2 and a Lewis Acid in the Presence of an Activation Energy Source,[23] Such as Heat,[24] Glow-Discharge,[23,25] Bremsstrahlung,[26] or UV Photolysis.[27] This method is well suited for the synthesis of NF_4^+ salts according to

$$NF_3 + F_2 + MF_5 \xrightarrow{\Delta E} NF_4^+MF_6^- \tag{5}$$

However, many attempts in our laboratory to apply this me-

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Table I. X-ray Data for ClF_6AsF_6[a]

d(obsd), Å	d(calcd), Å	I/I_0	hkl
3.35	3.35	100	220
2.855	2.858	25	331
2.740	2.737	60	222
2.179	2.175	15	331
2.120	2.120	25	420
1.936	1.935	65	422
1.826	1.824	10	511/333
1.677	1.676	45	440
1.601	1.602	15	531
1.580	1.580	70	600/442
1.498	1.499	20	620
1.428	1.429	25	622
1.367	1.368	10	444
1.313	1.315	25	640
1.265	1.267	25	642

[a] Cu Kα radiation and Ni filter; space group $Pa3$; face-centered cubic; $a = 9.47$ Å; $Z = 4$; $V = 849.3$ Å^3; d(calcd) = 2.631 g cm^{-3}.

thod to ClF_6^+ were unsuccessful because these activation energy sources decompose ClF_5 to F_2 and ClF_3 with the latter reacting instantaneously with strong Lewis acids to form ClF_2^+ salts.

(ii) Reaction of PtF$_6$ with a Lower Fluoride. As shown in (1) and (2), this method has successfully been applied to the synthesis of ClF_6^+ salts.[3-5] However, attempts to prepare NF_4^+ salts in the same manner have failed. For the preparation of NF_4PtF_6, elevated temperature and pressure are required,[28] i.e. conditions under which PtF_6 decomposes to PtF_5 and F_2, hereby corresponding to reaction 5 of method i.

(iii) Reaction of KrF$_2$ with a Lower Fluoride in the Presence of a Strong Lewis Acid. This method has successfully been used for the synthesis of BrF_6^+ [21] and NF_4^+ [29,30] salts

$$NF_3 + KrF_2 + MF_5 \rightarrow NF_4^+MF_6^- + Kr \qquad (6)$$

$$BrF_5 + KrF_2 + MF_5 \rightarrow BrF_6^+MF_6^- + Kr \qquad (7)$$

The most promising method for the synthesis of pure ClF_6^+ salts appeared to be method iii, the reaction of ClF_5 with KrF_2 in the presence of a Lewis acid. Indeed, it was found that KrF_2–Lewis acid adducts are capable of oxidatively fluorinating ClF_5 to ClF_6^+. It was found advantageous to preform the well-known adducts[9,21,31,32] between KrF_2 and the Lewis acids, AsF_5 and SbF_5, before addition of the ClF_5. The yields of ClF_6^+ salts were as high as 11%, based on the amount of KrF_2 used in the reaction. The reactions proceeded whether KrF^+ or $KrF^+\cdot nKrF_2$ salts were used as starting materials, although the ClF_6^+ yields, based on KrF_2, appeared higher when KrF^+ salts were used. An excess of ClF_5 as a solvent gave the highest yields of ClF_6^+ salts. Addition of anhydrous HF as a diluent significantly reduced the ClF_6^+ yield.

The $ClF_6^+AsF_6^-$ salt could readily be prepared in pure form because the byproduct $ClF_4^+AsF_6^-$ is unstable at ambient temperature[20] and because AsF_6^- does not form stable polyanions with AsF_5. For $ClF_6^+SbF_6^-$, the stability of $ClF_4^+SbF_6^-$ [20] and the tendency of SbF_5 to form stable polyanions did not permit isolation of the pure compound.

Properties of $ClF_6^+AsF_6^-$ and $ClF_6^+SbF_6^-$. Both compounds are white, crystalline, hygroscopic solids that are stable at room temperature. As a result of the above described experimental difficulties, only $ClF_6^+AsF_6^-$ could be prepared in a pure state and therefore was characterized more thoroughly than $ClF_6^+SbF_6^-$. The $ClF_6^+AsF_6^-$ salt is stable up to 110 °C. Above this temperature it begins to slowly decompose according to

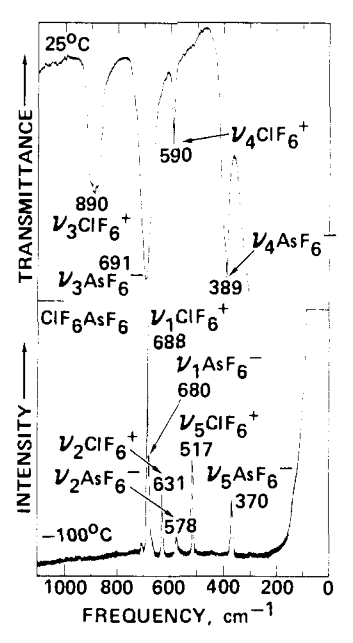

Figure 1. Infrared and Raman spectra of solid ClF_6AsF_6 and assignments to the ions in point group O_h. The broken line is due to absorption by the AgCl window material.

$$ClF_6AsF_6 \rightarrow ClF_5 + F_2 + AsF_5 \qquad (8)$$

The infrared spectra of the gaseous decomposition products showed ClF_5 and AsF_5 in a 1:1 mole ratio.

The X-ray powder diffraction data of ClF_6AsF_6 are given in Table I. The lines for hkl = 110 and 200 could not be observed by our technique due to an intense broad background peak below a 2θ value of 20°. The observed data show that ClF_6AsF_6 is isotypic with IF_6AsF_6[33,34] and BrF_6AsF_6,[16] although surprisingly the unit cell dimension of ClF_6AsF_6 (9.47 Å) is only slightly smaller than that of IF_6AsF_6 (9.49 Å)[33,34] and larger than that of BrF_6AsF_6 (9.39 Å).[16] A more detailed study for this series of compounds is needed to verify this effect.

The ^{19}F NMR spectra of these salts were recorded in anhydrous HF solutions at 29 °C. In addition to a broad unresolved resonance due to rapidly exchanging HF and the anions, a sharp signal was observed at 383.3 ppm downfield from external $CFCl_3$. In good agreement with a previous report,[35] the signal consisted of two sharp (half-width ~5 Hz) sets of quadruplets of equal intensity due to the ^{35}Cl and ^{37}Cl isotopes ($I = {}^3/_2$) with $J_{^{35}ClF}$ = 340 Hz, $J_{^{37}ClF}$ = 283 Hz, and $J_{^{35}ClF}/J_{^{37}ClF}$ = 1.201.

The vibrational spectra of $ClF_6^+AsF_6^-$ are shown in Figure 1, together with a listing of the observed frequencies and assignments for the two ions in point group O_h. The only band not marked in Figure 1 is the weak Raman band at 706 cm^{-1}, which can be assigned to $2\nu_6$ ($A_{1g} + E_g + F_{1g} + F_{2g}$) of ClF_6^+ being in Fermi resonance with ν_1 (A_{1g}) at 688 cm^{-1}. The value of 353 cm^{-1} thus obtained for the infrared and Raman-inactive ν_6 (F_{2u}) mode is in excellent agreement with the value of 347 cm^{-1} reported for the isoelectronic SF_6 molecule.[36] The frequencies for ClF_6^+ in its SbF_6^- salt were within experimental error identical with those of the AsF_6^- salt and therefore are not listed separately. These vibrational spectra confirm our previous assignments[5] for ClF_6^+, which had to be made for

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Table II. Symmetry and Valence Force Constants (mdyn/Å) of ClF_6^+ Compared to Those of BrF_6^+, IF_6^+, SF_6, SeF_6, and TeF_6

assign (O_h)	$^{35}ClF_6^+$ freq, cm^{-1}	force constants	ClF_6^+ (AH)[a]	SF_6 (AH)[b]	SF_6 (H)[c]	BrF_6^{+d}	$SeF_6{}^e$	IF_6^{+d}	$TeF_6{}^f$
		Symmetry Force Constants							
A_{1g}	ν_1 688	$F_{11} = f_r + 4f_{rr} + f_{rr'}$	5.298	6.70	6.845	4.88	5.61	5.61	5.50
E_g	ν_2 631	$F_{22} = f_r - 2f_{rr} + f_{rr'}$	4.456	4.61	4.715	5.02	4.85	6.00	5.08
F_{1u}	ν_3 894	$F_{33} = f_r - f_{rr'}$	5.200	5.30	5.465	4.82	4.93	5.23	4.98
	ν_4 590	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	0.957	1.034	1.051	0.63	0.646	0.45	0.40
		$F_{34} = 2(f_{r\alpha} - f_{r\alpha''})$	0.935	0.90	0.907	0.41	0.46	0.21	0.24
F_{2g}	ν_5 517	$F_{55} = f_\alpha - 2f_{\alpha\alpha'} + f_{\alpha\alpha'''}$	0.748	0.765	0.780	0.46	0.453	0.32	0.27
F_{2u}	ν_6 347	$F_{66} = f_\alpha - 2f_{\alpha\alpha} + 2f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	0.674	0.670	0.693		0.389		0.22
		Valence Force Constants							
		f_r	4.968	5.30	5.445	4.90	5.02	5.42	5.10
		f_{rr} (adjacent bonds)	0.140	0.348	0.355	−0.03	0.13	−0.07	0.07
		$f_{rr'}$ (opposite bonds)	−0.232	0.003	−0.020	0.08	0.09	0.19	0.12
		$f_\alpha - f_{\alpha\alpha'}$ ($\approx f_\alpha$)	0.782	0.809	0.826		0.49		0.30
		$f_\alpha - f_{\alpha\alpha'''}$	0.816	0.852	0.872		0.52		0.31
		$f_{r\alpha} - f_{r\alpha''}$	0.468	0.45	0.454	0.21	0.23	0.11	0.12

[a] Using observed frequencies and a ^{35}Cl–^{37}Cl isotopic shift of 13.1 cm^{-1} for ν_3. PED for F_{1u}: ν_3, 1.21 (3), 0.24 (4), −0.46 (3, 4); ν_4, 0.98 (4), 0.02 (3, 4). [b] Using observed frequencies.[36] [c] Using harmonic frequencies.[36] [d] Modified valence force field values from ref 16, assuming F_{44} = minimum. [e] Data from ref 37. [f] Data from ref 38.

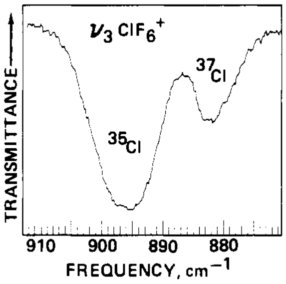

Figure 2. Infrared spectrum of the ν_3 (F_{1u}) band of ClF_6^+ in solid ClF_6SbF_6 recorded with 20-fold scale expansion under higher resolution conditions.

rather complex mixtures and therefore were somewhat tentative. Furthermore, the fact that both ClF_6^+ and AsF_6^- show no detectable deviations from the O_h selection rules suggests little or no ion interaction or distortion in $ClF_6^+AsF_6^-$, as expected for these coordinatively saturated ions. The structure of ClF_6AsF_6 can be visualized as a closest fluoride packing with Cl and As occupying some of the interstices in the lattice.

Under higher resolution conditions, the infrared spectra of ClF_6AsF_6 and ClF_6SbF_6 showed a splitting of the ν_3 (F_{1u}) band into two components (see Figure 2). These splittings are due to the ^{35}Cl and ^{37}Cl isotopes, which have a natural abundance of 75.4 and 24.6%, respectively. From a series of measurements the chlorine isotopic shifts for ν_3 (F_{1u}) of ClF_6^+ were found to be 12.8 ± 0.3 cm^{-1} for ClF_6AsF_6 and 13.4 ± 0.3 cm^{-1} for ClF_6SbF_6. On the basis on these data, a value of 13.1 ± 0.3 cm^{-1} was used for the force field computation of ClF_6^+.

General Valence Force Field of ClF_6^+. Modified valence force fields (MVFF) have previously been reported for IF_6^+,[33] BrF_6^+,[16] and ClF_6^+[5,16] by using for the underdetermined F_{1u} block (two frequencies; three symmetry force constants) the mathematical constraint F_{44} = minimum. A test of this constraint for the isoelectronic series TeF_6, SeF_6, and SF_6 for which fully determined general valence force fields (GVFF) are known[36–38] showed that F_{44} = minimum is a good approximation for TeF_6 and SeF_6.[16] However, for the lighter SF_6, which is isoelectronic with ClF_6^+, this approximation did not duplicate the GVFF values[36] very well. Therefore, for ClF_6^+ a second force field based on a transfer of the $f_{rr'}$ value of the GVFF of SF_6 to ClF_6^+ was preferred.[5] In the resulting force field, however, the value of the Cl–F stretching force constant (4.68 mdyn/Å)[5] was smaller than that found for ClF_2^+ (4.7 mdyn/Å);[39] a surprising result in view of the general trends observed for a large number of halogen fluorides.[40]

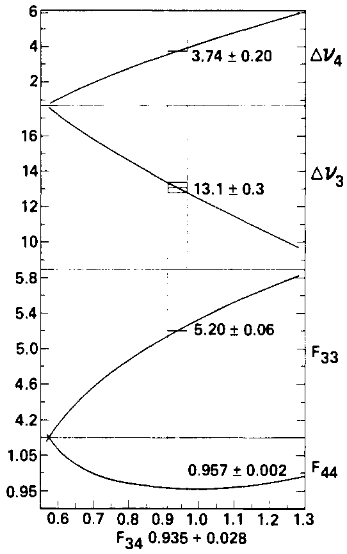

Figure 3. Solution range of the F_{1u} block symmetry force constants (mdyn/Å) of ClF_6^+ with the observed chlorine isotopic shift (13.1 ± 0.3 cm^{-1}) as a constraint. The horizontal and the broken vertical lines indicate the preferred values and their uncertainties, respectively.

The observation of the chlorine isotopic shift for ν_3 (F_{1u}) of ClF_6^+ in this study provided the additional data point required for the computation of a GVFF for ClF_6^+. The force field was computed by a previously described method[41] using the $^{35}ClF_6^+$ frequencies given in Table II and a ^{35}Cl–^{37}Cl isotopic shift of 13.1 ± 0.3 cm^{-1} for ν_3 (F_{1u}). In the absence of anharmonicity constants, the observed frequencies were used for the calculation of an anharmonic GVFF. On the basis of comparison between the anharmonic and the harmonic GVFF of isoelectronic SF_6 (see Table II),[36] the anharmonicity cor-

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(42) The compound claimed to be $ClF_6^+CuF_4^-$ has in the meantime been identified as $[Cu(H_2O)_4][SiF_6]$ (von Schnering, H. G.; Vu, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 408).

rections should have only a minor influence on the force field.

To obtain an estimate for the uncertainties of the F_{1u} force constants of ClF_6^+, the relevant parts of the F_{33} and F_{44} ellipses of ClF_6^+ and the corresponding ^{35}Cl–^{37}Cl isotopic shifts of ν_3 and ν_4 were computed as a function of F_{34}. As can be seen from Figure 3, the resulting uncertainties in the force constants are very small and the force field of ClF_6^+ is rather well determined.

A comparison of the GVFF of ClF_6^+ (see Figure 3 and Table II) with the two previously published modified valence force fields[5,16] shows that F_{44} = minimum is a much better constraint than the transfer of the $f_{rr'}$ value from SF_6 to ClF_6^+. Also, the resulting Cl–F stretching force constant value of 4.97 mdyn/Å for ClF_6^+ is, as expected for a perfluoro cation in its highest oxidation state,[40] the highest value found to date for a Cl–F bond and agrees with the good thermal stability found for these ClF_6^+ salts. A comparison of the ClF_6^+ force field with those of BrF_6^+ [16] and IF_6^+ [33] (see Table II) shows the expected trends.[40] The stretching force constant drops slightly from ClF_6^+ to BrF_6^+ and then markedly increases for IF_6^+. The deformation constants decrease from ClF_6^+ toward IF_6^+, as expected from the increase in bond lengths. The stretch–stretch interaction constants f_{rr} and $f_{rr'}$ show smooth trends from ClF_6^+ toward IF_6^+, similar to those observed for the isoelectronic SF_6, SeF_6, TeF_6 series, although the relative contributions from f_{rr} and $f_{rr'}$ are different within each series. A comparison of the GVFF of ClF_6^+ with that of SF_6 (see Table II)[36] also shows excellent agreement, except for the above noted difference in the relative contribution from f_{rr} and $f_{rr'}$.

Conclusion. The KrF^+ cation is capable of oxidizing ClF_5 to ClF_6^+ and provides a method for the synthesis of pure ClF_6^+ salts. Thus, KrF^+ is the first oxidative fluorinator capable of producing all three of the presently known coordinatively saturated complex fluoro cations, NF_4^+, BrF_6^+, and ClF_6^+. The synthesis of pure ClF_6AsF_6 permitted a better characterization of the ClF_6^+ cation and the determination of a general valence force field for ClF_6^+. The Cl–F bond in ClF_6^+ (4.97 mdyn/Å) is the strongest Cl–F bond presently known, suggesting highly covalent bonds with sp^3d^2 hybridization of the valence electrons of chlorine. By analogy with the known NF_4^+ chemistry, the existence of numerous stable ClF_6^+ salts is predicted.

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Registry No. ClF_6AsF_6, 86527-33-5; ClF_6SbF_6, 86527-34-6; ClF_6^+, 38217-33-3; KrF_2, 13773-81-4; AsF_5, 7784-36-3; ClF_5, 13637-63-3; SbF_5, 7783-70-2.

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trans-$[(en)_2Co(Cl)(S_2O_3)]$, Na[*trans*-$[(en)_2Co(C_2O_4)(S_2O_3)]]$, *trans*-$[(en)_2Co(NCO)(S_2O_3)]$, and the Nature of $[(en)_2Co(OH_2)(S_2O_3)]^+$ in Aqueous Solution

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The preparation and characterization of the title complexes are described. The chloro complex rapidly aquates at pH 5–6, and the oxalato and cyanato complexes undergo acidolyses in dilute $HClO_4$, to form a common intermediate, *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, which subsequently equilibrates to a mixture of cis and trans isomers. Kinetics of the cyanato complex acidolysis are presented and compared with those of HNCO and of $[(NH_3)_5Co(NCO)]^{2+}$.

Introduction

In a previous report,[1] the synthesis of *trans*-(thiosulfato)(aniono)bis(ethylenediamine)cobalt(III) complexes by anation of a brown aqueous cation has been described. This cation, isolated by ion-exchange chromatography, was formulated as *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ largely on the basis of its UV spectroscopic parameters and its labile substitution chemistry; although its stoichiometry appeared certain, its geometric configuration was only inferred. No corresponding brown solid was obtained; indeed, attempts to prepare the perchlorate salt produced a red, bidentate (O,S) thiosulfato complex, $[(en)_2Co(S_2O_3)]^+$,[2] and attempts to isolate a chloride salt[1] resulted in the production of a green solid of variable composition containing excess Cl. Although the aqua in *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ is readily substituted,[1] the corresponding thiocyanato- and nitrito-*N* complexes are relatively inert to aquation even in dilute acid. In an attempt to produce complexes with more labile trans substituents, we have prepared three new complexes in the series *trans*-$[(en)_2Co(X)(S_2O_3)]^{0,-}$, X = Cl^-, NCO^-, $C_2O_4^{2-}$. We report here their isolation, characterization, and chemistry, which establishes the nature of aqueous $[(en)_2Co(OH_2)(S_2O_3)]^+$.

Experimental Section

General Data. For chromatographic elutions, LiCl and hydrated $NaClO_4$ and $LiClO_4$, as obtained from G. F. Smith Chemical Co., were prepared as concentrated stock solutions and filtered before use. For the acidolysis kinetic experiments, doubly vacuum-distilled $HClO_4$ (70–72%, G. F. Smith) and $LiClO_4$ recrystallized from H_2O were used to prepare stock solutions. A chloroacetic acid–chloroacetate buffer was prepared from Li_2CO_3 and aqueous chloroacetic acid, and the pH values were determined with a pH meter calibrated at μ = 1.00 M ($LiClO_4$). Deuterium oxide (99.85 atom % D) was obtained from Aldrich Chemical Co. Other common chemicals were of reagent

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