in preparing for such measurements.

The major results of the study are, of course, the two binding constants. These are not exactly comparable to the binding constants between ZnTPP and pyridine, but certain features are clear. The numbers quoted (2327 M^{-1} for ZnTPP binding to PVP in CH_2Cl_2 and 2.74×10^8 M^{-1} for ZnTPP binding to PVP on silica from benzene solution) are limiting binding constants that avoid any concern with steric interactions among the ZnTPP molecules. This is because the measurement on solution PVP was made at such low concentrations of ZnTPP that a given polymer had, on the average, less than one bound ZnTPP and because the model used for surface adsorption considered explicitly the limited number of adsorption sites available.

The result obtained with PVP in solution is expected. CH_2Cl_2 is only a moderately good solvent for PVP; the polymer is somewhat contracted and, thus, not all the pyridyl groupings are available for adsorption. This, added to any steric repulsion between the ZnTPP and portions of the polymer to which the molecule is not bonded, makes the fall in binding constant understandable.

The very large binding constant of ZnTPP to the modified surface is harder to understand. Poly(4-vinylpyridine) is believed to adsorb to a surface with only a few segments of the molecule in intimate contact with the surface. The rest of the molecule is essentially free and extends out into the solution, assuming a structure similar to the structure a molecule has in solution.[28,29] This suggestion is based on the observation that a large fraction of the pyridyl groups are available for reaction in the adsorbed system. This observation applies to our system, the polymer adsorbed onto a silica surface, as well as to the system for which it was originally made, PVP adsorbed onto graphite.

Our observations show that the model needs modification to deal with the reaction of ZnTPP with the adsorbed polymer. First, the equilibrium constants yield a $\Delta G°$ of transfer of ZnTPP from pyridine in solution to a pyridyl of the adsorbed polymer of -6393 cal mol^{-1}. $\Delta G°$ of transfer from pyridine to a pyridyl of the polymer in solution is much smaller and is of the opposite sign, $\Delta G° = +201$ cal mol^{-1} (in CH_2Cl_2). Second, the molar extinction coefficient of ZnTPP absorbed on the modified surface is not the same as that of the pyridine complex in solution. As mentioned above, easily the most obvious explanation of the change in molar extinction coefficient is that the ZnTPP is oriented by the surface.

Some of the effects we see must be due to the size of the porphyrin molecule, which is not small compared with other dimensions in the system. The porphyrin molecules are 14 Å on a side, in the sense that a square drawn around its plane would need to have such a length. A polymer film having the density of the solid would only be 10 Å thick to provide the observed area density of the pyridyl groupings. The strong preferential orientation of the porphyrin is, thus, not expected.

It is not possible to discuss the thermodynamic aspects of the adsorption of the ZnTPP without a more detailed model of the modified surface. It seems more likely, however, that some degree of organization of the PVP by the surface is responsible for these effects as well.

Conclusions

Zinc tetraphenylporphyrin is found to adsorb reversibly onto silica surfaces modified with poly(4-vinylpyridine). The adsorption obeys a simple isotherm, but the thermodynamics of adsorption is quite different from that of binding to a polymer in solution, with the effect of making adsorption very efficient. These results will perhaps be helpful to those who wish to use porphyrin compounds in interfacial systems, perhaps as sensitizers.

Registry No. Zinc tetraphenylporphyrin, 14074-80-7; poly(4-vinylpyridine) (homopolymer), 25232-41-1; vitreous silica, 60676-86-0.

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Protonation and Aquation of Chromium(III)/Ethanolamine Complexes in Aqueous Solution

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Several Cr(III) complexes with amino alcohols have been prepared, and the solution chemistry of the tris(2-aminoethanol) complex has been studied in detail. Addition of excess strong acid to solutions containing $Cr(Eta)_3{}^0$ (Eta = bidentate aminoalkoxy) results in the following sequence of reactions: stage I, instantaneous protonation to produce bidentate $Cr(EtaH)_3{}^{3+}$ (EtaH = 2-aminoethanol); stage II, rapid (complete in ~10 min at 20 °C) conversion to monodentate $Cr(EtaH)_3(OH_2)_3{}^{3+}$ by ring opening at the alcohol function; stage III, slower stepwise aquation of the N-bonded ethanolamine to produce $Cr(OH_2)_6{}^{3+}$. The first-order rate constants in stage III (25 °C, $\mu = 0.10$) are $k_{3\to2} = 2.3 \times 10^{-4}$ s^{-1}, $k_{2\to1} = 1.7 \times 10^{-5}$ s^{-1}, and $k_{1\to0} = 6.4 \times 10^{-7}$ s^{-1}. Aquation rates in stages II and III ($k_{1\to0}$) are much faster than normal for Cr(III) complexes but have a precedent in the Cr(III)/ethylene glycol system.

Introduction

With the exception of the amino acids, there has been relatively little study of bidentate ligand complexes containing one nitrogen and one oxygen donor. There has also been relatively little reported on complexes containing ligands with alcohol functional groups as binding sites, probably because the oxygen atoms are usually poor donor atoms.

Some earlier work[1-5] on ethanolamine complexes of Cr(III) was largely preparative in nature and did not provide a con-

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vincing characterization of the solution chemistry of the complexes. Thus, structures were often proposed on the basis of empirical composition only and solution chemistry was interpreted on the basis of overall spectral changes with no attempt to isolate individual species. In this paper we report a systematic study of the Cr(III)/2-aminoethanol system and preparative results on some other amino alcohols. The following symbols are used: EtaH for 2-aminoethanol, AprH for 2-amino-1-propanol, *i*-PraH for 1-amino-2-propanol, and *n*-PraH for 3-amino-1-propanol. In each case the H represents the hydrogen of the alcohol group.

Experimental Section

Materials and Procedures. Organic compounds were obtained from Aldrich or Eastman Kodak and other chemicals from Fisher; all were used without further purification. Chromium was determined via atomic absorption (Jarrell-Ash 82-360) and elemental analysis (N, H, C, O) by ArRo Laboratories (Joliet, IL). IR spectra (in KBr pellets) were taken on a Beckman 4240, X-ray powder patterns on a Norelco XRG-2680 (Mo Kα1 or Cu Kα1 radiation), and visible spectra on a Beckman 25; conductance was determined with a Leeds and Northrup bridge using an Aminco dip cell.

Synthesis. $Cr(Eta)_3 \cdot 3H_2O$ was prepared by reaction of 15.0 g (0.095 mol) of anhydrous $CrCl_3$ with a mixture of 90 mL (1.5 mol) of 2-aminoethanol and 20 mL of H_2O. The solution was stirred for about 24 h, the resulting viscous product was allowed to stand another 24 h, some ethanol was added, and crystals were collected by filtration. The crystals were washed with 10-mL portions of 80% ethanol until the supernatant was nearly colorless and then dried in a desiccator. This method is faster and more convenient than those previously reported[2b,3a]. Yield based on Cr was 45%, and chloride tests were negative. Anal. Calcd: Cr, 18.18; N, 14.69; C, 25.17; H, 8.39. Found: Cr, 18.21; N, 14.75; C, 24.73; H, 8.44.

$[Cr_2(Eta)_3(EtaH)_3]X_3$ ($X = I^-, ClO_4^-$) was prepared by addition of 0.5 g (1.74 mmol) of $Cr(Eta)_3 \cdot 3H_2O$ to 100 mL of saturated aqueous NH_4X, and crystals were collected after about 30 min. Yields: $X = I^-$, 89%; $X = ClO_4^-$, 94%. Anal. Calcd: Cr, 13.59; N, 10.97. Found: (ClO_4^- salt): Cr, 14.15; N, 10.78. The visible spectrum was quantitatively identical with that of the I^- salt. Hydrates of similar compounds ($X = Cl^-, Br^-, NO_3^-, SO_4^{2-}$) can be prepared from ethanol slurries.[3a]

$[Cr(Eta)_2(EtaH)(OH_2)]Cl$ was prepared by a slight modification of a previous method[3b] using $[CrCl_2(OH_2)_4]Cl \cdot 2H_2O$ as starting material; yield 28%. Anal. Calcd: Cr, 18.15; N, 14.66; C, 25.13; H, 7.33. Found: Cr, 18.28; N, 14.37; C, 26.80; H, 6.86.

$Cr(L)_3 \cdot 3H_2O$ (L = Apr, *i*-Pra) were prepared as described above for $Cr(Eta)_3 \cdot 3H_2O$. With *n*-PraH, however, the product was identified as $[Cr(n\text{-}Pra)_2(n\text{-}PraH)(OH_2)]Cl$. Reaction with 2-amino-2-methyl-1-propanol was very slow, and no product was isolated.

Separation of Solute Species. SP-Sephadex C-25 (Pharmacia) was used in 1 cm × 20 cm columns with 10-psig external pressure to separate complexes. A trial run showed complete separation (with 95% recovery) for a mixture of the ions (in order of appearance) $Cr_2(Eta)_3(EtaH)_3^{3+}$, $Cr(en)_3^{3+}$, and $Cr(H_2O)_6^{3+}$, thus confirming the earlier report[6] that ions with the same charge can be separated. Elutions used 0.1 M NaCl or 0.5 M $NaClO_4$ (with 2M NaCl needed to remove the aquo ion).

Results

$Cr(Eta)_3 \cdot 3H_2O$. Elemental analysis and conductance (a 10^{-3} M solution had a molar conductance of 7 Ω^{-1} after 1.5 min) agreed with earlier reports[3a] and established the electrical neutrality of the species, a conclusion further verified by complete lack of retention on a SP-Sephadex C-25 column (Na^+ form). Efforts to obtain single crystals suitable for X-ray structure determination were unsuccessful, but some additional experiments were performed to distinguish between the chelate $Cr(Eta)_3^0$ and the monodentate alternatives, viz. $Cr(Eta)_3(OH_2)_3$ or $Cr(EtaH)_3(OH)_3$. Thus the visible spectra of the compound (summarized in Table I) are the same in water and 1 M NaOH, which would not be expected for a complex with water molecules or hydroxide ions in the primary coordination sphere. Furthermore, evidence is cited below that the tris chelate cation $Cr(EtaH)_3^{3+}$ is formed on dissolving the solid in strong acid. It therefore seems certain that the solute species produced on dissolving solid $Cr(Eta)_3 \cdot 3H_2O$ in water (or alkali) is the tris chelate containing three anionic alkoxide ligands. Detailed analysis of the IR spectrum was precluded by overlap of O–H and N–H stretching frequencies.

Table I. UV-Vis Spectra of Selected Cr(III)/Amino Alcohol Species

species	λ_{max} (ϵ)	ref
$Cr[Eta]_3^0$	407 (117), 545 (122)	*a*
	409 (126), 555 (127)	28[b]
	412 (109), 569 (116)	26[b]
$Cr[Apr]_3^0$	405 (107), 545 (109)	*a*
$Cr[i\text{-}Pra]_3^0$	405 (102), 545 (105)	*a*
$Cr[EtaH]_3^{3+}$	380 (73), 510 (100)	*a*
$Cr[AprH]_3^{3+}$	378 (58), 505 (88)	*a*
$Cr_2[Eta]_3[EtaH]_3^{3+}$	385 (68), 516 (99)	*a*
$Cr_2[Apr]_3[AprH]_3^{3+}$	386 (56), 520 (92)	*a*

[a] This work; all values extrapolated to time of mixing. [b] Estimated from published figures.

Stage I: Protonation

$$Cr[Eta]_3^0 \rightarrow \{Cr[Eta]_2[EtaH]^+\} \rightarrow \{Cr[Eta][EtaH]_2^{2+}\} \rightarrow Cr[EtaH]_3^{3+}$$

Stage II: Alcohol Aquation

$$Cr[EtaH]_3^{3+} \rightarrow \{Cr[EtaH]_2(EtaH)(OH_2)^{3+}\} \rightarrow \{Cr[EtaH](EtaH)_2(OH_2)_2^{3+}\} \rightarrow Cr(EtaH)_3(OH_2)_3^{3+}$$

Stage III: Amine Aquation

$$Cr(EtaH)_3(OH_2)_3^{3+} \xrightarrow{k_{3\rightarrow2}} Cr(EtaH)_2(OH_2)_4^{3+} \xrightarrow{k_{2\rightarrow1}} Cr(EtaH)(OH_2)_5^{3+} \xrightarrow{k_{1\rightarrow0}} Cr(OH_2)_6^{3+}$$

Figure 1. Reaction summary for $Cr(Eta)_3$ in acid: [], bidentate ligands; (), monodentate ligands; {}, species that have not been directly identified.

Despite the conclusion that the water is present as "crystal" water, it proved to be impossible to remove the water without decomposition of the compound. Drying at 50 °C, warming with ethanol, and stirring for several days at room temperature with 2,2-dimethoxypropane all led to formation of blue-gray solids with essentially identical IR spectra and X-ray diffraction powder patterns[7] corresponding to $Cr(OH)_3$. It appears likely that the Cr species are stabilized in the solid by strong hydrogen bonding involving the chelated alkoxide donor atoms.

$[Cr_2(Eta)_3(EtaH)_3](ClO_4)_3$. The solid compound was characterized by elemental analysis and by comparison of X-ray powder and IR spectra with those of an authentic sample of the analogous cobalt(III) complex, $[Co_2(Eta)_3(EtaH)_3](ClO_4)_3 \cdot {}^1/_2H_2O$, kindly supplied by J. Bertrand, who had previously determined its crystal structure.[8] The 15 most intense interplanar spacings matched with an average (Cr–Co) difference of 0.047 ± 0.019 Å. Additionally, the IR spectra (3600–400 cm^{-1}) are nearly identical. These similarities provide strong evidence that the chromium compound exists in the solid as a hydrogen-bonded dimer with, in effect, three protons holding two facial $Cr(Eta)_3^0$ molecules together. The

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short O–O distance (average 2.42 Å) in the cobalt dimer indicates a strong hydrogen bond (cf. ice 2.75 Å) and, incidentally, provides further insight into the difficulty of removing H_2O from $Cr(Eta)_3 \cdot 3H_2O$.

Solution Chemistry. Solutions of $Cr(Eta)_3 \cdot 3H_2O$ in excess acid undergo an extensive series of chemical changes ultimately producing $Cr(OH_2)_6^{3+}$. These reactions will be divided into three stages (protonation, alcohol group aquation, and amino group aquation) for discussion purposes. (See Figure 1 for summary.)

Stage I: Protonation. Solutions with identical UV–vis absorption spectra can be prepared (1) by dissolving either $Cr(Eta)_3 \cdot 3H_2O$ or $[Cr_2(Eta)_3(EtaH)_3]X_3 \cdot nH_2O$ in 1 M $HClO_4$ or (2) by adding exactly 3 mol of $HClO_4$/mol of Cr to a solution of $Cr(Eta)_3 \cdot 3H_2O$ in water. The predominant species in these acidic solutions has been identified as the tris chelate $Cr(EtaH)_3^{3+}$ on the basis of the following observations:

(1) The absorption spectrum (Table I) shows wavelength maxima and intensities expected for the Cr^{III} (3O,3N) chromophore. The shifts in position of absorption maxima on protonation of 30 ± 5 nm are very similar to other cases[9] of protonation of oxygen donor atoms on Cr(III).

(2) Immediate neutralization of excess H^+ to pH $\simeq 9$ produces a solution with a spectrum identical with that of $Cr(Eta)_3 \cdot 3H_2O$ alone in water.

(3) Addition of excess hydroxide (as previously noted) produces no further spectral change. Stage I of the reaction of $Cr(Eta)_3$ with acid can therefore be ascribed to very rapid proton equilibria in which the coordinated alkoxide groups are converted to alcohol groups.

Further information on the protonation was obtained from pH and absorption spectra measurements as a function of added acid or base. Because of the substitution lability of the systems, these experiments were done on a "point by point" basis over the pH range 1.0–9.2. The principal feature of the titration curve for $Cr(Eta)_3^0$ was an inflection point at 1.5 mol of added H^+/mol of complex, suggesting some sort of association between solute species. (This conclusion is also supported by concentration-dependent absorption spectra and will be analyzed more fully in a separate publication.) Ignoring the above complexity, we obtained estimates of the stepwise pK_a values for $Cr(EtaH)_3^{3+}$ in the usual way: these values are $pK_1 \sim 3.0$, $pK_2 \sim 5.1$, and $pK_3 \sim 8.0$.

Stage II: Alcohol Aquation. Following protonation, irreversible changes occur that are attributed to aquation at the alcohol sites, converting the bidentate ligands to monodentate. As expected for a process with such a minor change in chromophore, there is no change in UV–vis peak positions, although marked decreases in peak intensities are observed. Neutralization to pH $\simeq 9$ fter increasing periods of time results in successively smaller spectral changes until, after 10 min at 25 °C, the reaction appears to be nearly complete. Estimating 90% completion leads to $t_{1/2} \simeq 3$ min for the overall (three-step) aquation.

Stage III: Amine Aquation. The final stage of the reaction sequence involves stepwise aquation of the monodentate N-bonded 2-aminoethanol ligands formed in stage II. Since these aquations are moderately slow and are accompanied by substantial spectral changes (in both peak positions and intensities), it has been possible to determine the individual rate constants (Table II).

Table II. Experimental Rate Constants for Stepwise Aquation of Monodentate 2-Aminoethanol Ligands of $Cr(EtaH)_3(OH_2)_3^{3+}$ [a]

	10^5k, s^{-1}			
species	30 °C	40 °C	45 °C	49 °C
$Cr(EtaH)_3(OH_2)_3^{3+}$	38.5	102	163	239
$Cr(EtaH)_2(OH_2)_4^{3+}$	3.1	9.8	17.3	26.7
$Cr(EtaH)(OH_2)_5^{3+}$	0.12	0.37	0.64	0.99

[a] See text for extrapolated values at 25 °C. All adjusted to 1 M ionic strength with $NaClO_4$.

Following the fairly rapid aquation in stage II, acidic solutions prepared from $Cr(Eta)_3^0$ or $[Cr_2(Eta)_3(EtaH)_3]X_3 \cdot nH_2O$ exhibit spectral changes characterized by peak shifts and decreases in intensity, resulting in a solution with a spectrum identical with that of $Cr(OH_2)_6^{3+}$. Since there is no evidence of reversibility, these changes were analyzed by assuming three consecutive first-order aquations to obtain rate constants at 30, 40, 45, and 49 °C. The following rate constant and thermodynamic values were obtained (extrapolated to 25 °C): $k_1 = 2.3 \times 10^{-4}\ s^{-1}$, $k_2 = 1.7 \times 10^{-5}\ s^{-1}$, $k_3 = 6.4 \times 10^{-7}$; $\Delta H_1{}^* = 18$ kcal mol^{-1}, $\Delta S_1{}^* = -15$ cal mol^{-1} K^{-1}; $\Delta H_2{}^* = 21$ kcal mol^{-1}, $\Delta S_2{}^* = -9$ cal mol^{-1} K^{-1}; $\Delta H_3{}^* = 21$ kcal mol^{-1}, $\Delta S_3{}^* = -16$ cal mol^{-1} K^{-1}. Reaction rates were independent of H^+ concentration in the range 0.10–1.0 M in solutions with constant ionic strength (total [perchlorate] = 1.0 M with added $NaClO_4$).

To confirm the above values for k_2 and k_3, additional experiments were done by using solutions containing $Cr(EtaH)_2(OH_2)_4^{3+}$ or $Cr(EtaH)(OH_2)_5^{3+}$ (prepared by ion-exchange separation of partially aquated solutions) as the initial chromium species.

Discussion

Protonation Equilibria. The estimated pK_a values for the tris chelate $Cr(EtaH)_3^{3+}$ can be compared with previous results[10] on cobalt complexes containing ligands with alcohol donor groups. Thus, $Co(en)_2(EtaH)^{3+}$ (en = ethylenediamine) has a $pK_1 = 3.5$, in good agreement with 3.0 for $Cr(EtaH)_3^{3+}$ in the present work. Although there is no direct analogy for K_2 and K_3, it is known that pK increases by 2 units for the stepwise acid dissociation[11] of *cis*-$Co(en)_2(OH_2)_2^{3+}$. These results provide an additional example[12] of enhanced acidity of protic chelated ligands.

Aquation Kinetics. The extremely rapid aquation of the alcohol oxygen to produce the monodentate $Cr(EtaH)_3(OH_2)_3^{3+}$ is unusual for Cr(III) but has a precedent in several other systems. The most analogous system is 1,2-ethanediol (ethylene glycol) for which a rate constant of $4.8 \times 10^{-3}\ s^{-1}$ at 25 °C has been reported[13] for the conversion of bidentate $Cr(OH_2)_4G^{3+}$ to monodentate $Cr(OH_2)_5G^{3+}$, where G = 1,2-ethanediol. Also unusual in the glycol system is an equilibrium that favors the monodentate form in marked contrast to the nitrogen analogue 1,2-diaminoethane (ethylenediamine). These enhanced labilities and decreased stabilities have been shown to be a function of ring size in a study[14] comparing 1,3-propanediol with 1,2-propanediol complexes of Cr(III), with only the latter system showing the effects. Similar labilizations of Cr(III) complexes have also been reported[15] for several oxyanions; it has been suggested that these labilizations arise from breaking of the nonmetal–oxygen bonds within the ligands rather than Cr(III)–oxygen bonds.

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

	10^6k, 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.]

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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*-Pra)$_3$, 86834-55-1; [Cr(*n*-Pra)$_2$(*n*-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.

Contribution from Rocketdyne, A Division of
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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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