values of pK_{OH} of the phenol group of the complex ($K_{OH} = Q_1K_W$) as 10.9 ± 0.1 and 10.7 ± 0.2 at 30 and 35 °C, $I = 1$ M, respectively. These are very similar to the values of pK_{OH} obtained for *cis*-$[Co(en)_2(NH_3)O_2CC_6H_4OH]^{2+}$ (11.22 at 29.5 °C, $I = 1$ M)[11] and *cis*-$[Co(en)_2(imidazole\text{-}H)O_2CC_6OH]^+$ (10.99 at 30 °C, $I = 0.3$ M).[4]

Typically, the aquation rate constants, k_1, of complexes of the type $[N_5CoOCOC_6H_4O]^+$ are of the order of magnitude 10^{-5} s^{-1}, while the base hydrolysis constants, k_2, are around 10^{-4} s^{-1} M^{-1} (see entries 1, 2, and 3 in Table II). In contrast, the tetren species is very much more reactive than the previously studied analogues, with both k_1 and k_2 values greater by a factor of $\sim 10^4$ (entry 4 in Table II). A molecular model of ($\alpha\beta S$)-$[Co(tetren)OCOC_6H_4O]^+$ ion reveals that the phenoxide oxygen must occupy a position in close proximity to one of the terminal NH_2 groups of the tetren ligand. This favors internal acid–base equilibration through hydrogen bonding of the type $-NH_2\cdots OC_6H_4OCO- \rightleftarrows -NH\cdots HOC_6H_4OCO-$, thus generating what amounts to the more reactive conjugate-base form of the complex ion. Thus the present work lends support to the mechanism previously suggested for the aquation of the $(en)_2(NH_3)$, $(trien)(NH_3)$, and $(en)_2(im\text{-}H)$ analogues, except that the effect is much greater for the tetren species. Further corroboration of this concept is provided by the proposal by Poon and Tobe[16] that the facile cis → trans isomerization of $[Co(cyclam)(OH)(OH_2)]^{2+}$ is promoted by intramolecular proton transfer from an amine ligand to the hydroxo ligand. The pK_{OH} of the phenol group of the salicylato complex is at least 6 units greater than the first pK of the aqua ligand of *cis*-$[Co(cyclam)(OH_2)_2]^{3+}$ (pK = 4.9 at 25 °C and $I = 0.5$ M, $NaClO_4$),[16] so the accelerating influence of the phenoxide group should be even more substantial. It should be noted that various types of N_5CoX^{2+} complexes aquate at very low rates (entries 5–11 in Table II), mainly as a result of low $\Delta S^{\ddagger}$ values. The highly positive activation entropies for the k_1 path of all four of the salicylato species may indeed result from the contribution of ΔS° from the internal conjugate-base equilibration, for which a large positive entropy change could well result from changes in the solvation pattern.

Turning now to the base hydrolysis reaction described by k_2, the tetren salicylato is, as mentioned above, much more reactive than any of the other comparable salicylato species or even than the other singly charged complex ion, the S-bonded tetren sulfito complex (entry 14). However, the tetren salicylato ion is not unusually reactive as compared to various other complexes of the $[N_5CoX]^{2+}$ family, which are seen to fall within a very wide range of reactivity ($10^{-2} \leq k_2 \leq 10^4$ at 25 °C — see entries 5–13 in Table II). The $[N_5Co(sal)]^+$ species are unusual in these comparisons in that k_2 differs from k_1 by only an order of magnitude, while for all the other species for which the appropriate data are tabulated the rate ratios are within the range $10^5 \leq k_2/k_1 \leq 10^{12}$. This observation further supports our concept of an "internal S_N1cB" mechanism for the k_1 path for the salicylato complexes, since further increase of $[OH^-]$ would be expected to promote the second-order k_2 path, but not with a large increase, conjugate-base conditions having already been established. It is also worth noting that the large increase in base hydrolysis rate (k_2 path) on changing from *cis*-$[Co(en)_2(NH_3)(OCOC_6H_4O)]^+$ to the tetren analogue is paralleled by a similar large increase in changing from *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ to its tetren analogue. Apparently these parallel rate contrasts are the result of the change in the nature of the N_5 grouping, not of anything inherently very different in the $(OCOC_6H_4O)^{2-}$ ligand as compared to the Cl^- ligand, except for the change in overall charge of the complex ion. Other things being equal, it is apparent that the doubly charged species are more receptive to the S_N1cB mechanistic requirements than are those of single charge.

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Hydrogen Bonding. 11. Infrared Study of the Water–Chloride Ion Cluster in Tetraethylammonium Chloride Hydrate[1]

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In previous work we have demonstrated that tetramethylammonium fluoride hydrate[3,4] and tetraethylammonium fluoride hydrate[5] contain discrete $H_4O_2F_2^{2-}$ water–fluoride clusters and have proposed that these clusters can be described as a tetrahedron of electronegative atoms with bridging protons on the faces of the tetrahedron.[6] This structure is consonant with theoretical treatments of tetrahedral clusters by Kettle[7] or Hoffmann,[8] with the protons interacting with the $A_1 + T_2$ face-centered bonding orbitals. Such a cluster would be isoorbital with, for example, methyllithium tetramer;[7,9] however, the electronegative atoms in the fluoride monohydrate cluster would facilitate the presence of electrons in the remaining $E + T_1 + T_2$ orbitals much as the electronegative atoms in a three-centered hydrogen bond[10] facilitate the presence of nonbonding electrons, in contrast to the hydrogen bridge bond in boranes.[11]

Structural information on these unique and extraordinarily stable hydrates would be of considerable interest; however, both of the fluoride monohydrates studied are obtained by dehydration of higher solid hydrates and are thus fine, micro-

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Table I. Infrared Spectral Assignments for Water-Anion Clusters in Tetramethylammonium Fluoride Hydrate-d_2 and Tetraethylammonium Chloride Hydrate and Hydrate-d_2[a,b]

band[c]	Symmetry under[c]			$F^-\cdot D_2O$[c]	$Cl^-\cdot D_2O$	$Cl^-\cdot H_2O$		$\nu(H)/\nu(D)$[d]
	T_d	C_{4h}	C_{2v}	10 K	300 K	300 K	10 K	
ν_6 unsym XH str	t_2	a_u	a_1	2465 (s)	2554 (s)	3430 (sh)	3420 (vs)	1.34
		e_u	b[e]	2340 (vs)	2474 (s)	3373 (vs)	3360 (vs)	1.36
			b	2235 (vs)	2385 (m)	3256 (s)	3265 (s)	1.37
ν_7 unsym XH bend	t_2	e_u	b	1280 (m)	*f*	*f*	*f*	
			b	1270 (m)	*f*	*f*	*f*	
		a_u	a_1	1170 (s)	*g*	1637 (s)	1635 (s)	1.39[h]
ν_8 unsym X_4 def	t_2	e_u	b	655 (vs)	465 (s)	*i*	638 (vs)	
			b	635 (s)	442 (vs)	615 (vs)	615 (s)	1.39
		a_u	a_1	590 (vs)	377 (s)	536 (vs)	542 (vs)	1.42

[a] Units are wavenumbers (cm^{-1}). [b] Abbreviations: weak, w; medium, m; strong, s; very strong, vs; shoulder, sh; unsym, unsymmetrical; str, stretch; def, deformation. X stands for electronegative atom (O, F, Cl). [c] From ref 4. [d] Observed for tetraethylammonium chloride hydrates at 300 K; $\nu(H)/\nu(D)$ ratios for hydrogen bonds are expected to be less than 1.41.[17] [e] Cannot assign b_1 (Cl against O–O rock) and b_2 (O against Cl–Cl rock) at this time. [f] Not observed. [g] Apparently masked by cation peak at 1183 cm^{-1}. [h] Estimated (see *g*). [i] Vibrations of B symmetry not resolved at 300 K.

crystalline powders unsuitable for single-crystal diffraction studies. We now find that tetraethylammonium chloride hydrate contains a water–chloride cluster similar to the water–fluoride clusters previously reported; this is our first observation of the incorporation of chloride ion into such a species. Moreover, tetraethylammonium chloride hydrate can be recrystallized to yield large, single prisms which should be suitable for diffraction study.

Experimental Section

Aldrich tetraethylammonium chloride hydrate was used as supplied; thermogravimetric analysis showed the material to contain 1.16 mol of water per mole salt. A portion of this material was ground to a powder, covered with a quantity of reagent acetone sufficient to dissolve about half of the sample, and heated under reflux overnight. After this time, the powder had disappeared and a mass of small white prisms had formed. NMR analysis[5] showed the material to be $(C_2H_5)_4N$-$Cl\cdot1.00H_2O$. Continued refluxing will give larger crystals—up to 1 cm in length—however, traces of triethylammonium chloride appear in the material (see Discussion). Tetraethylammonium chloride hydrate-d_2 was prepared by dissolving the monohydrate in 99.7% D_2O and removing the solvent in vacuo; this process was repeated three times to yield $(C_2H_5)_4NCl\cdot1.18D_2O$. An infrared spectrum showed the sample to be free of H_2O. Tetraethylammonium hexafluorosilicate was prepared by neutralizing Alpha hexafluorosilicic acid with Eastman Kodak White Label tetraethylammonium hydroxide solution. Water was removed in vacuo and the solid taken up in ethanol, precipitated with ether, and dried in vacuo at 25 ° for 4 h. An infrared spectrum showed the presence of hexafluorosilicate ion[12] and the absence of solvent.

With the exception of the recrystallization, all operations were carried out in a glovebox under dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls on CsI plates. The Nujol was predried by dissolution in pentane, treatment with Linde 4-A molecular sieve, and removal of solvent in vacuo. An Air Products and Chemicals Displex CSW-202 two-stage helium refrigerator equipped with KBr windows was used for the low-temperature spectrum.

Discussion

An isolated face-protonated X_4H_4 cluster of T_d symmetry would show three infrared-active T_2 bands; this is observed for the water–fluoride cluster in tetraethylammonium fluoride hydrate.[5] In the progression tetraethylammonium fluoride hydrate, tetraethylammonium fluoride hydrate-d_2, tetramethylammonium fluoride hydrate, tetramethylammonium fluoride hydrate-d_2, we see each T_2 fundamental first split into two bands, and subsequently one of these bands split again. This splitting has been discussed[4] in terms of increasing distortion of the anion toward C_{2v} symmetry caused by increased lattice interactions in the tetramethylammonium salts coupled with weaker hydrogen bonds in the deuterated species. The assignments of vibrations under various symmetries are shown in Table I; in all cases, as expected,[13] only those bands derived by factorization of the T_2 vibrations, which have large intrinsic transition moments in the free ions, are observed.

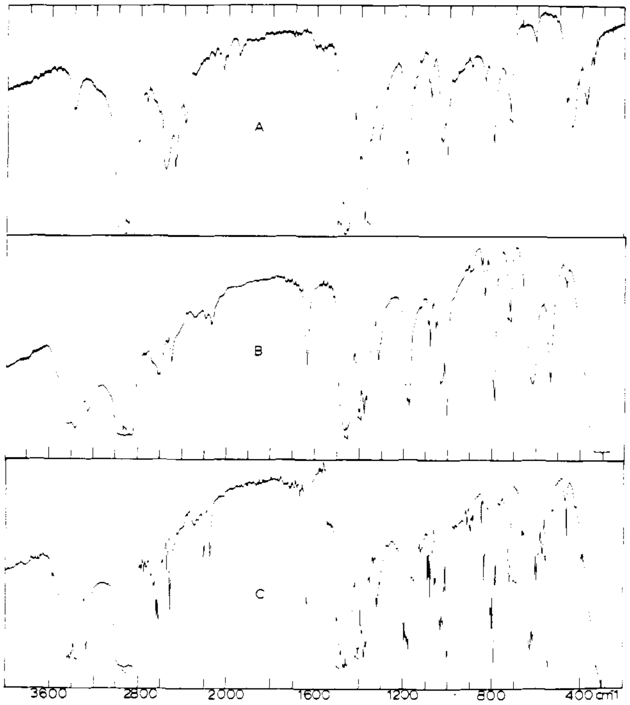

Figure 1. Infrared spectra of (A) tetraethylammonium chloride hydrate-d_2 at 300 K (CsI plates), (B) tetraethylammonium chloride hydrate at 300 K (CsI plates, KBr windows), and (C) tetraethylammonium chloride hydrate at 10 K (CsI plates, KBr windows). Peaks marked N are from Nujol. Peak at 3395 cm^{-1} in A is H_2O on plates used.

The infrared spectra of the water–chloride clusters in tetraethylammonium chloride hydrate and hydrate-d_2 (Figure 1) are strikingly similar to those of the corresponding tetramethylammonium fluoride hydrates, particularly in the deformation region, where narrow, intense bands attest to the presence of strongly tricoordinated electronegative atoms.[14] The stretching bands of the water–chloride clusters are found at higher energy and the deformation bands at lower energies than in the water–fluoride clusters, as expected for the lower

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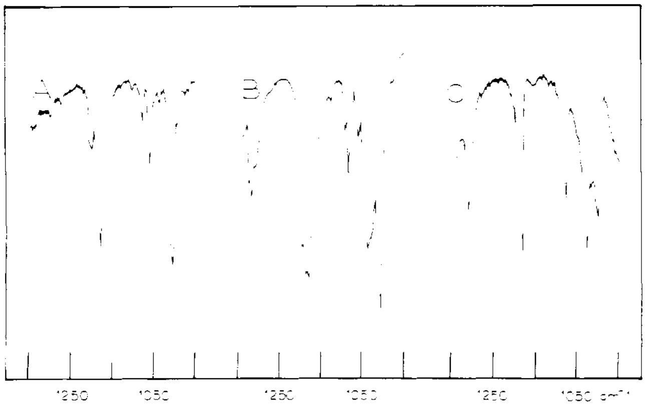

Figure 2. Infrared spectra (Nujol mulls on CsI plates) of the 1350–950 cm^{-1} region for tetraethylammonium ion in the (A) chloride, (B) chloride monohydrate, and (C) hexafluorosilicate.

electronegativity of chlorine relative to fluorine; otherwise the band shapes and splittings are nearly identical. The water–chloride clusters show significant bias toward C_{2v} symmetry; the chloride hydrate-d_2 spectrum at 300 K closely resembles that of the fluoride hydrate-d_2 at 10 K (Table I). Also, in the spectrum of the chloride hydrate at 10 K, the stretching and deformation bands are resolved into their $A_1 + B_1 + B_2$ components (Figure 1 and Table I), which is not true for tetramethylammonium fluoride hydrate. Whether this somewhat greater departure from T_d symmetry arises from lattice effects or from the greater dissimilarity between oxygen and chlorine as compared to oxygen and fluorine cannot be determined at this time.

From extensive cation infrared spectra–crystal structure correlations for tetramethylammonium ion salts,[15] we were able to show[3,4] that tetramethylammonium fluoride hydrate most probably has a unit cell isomorphous with that of the hexafluorosilicate, which contains a dinegative ion with radius equal to that calculated for the proposed $H_4O_2F_2^{2-}$ ion. No such array of structural data is available for tetraethylammonium ion salts; however, we find that the infrared spectrum of the tetraethylammonium cation in the chloride hydrate differs from that in the chloride and again resembles closely that in the hexafluorosilicate (Figure 2). In the 1350–950-cm^{-1} region, the chloride shows two doublets at 1194–1177 and 1073–1057 cm^{-1} and a singlet at 1003 cm^{-1}. The 1003-cm^{-1} band remains unchanged in both the chloride hydrate and the hexafluorosilicate; however, in the chloride hydrate the doublets have collapsed into structured singlets at 1177 and 1077 cm^{-1}, while the hexafluorosilicate shows two singlets at 1185 and 1077 cm^{-1}. More striking is the appearance of two new bands in the spectra of both the chloride hydrate and the hexafluorosilicate at 1316 and 1034 cm^{-1} and 1314 and 1030 cm^{-1}, respectively; these bands are entirely absent in the spectrum of the chloride (Figure 2).

Several weak bands appear in the 2800–2000-cm^{-1} region of the infrared spectrum of tetraethylammonium chloride hydrate, and these can be seen more clearly in the 10 K spectrum of this sample (Figure 1). The two bands at 2205 and 2145 cm^{-1} are reasonably ascribed to combination bands of the XH bend with the two X_4 deformation bands of the water–chloride cluster. The group of bands between 2700 and 2500 cm^{-1} have been identified as the characteristic N–H stretching bands of triethylammonium chloride. In pure triethylammonium chloride, these bands are extremely intense; the N–H band has five times the absorption of the next strongest band, at 1040 cm^{-1}, in the spectrum of triethylammonium chloride. Neither the 1040-cm^{-1} band nor any other bands ascribable to triethylammonium chloride can be detected in the chloride hydrate spectra at either 300 or 10 K; the presence of this small quantity of the triethylammonium salt does not perturb the spectrum of the hydrate.

Triethylammonium chloride is presumed to arise from β-hydrogen removal from tetraethylammonium ion by chloride ion to yield triethylamine, hydrogen chloride, and ethylene; similar Hofmann elimination has been shown for tetraethyl-[5] and tetrapropylammonium[16] fluorides but has not been previously reported with chloride ion. The commercial tetraethylammonium chloride hydrate starting material is free of triethylammonium chloride, and the amount of the triethylammonium salt increases slowly with time of reflux. The sample of chloride hydrate used for the low-temperature spectrum was ground from a large crystal obtained after several days of reflux; rapid recrystallization yields chloride hydrate free of triethylammonium chloride.

In conclusion, we believe that the water–chloride species in tetraethylammonium chloride hydrate is closely related structurally to the water–fluoride cluster in tetraalkylammonium fluoride hydrates. Since crystalline material can be prepared easily by recrystallization from acetone, we suggest that diffraction studies on this hydrate would be highly desirable. We do not have facilities for such studies ourselves but would be pleased to furnish crystals to persons interested in this material.

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Electrochemistry of Main-Group Phthalocyanines

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Metallophthalocyanines have been the subject of several electrochemical investigations,[1-9] but no systematic study as a function of central metal ion has been published. We have recently completed a study of the electrochemistry of main-

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