L* = PhP(Me)(α-np). A solution of $[RuCH_3(CO)_2(NCMe)(PMe_3)_2][BF_4]$ (0.584 g, 0.001 mol) in methylene chloride (100 mL) was reacted with 1 equiv of the corresponding phosphine L* at room temperature for $^1/_2$ h. The complex was precipitated by addition of pentane. The white solid was collected, washed, and dried under vacuum; yields were quantitative. IR and NMR data are given in Table II.

Anal. Calcd for $BC_{20}F_4H_{38}O_3P_3Ru$ (L* = PhP(Me)(O-*t*-Bu)): C, 39.55; H, 6.31; P, 15.30. Found: C, 39.42; H, 6.27; P, 14.91.

Preparation of $(RuCH_3(CO)_2(PhP(Me)(\alpha\text{-np}))(PMe_3)_2)(BPh_3)$. This complex was obtained from $RuICH_3(CO)_2(PMe_3)_2$ by using the procedure described above for $[FeCH_3(CO)_2L^*(PMe_3)_2][BPh_4]$, at −20 °C (method B).

Preparation of $(RuCH_2Ph(CO)_2(PhP(Me)(O\text{-}t\text{-}Bu))(PMe_3)_2)(BF_4)$. A solution of $[RuCH_2Ph(CO)_3(PMe_3)_2]_1[BPh_4]$ (0.747 g, 0.001 mol) in methylene chloride (100 mL) was reacted with 1 equiv of PhP(Me)(O-*t*-Bu) 0.195 g, 0.001 mol) in methylene chloride (50 mL) for 1 h at 20 °C to eliminate 1 equiv of CO (method A). The complex was precipitated by addition of pentane. The white solid was collected, washed, and dried under vacuum.

IR and NMR data are given in Tables II and IV.

Acknowledgment. The authors are indebted to Dr. C. Brevard (Bruker) for the computer simulation of X_9ABY_9 spin systems and for running the ^{13}C spectrum at 62.8 MHz. We also thank Dr. C. Charrier (Laboratoire SNPE, CNRS, Thiais, France) for measuring the ^{31}P spectra, M. J. Pouet for recording ^1H spectra, and Prof. J. F. Harrod and Prof. M. J. Mc Glinchey for helpful discussions.

Registry No. **1**·BPh_4 (M = Fe, L* = NCMe, R = Me), 89616-74-0; **1**·BPh_4 (M = Fe, L* = py, R = Me), 94249-34-0; **1**·BPh_4 (M = Fe, L* = PMe_3, R = Me), 89616-71-7; **1**·BPh_4 (M = Fe, L* = $P(OMe)_3$, R = Me), 89557-49-3; **1**·BPh_4 (M = Fe, L* = NCCH(Me)Cl, R = Me), 94249-36-2; **1**·BPh_4 (M = Fe, L* = PhP(*o*-C_6H_4OMe)(Me), R = Me), 94278-56-5; **1**·BPh_4 (M = Fe, L* = PhP(CH_2Ph)(Me), R = Me), 94249-54-4; **1**·BPh_4 (Me = Fe, L* = PhP(Me)(Et), R = Me), 94249-42-0; **1**·BPh_4 (M = Fe, L* = PhP(Me)(NEt_2), R = Me), 94249-56-6; **1**·BPh_4 (M = Fe, L* = PhP(Me)(OMe), R = Me), 94249-38-4; **1**·BPh_4 (M = Fe, L* = PhP(Me)(OPh), R = Me), 94249-58-8; **1**·BPh_4 (M = Fe, L* = PhP(Me)(O-*t*-Bu), R = Me), 94249-40-8; **1**·BPh_4 (M = Fe, L* = PhP(Me)(OMe), R = COMe), 94249-32-8; **1**·ClO_4 (M = Fe, L* = PhP(Me)(OMe), R = COMe), 94278-52-1; **1**·BF_4 (M = Ru, L* = NCMe, R = Me), 94249-50-0; **1**·BF_4 (M = Ru, L* = PPh_3, R = Me), 94278-58-7; **1**·BF_4 (M = Ru, L* = PMe_3, R = Me), 94249-60-2; **1**·BF_4 (M = Ru, L* = PhP(OMe)(α-np), R = Me), 94249-62-4; **1**·BF_4 (M = Ru, L* = PhP(Me)(α-np), R = Me), 94249-52-2; **1**·BF_4 (M = Ru, L* = PhP(*o*-C_6H_4OMe)(Me), R = Me), 94249-64-6; **1**·BF_4 (M = Ru, L* = PhP(Me)(CH_2Ph), R = Me), 94249-66-8; **1**·BF_4 (M = Ru, L* = PhP(Me)(O-*t*-Bu), R = Me), 94249-68-0; **1**·BPh_4 (M = Ru, L* = PhP(Me)(α-np), R = Me), 94278-59-8; **1**·BF_4 (M = Ru, L* = PhP(Me)(O-*t*-Bu), R = CHPh), 94278-54-3; **2**·BPh_4 (M = Fe, R = Me), 82660-92-2; **2**·ClO_4 (M = Fe, R = Me), 94294-06-1; **2**·BPh_4 (M = Ru, R = Me), 94249-45-3; **2**·BPh_4 (M = Ru, R = CH_2Ph), 94249-47-5; **4** (M = Fe, X = Cl), 78306-62-4; **4** (M = Fe, X = Br), 78306-64-6; **4** (M = Fe, X = I), 33542-07-3; **4** (M = Ru, X = Cl), 94345-81-0; **4** (M = Ru, X = Br), 94249-48-6; **4** (M = Ru, X = I), 88003-88-7; **5** (M = Fe, L* = PMe_3, X = I), 94345-80-9; **5** (M = Ru, L* = PMe_3, X = I), 94249-43-1; $Ru(CO)_3(PMe_3)_2$, 75687-45-5; Me_2Cd, 506-82-1; (α-np)$_2$Cd, 66338-72-5; PhP(Me)Cl, 15849-86-2; (α-np)P(Me)Cl, 94235-64-0; PhP(O-*t*-Bu)Cl, 94235-65-1; PhP(NEt_2)Cl, 4073-31-8; PhP(Me)(*o*-C_6H_4OMe), 1485-88-7; PhP(Me)(CH_2Ph), 23275-37-8; PhP(Me)(α-np), 38851-76-2; PhP(Me)(OMe), 94235-66-2; PhP(OMe)Ph, 4020-99-9; PhP(α-np)OMe, 94278-51-0; PhP(Me)(O-*t*-Bu), 94249-30-6; PhP(Me)(NEt_2), 708-90-7; PhP(Me)(Et), 15849-84-0; $(Ph_4P)Cl$, 2001-45-8; $(Ph_3MeP)Br$, 1779-49-3; NCCH(Me)Cl, 1617-17-0; dichlorophenylphosphine, 644-97-3.

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Formation and Stabilization of Anionic Metal Complexes in Concentrated Aqueous Quaternary Ammonium Salt Solutions

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Anionic complexes of transition metals were stabilized in aqueous solutions containing high concentrations of various short-chain quaternary ammonium salts. Compounds with longer paraffin chains were effective in much less concentrated solution. Complex ions were detected spectrophotometrically. $FeCl_4^-$, which is usually formed in concentrated HCl, was the predominant Fe(III) complex in 30 *m* choline chloride containing only 0.12 M HCl. A yellow transitory Tc(VII) chloro-addition intermediate, formed in the reduction of TcO_4^- by concentrated HCl, was stabilized when the solution also contained 25 *m* choline chloride. Its spectrum, as well as the isolation of an already known Tc(VII) bipyridyl complex, is reported. Concentrated organic electrolytes also stabilized Tc(V) oxide halides against disproportionation and Tc(IV) hexahalides against hydrolysis. Halochromates of Cr(VI) were formed and stabilized in dilute acid containing quaternary ammonium salts. Their UV spectra showed the well-resolved vibronic fine structure associated with the symmetric chromium-to-oxygen charge-transfer band. It is known that these progressions are resolved in aprotic solvents, but not in aqueous acidic solution alone, and that the loss of fine structure in aqueous media is due to hydrogen bonding. The stabilization of anionic metal complexes and the resolution of vibronic structure in halochromates are probably consequences of water-structure-enforced ion pairing. The present work strongly suggests that the water molecules in immediate contact with the complex anions are more strongly hydrogen bonded to each other than to the complex.

Introduction

Quaternary ammonium salts of large anions, tetraalkylammonium perchlorates and perrhenates, for example, are considerably less soluble in water than in organic solvents. This illustrates a well-known general phenomenon—that compounds composed of two large ions, although insoluble in water, are often soluble in a variety of organic solvents—and has led to the widespread practice in inorganic chemistry of precipitating such compounds from water and then dissolving them in organic solvents for detailed physicochemical studies. It is particularly useful for the preparation and study of easily hydrolyzable anionic metal complexes.

On the other hand, quaternary ammonium salts in concentrated aqueous solution are salting-in agents.[1] Tetra-*n*-butylammonium perchlorate, for example, is strongly salted into water by concentrated tetra-*n*-butylammonium bromide in spite of the common ion effect.[2] This suggests that quaternary ammonium salts might salt in anionic metal complexes.

There is also reason to believe that concentrated aqueous solutions of quaternary ammonium salts would stabilize as well as solubilize reactive metal complexes. This is suggested by results of extraction studies with strongly basic anion-exchange resins. Such resins, which can be viewed as three-dimensional insoluble

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quaternary ammonium salts, can selectively extract anionic metal complexes from aqueous solution under conditions where very little complex is originally present.[3] Liquid ion exchangers based on amine or quaternary ammonium salts can also stabilize and extract anionic metal complexes.[4]

In the present paper, a number of anionic transition-metal complexes were studied spectrophotometrically in aqueous concentrated quaternary ammonium salt solutions in order to determine whether stabilization would take place. These included (1) Fe(III) chloro complexes, (2) Tc(VII), Tc(V), and Tc(IV) halo and oxo halo complexes, and (3) chromium(VI) halo compounds where the resolution of vibronic fine structure was observed.

Experimental Section

Materials. Choline chloride ((2-hydroxyethyl)trimethylammonium chloride) was purchased from Sigma Chemical Co. and recrystallized from ethanol. Tetra-*n*-butylammonium bromide, electrometric grade, and tetra-*n*-butylammonium chloride hydrate were obtained from Southwestern Analytical Chemicals, Inc., and were used without further purification. Tetra-*n*-pentylammonium chloride was purchased from Eastman Chemical Co. Ferric chloride, potassium dichromate, and other reagent chemicals were purchased from Fisher Scientific Co. They were the highest grade available and were used without further purification. Ammonium pertechnetate in solution was supplied by the New England Nuclear Corp. Tetra-*n*-butylammonium oxotetrachlorotechnetate(V), $[(n\text{-Bu})_4\text{NTcOCl}_4]$, was prepared as described by Davison et al.[5] The Tc(IV) anions, TcCl_6^{2-} and TcBr_6^{2-}, were prepared by reduction of TcO_4^- in concentrated HCl and HBr, respectively,[6] and isolated as the tetra-*n*-butylammonium salts. The absorption spectra of solutions of these salts were in agreement with published data.[5,7] Partially quaternized poly(vinylpyridinium bromide) was a gift from Dr. F. Eirich of the Polytechnic Institute of New York.

General Methods. The quaternary ammonium salt solutions were prepared on a molal (*m*) basis, and the transition-metal compounds were then dissolved in these solutions on a molar (M) basis. Most of the studies were conducted in 20–30 *m* choline chloride. Complex ions were detected spectrophotometrically by using a Beckman Acta recording spectrophotometer. IR spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

Fe(III) and Cr(VI) complex ions were prepared by adding aliquots of stock solutions of $\text{FeCl}_3\cdot6\text{H}_2\text{O}$ in 12 M HCl or of potassium dichromate in dilute perchloric acid to solutions of the quaternary ammonium salts.

Tc halogenate and oxo halogenate ions were prepared as follows: (1) addition of pertechnetate to concentrated HCl, or to choline chloride dissolved in concentrated HCl, to yield—depending on time and temperature—the Tc(VII), Tc(V), or Tc(IV) oxo halogenate ion; (2) addition of the oxo halogenate—either as the solid tetra-*n*-butylammonium salt or as the complex already formed in concentrated HCl—to the quaternary ammonium salt solutions.

Results and Discussion

Fe(III) Chloro Complexes. The absorption spectrum of Fe(III) in concentrated HCl is predominantly that of the tetrahedral FeCl_4^- anion. This anion is the limiting mononuclear complex formed by dilute Fe(III) in concentrated HCl.[8] Some octahedral complexes may be present but would contribute little to the spectrum. FeCl_4^- is unstable in dilute acid and hydrolyzes, forming lower chloro and various hydroxy complexes in proportions depending on pH and other factors. In dilute HCl and water, the spectra of any Fe(III) chloro complexes are obscured by the strong light absorption due to the various hydroxy complexes.[9]

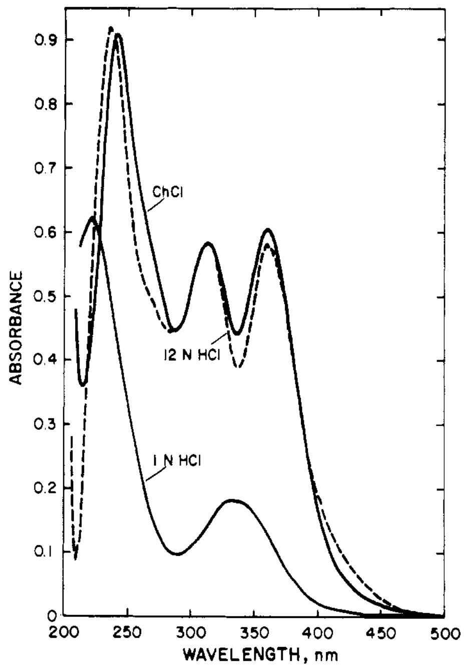

Figure 1. Optical spectra of $\text{FeCl}_3\cdot6\text{H}_2\text{O}$ (1.05×10^{-4} M) in 1 M HCl, in 12 M HCl, and in 30 *m* choline chloride containing 0.12 M HCl.

Figure 1 shows the absorption spectra of 1.05×10^{-4} M solutions of ferric chloride in concentrated HCl, in 30 *m* choline chloride, and in 1 M HCl. The choline chloride solution also contained HCl, but at a concentration of 0.12 M. The spectra in the choline chloride solution and in 12 M HCl are nearly identical and resemble the limiting spectrum of Fe(III) in concentrated HCl reported by Gamlen and Jordan.[8] The spectrum in the quaternary solution was unchanged for at least several days. At concentrations of choline chloride below 30 *m*, the yield of FeCl_4^- was lower. High yields of FeCl_4^- were also obtained in 2 *m* tetra-*n*-butylammonium chloride and in 1 *m* tetra-*n*-pentylammonium chloride solutions. Spectra (not shown) of Fe(III) in 20 *m* LiCl and in saturated CsCl, both containing 0.12 M HCl, indicated hydrolysis.

The close resemblance of the spectra of Fe(III) in concentrated HCl and in the organic electrolytes argues that FeCl_4^- is the predominant species in all four solutions. It is resistant to hydrolysis in the organic salt system despite the low concentration of acid. A high chloride ion concentration by itself is not sufficient; from the LiCl and CsCl experiments it is clear that a major stabilizing effect is associated with the quaternary ammonium ions.

Halogenate Complexes of Technetium. The addition of pertechnetate (TcO_4^-) to concentrated aqueous halo acids leads to the reduction of technetium with the replacement of some or all of the oxygens by halogen. Solid oxohalotechnetates of Tc(V) and halotechnetates of Tc(IV) are obtained from concentrated acidic solution as either the cesium or tetra-*n*-butylammonium salts; they are soluble in organic solvents. In dilute acid or water the Tc(V) complexes disproportionate,[10] and the Tc(IV) complexes hydrolyze to insoluble TcO_2.[7a]

It is known that when pertechnetate is added to concentrated HCl, a transient yellow color appears before the solution develops the greenish yellow color of the Tc(V) oxochloro anion. Davison et al. suggested that the yellow species is a Tc(VII) chloro-addition product with the formula $[\text{TcO}_3\text{Cl}_3]^{2-}$.[11] They based this proposal on (1) an analogy with a Re(VII) chloro-addition product isolated as the solid cesium salt from concentrated HCl and characterized by spectroscopy and X-ray crystallography[12] and (2) their isolation of a Tc(VII) bipyridyl complex from an acidified ethanol solution

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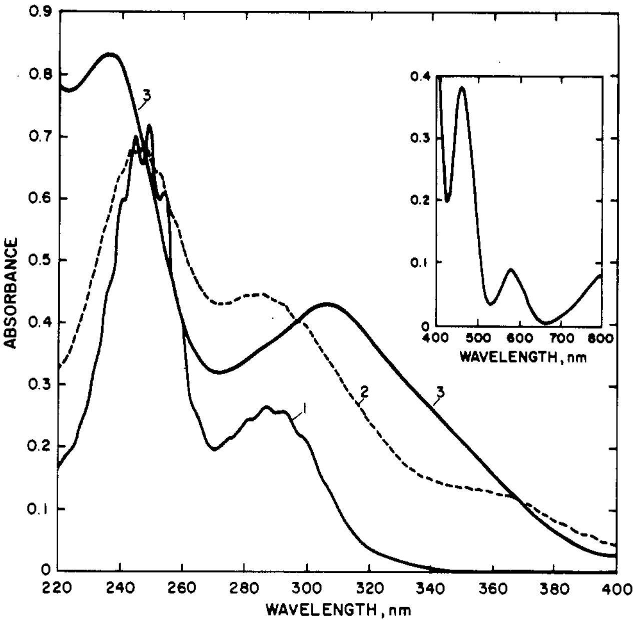

Figure 2. Electronic spectral changes accompanying the reduction of TcO_4^-: (1) spectrum of TcO_4^- in 25 *m* choline chloride without HCl; (2) spectrum 1 min and (3) spectrum 15 h after adding TcO_4^- (1.1×10^{-4} M) to choline chloride in concentrated HCl. Insert: visible spectrum of TcO_4^- (0.018 M) after 4 days in acidic choline chloride.

containing TcO_4^- and bipyridyl. Addition of bipyridyl to the already acidified pertechnetate–ethanol solution resulted in the precipitation of a Tc(V) bipyridyl complex.

In place of the almost instantaneous reduction of TcO_4^- in concentrated HCl, we found that virtual saturation of the latter with choline chloride retarded the redox reaction. The solution stayed bright yellow for several hours, and its spectrum was unlike that reported[7a,11] for either the TcO_4^- or the Tc(V) oxo chloro anion. By the next day, the solution had turned greenish yellow and its spectrum was that of the Tc(V) complex. These spectra are shown in Figure 2.

Figure 2 compares the UV spectrum of TcO_4^- in 25 *m* choline chloride and the UV spectrum of pertechnetate added to 25 *m* choline chloride in concentrated HCl; the latter spectrum was obtained within 2 min of the addition. The figure also shows the spectrum of the solution after 15 h of standing at room temperature. The insert shows the characteristic low-intensity absorption bands in the visible absorption spectrum of a more concentrated solution of TcO_4^- added to the acidic choline chloride 4 days after mixing. The absorptivity coefficients of the Tc(V) oxo chloro anion were almost identical with those observed after 15 h of standing. These spectra show that the initial effect of acidic choline chloride on TcO_4^- is an increase in intensity at the 290-nm peak and a considerable broadening and extension of this band into the visible region.

The slow conversion of the yellow species to a Tc(V) ion argues that the transient intermediate in the HCl reduction of pertechnetate is a Tc(VII) complex. As further evidence that it is a Tc(VII) compound, the addition of bipyridyl 1 h after mixing TcO_4^- and the choline chloride–HCl solution still yielded the previously described[11] Tc(VII) bipyridyl complex with a 46% yield. If the bipyridyl was present at the time of mixing, the yield was 60%. Both complexes had the same infrared and melting point characteristics as the Tc(VII) bipyridyl complex reported by Davison et al.[11]

High concentrations of organic electrolyte also stabilized Tc(V) and Tc(IV) complex ions. The absorption spectrum, not shown, of the Tc(V) complex, formed in concentrated HCl and added as an aliquot to 25 *m* choline chloride (final HCl concentration 0.01 M), was similar to the spectrum of the tetra-*n*-butylammonium salt dissolved in choline chloride. Both spectra resembled the spectrum of Tc(V) in methylene chloride reported by Davison et al.[11]

The spectra of Tc(V) in solutions of concentrated HCl, and in solutions prepared by adding aliquots of the latter to choline chloride, included a peak between 230 and 235 nm, a region below the UV cutoff point of methylene chloride. This peak, which was particularly intense in fresh solutions, is due in part to the presence of dissolved chlorine gas formed in the reduction of TcO_4^-. If the sample was flushed with nitrogen or allowed to stand for several hours, the absorptivity coefficient in this region was the same as that obtained by dissolving the tetra-*n*-butylammonium oxotetrachlorotechnetate(V) salt in the choline chloride solution. Molar absorptivity coefficients (M^{-1} cm^{-1}) of the tetra-*n*-butylammonium Tc(V) salt stabilized in 25 *m* choline chloride containing 0.1 M HCl are as follows: 840 nm, 9; 590 nm, 6; 480 nm, 22; 293 nm, 4300; 235 nm, 9200.

The Tc(IV) complex ions studied included $TcCl_6^{2-}$ and $TcBr_6^{2-}$. Molar absorptivity coefficients of the tetra-*n*-butylammonium salts of $TcCl_6^{2-}$ in 25 *m* choline chloride were 9900 at 342 nm, 6700 at 309 nm, and 17 000 at 243 nm. These values are similar to those reported in the literature for the hexachlorotechnetate ion in concentrated HCl.[7] The solution was stable for at least several days. The solid tetra-*n*-butylammonium salt of $TcBr_6^{2-}$ in 10 *m* tetra-*n*-butylammonium bromide was less stable; 70% decomposed within 18 h. The presence of 0.12 M HBr in the solution stabilized the complex for several days. Its molar absorptivity coefficients are as follows: 445 nm, 4800; 390 nm, 6100; 335 nm, 7300; 268 nm, 11 800.

Vibrational Fine Structure of Cr(VI) Halo Complexes. The electronic absorption spectra of polyatomic species often show vibrational fine structure in the gaseous and crystalline states, and in noninteracting solvents at low temperatures.[13] Such fine structure is rarely seen in water because of interaction with solvent molecules. A number of oxo anions of some transition metals are exceptions, among them MnO_4^-, ReO_4^-, and TcO_4^-.[14] Oxo anions of Cr(VI), on the other hand, show well-resolved vibronic fine structure in aprotic solvents but not in aqueous solution.[13] For example, the spectrum of the chlorochromate ion, the predominant anionic form[15] of Cr(VI) in HCl above 1 M, does not show the vibronic fine structure observable in organic solvents.[16] The chlorochromate anion is stable in 1 M HCl but hydrolyzes in water.[17]

The vibronic progressions in the chromate halo anion spectra are superimposed on an oxygen-to-chromium charge-transfer band; the fine structure comes from the excitation of a symmetric stretching mode in the CrO_3 group.[16] Such progressions are characteristic of ions with full C_{3v} symmetry. This band is centered at 355 nm.

We have examined the effects of concentrated quaternary ammonium salts and other electrolytes on the absorption spectra of 2.5×10^{-4} M potassium dichromate in solutions of two initial acidities: 1 M HCl and 0.025 M $HClO_4$. A solution of dichromate in 1 M HCl alone showed no vibronic fine structure. The addition of enough choline chloride to bring the latter to 25 *m* resolved individual vibronic bands very much like those reported for CrO_3Cl^- in aprotic solvents.[16]

It is not necessary to synthesize the CrO_3Cl^- moiety in 1 M HCl before adding solid choline chloride in order to obtain the vibronic progressions, since identical vibronic structure was observed in a 25 *m* choline chloride solution upon addition of potassium dichromate; the solution also contained 0.025 M perchloric acid. It can be concluded that in dilute acid, with sufficient quaternary ammonium chloride present, the chlorochromate complex will be formed.

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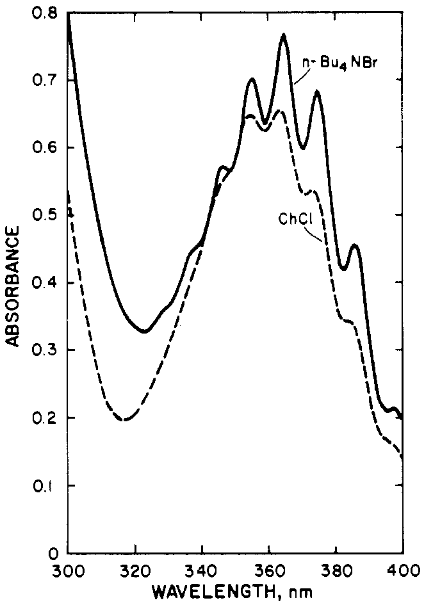

Figure 3. UV absorption spectra of $K_2Cr_2O_7$ (2.5×10^{-4} M) in 30 *m* choline chloride and in 5 *m* tetra-*n*-butylammonium bromide. Both solutions also contained 0.025 M $HClO_4$.

Figure 3 shows the absorption spectra of 2.5×10^{-4} M $K_2Cr_2O_7$ in 5 *m* tetra-*n*-butylammonium bromide and in 30 *m* choline chloride, both in the presence of 0.025 M perchloric acid. The vibronic bands of the bromochromate complex are quite marked. Their average spacing, 700 cm^{-1}, compares with a value of 650 cm^{-1} reported for this complex in aprotic solvents.[16]

Figure 4 compares the spectra of 2.5×10^{-4} M $K_2Cr_2O_7$ in a 1.2 M HCl solution that had been saturated with CsCl and in a 1.2 M HCl solution containing 5 *m* tetra-*n*-butylammonium chloride. The figure shows first that the stabilization of the CrO_3Cl^- vibrational levels is not due mainly to the halide ion in these concentrated solutions but second that the cation—presumably through its size—plays an important role. In the chlorochromate spectrum in 1.2 M HCl there are only traces of vibronic structure in the form of several faint inflection points. These become somewhat more distinct in the spectrum of the CrO_3Cl^- anion in saturated CsCl and are more strongly developed as actual bands in the tetra-*n*-butylammonmium chloride solution.

Vibronic progressions were also observed in a 1 M HBr solution containing 2.5×10^{-4} M dichromate and 2 mg/mL of a partially quaternized poly(vinylpyridinium bromide) and in a 1 M HBr solution containing 0.01 M cetyltrimethylammonium bromide, a concentration above the detergent's critical micelle concentration (cmc). No vibronic progressions were observed below the cmc. The appearance of the vibronic progression in these dilute polyelectrolyte solutions suggests that what is occurring in the concentrated quaternary ammonium salt solutions is also taking place in the immediate vicinity of these solutes, where there is a high (local) concentration of organic cations.

Choline chloride was used as the principal quaternary ammonium salt in most of this research. This is because we required a series of soluble quaternary ammonium salts for a more extensive investigation of the effects of different anionic counterions on the stabilization of metal complexes. Tetraalkylammonium perchlorates, iodides, and thiocyanates, for example, are too insoluble for this purpose. The corresponding choline salts, on the other hand, are quite soluble but like the chloride require extremely high concentrations for metal complex stabilization.

Long chain tetraalkylammonium chlorides and bromides produce the same stabilizing effects as the corresponding choline salts but at much lower concentrations. We have already noted that the formation of $FeCl_4^-$ was observed in a 2 *m* solution of tetra-*n*-butylammonium chloride and in 1 *m* tetra-*n*-pentylammonium chloride. A 2 *m* solution of tetra-*n*-butylammonium bromide showed the vibronic progressions of the CrO_3Br^- anion, and the vibronic progression of the chlorochromate anion was clearly apparent in 1 *m* tetra-*n*-pentylammonium chloride solution.

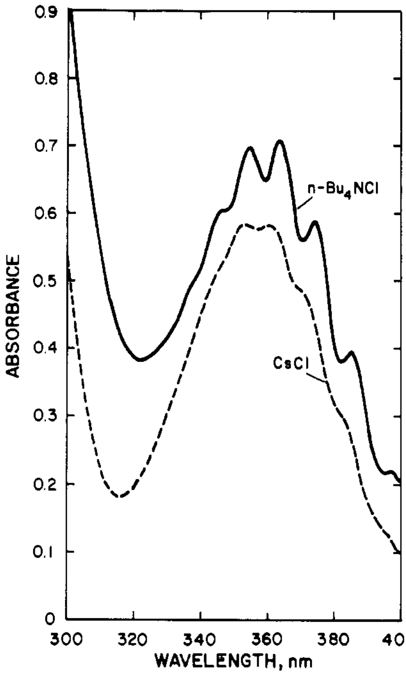

Figure 4. UV absorption spectra of $K_2Cr_2O_7$ (2.5×10^{-4} M) in 5 *m* tetra-*n*-butylammonium chloride and in saturated CsCl. Both solutions contain 1.2 M HCl.

We have extended to these less concentrated solutions certain concepts about the behavior of still more dilute aqueous quaternary ammonium salt solutions, in order to explain the solubilization and stabilization of anionic metal complexes.

Quaternary ammonium salts in water are believed to produce cages of hydrogen-bonded water molecules around their nonpolar paraffinic moieties.[18] Frank[19] explained some of their behavior in aqueous solution by the formation of a cation–cation pair, hypothesizing that with increasing concentration there was an increasing mutual stabilization of the H-bonded water cages around these cations. In his view, the expected electrostatic repulsion would be overcome by the free energy decrease associated with the H-bonded stabilization of the water cages. We postulate that the observed solubilization by tetra-*n*-butylammonium bromide of the normally insoluble tetra-*n*-butylammonium perchlorate[2] is due to the formation of such cation–cation pairs. This process is also responsible for the solubilization of the anionic metal complexes reported here.

Stabilization of the easily hydrolyzed metal anionic complexes by the organic salt solutions is explained by a different, but related, concept. In order to account for the unusually low activity coefficients in water of quaternary ammonium iodides, Diamond hypothesized that a new type of ion pair, which he called a water-structure-enforced ion pair, was formed.[20] If both the cation and the anion are large and poorly hydrated, they will associate closely with each other in order to minimize disturbances to the water structure in the immediate vicinity, and in turn, the water in immediate contact with the ion pair will become more strongly hydrogen bonded to the next water layer.

The almost complete loss of vibronic structure in aqueous acid solutions of halochromates has been attributed to hydrogen bonding between the complex anions and the water.[21] The restoration of vibronic progression in the quaternary ammonium salt solutions takes place because the hydrogen bonding between water molecules and the halochromate is reduced or eliminated. This means, as Diamond hypothesized, that the water in the immediate vicinity of the ion is more strongly hydrogen bonded

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to itself than to the halochromate. This also means that complex metal anions in general will be insulated to some extent from hydrolysis and other solvent-related reactions because there will be a paucity of free water molecules in their immediate vicinity.

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Registry No. $TcCl_6^{2-}$, 16972-03-5; $TcBr_6^{2-}$, 19443-24-4; CrO_3Cl^-, 15906-70-4; $FeCl_4^-$, 14946-92-0; choline chloride, 67-48-1; tetra-*n*-butylammonium chloride, 1112-67-0; tetra-*n*-pentylammonium chloride, 4965-17-7; poly(vinylpyridinium bromide), 32492-40-3; cetyltrimethylammonium bromide, 57-09-0.

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Crystal Structures of Mixed-Valency and Mixed-Metal Salts $A_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}X_6$ (A = Rb, Cs; M = Sb, Bi, In, Tl, Fe, Rh; X = Cl, Br). A Powder Neutron Diffraction Study

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The crystal structures of 11 mixed-valency and mixed-metal salts $A_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}X_6$ (A = Rb, Cs; M = Sb, Bi, In, Tl, Fe, Rh; X = Cl, Br) have been determined by powder neutron diffraction at 4.7 K and in several cases also at 298 and 423 K. Structures were refined by the Rietveld method. In five cases (A = Cs; M = Sb, Bi, Tl; X = Cl and A = Rb, Cs; M = Sb; X = Br), superlattice ordering of SbX_6^- and MX_6^{3-} was found (space group *I*4$_1$/*amd*) while the remainder were disordered (space group *Fm*3*m*). The presence of order or disorder correlates with the average $M^{III,V}$–X bond length. In $Rb_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Br_6$, the $SbBr_6^{n-}$ groups are also tilted from the 4-fold axis at 4.7 K (space group *I*4$_1$/*a*). $Cs_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ retains distinguishable $SbCl_6^-$ and $SbCl_6^{3-}$ up to 423 K. Other physical properties (vibrational spectra) are discussed in the light of the structural results.

Introduction

The hexahalogenoantimonate(III,V) salts $A_2Sb^{III}{}_{0.5}Sb^{V}{}_{0.5}X_6$ have long been recognized as prototypes of Robin–Day[1] class II mixed-valency behavior, and their structural simplicity makes them ideal starting models for an understanding of the dynamics of intervalence electron transfer in weak interaction systems. Surprisingly, their structures have presented a longstanding puzzle. Early X-ray powder diffraction work[2] indicated that the salts crystallize with a structure isomorphous with that of K_2PtCl_6 (space group *Fm*3*m*), leading to the conclusion that the $Sb^{V}X_6^-$ and $Sb^{III}X_6^{3-}$ units are either crystallographically equivalent or randomly distributed. Later, X-ray single-crystal diffraction[3,4] established the presence of a superlattice in A_2SbBr_6 (A = NH_4, Rb).

To evaluate physical properties of these mixed-valency compounds, it is essential to have precise structural information, e.g. the difference in site geometry and bond length around the ions of differing oxidation states. In the case of the hexahalogenoantimonates(III,V), there have been reports that electron transfer may be sufficiently fast at high temperature to make the Sb sites equivalent on the Mössbauer time scale. In additon, with increasing temperature, the Sb^{III}–Cl stretching mode becomes weaker, suggesting that the oxidation state may lose its discrete character as phonons are progressively excited.

Given that the X-ray scattering in Cs_2SbCl_6 and related chlorides is dominated by the heavy elements Cs and Sb, we have undertaken a detailed investigation of the structural properties of the hexahalogenoantimonates(III,V) and mixed-metal salts with general formula $A_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}X_6$ (A = Rb, Cs; M = Sb, Bi, In, Tl, Fe, Rh; X = Cl, Br) by powder neutron diffraction at temperatures from 4.7 to 423 K. A preliminary report of some of our results has appeared elsewhere.[5]

Experimental Section

All the compounds were prepared by standard methods[6,7] from HCl (or HBr) solutions of the constituent ions. X-ray powder diffraction was employed to ensure their purity. In order to suppress debromination, Rb_2SbBr_6 and Cs_2SbBr_6 were sealed in a tube under a bromine atmosphere. The powder neutron diffraction data were obtained on the high-resolution powder diffractometer, D1A, at the Institut Laue-Langevin, Grenoble, using neutrons with a mean wavelength of 1.909 Å. The samples were mounted in vanadium cans placed in a standard liquid-helium cryostat or an evacuable furnace. Diffraction data were collected in steps of 0.05°. The raw data from the 10 counters were merged by using Hewat's computer program.[8] After background subtraction, profile refinements were performed by using either the POWDER system[9] on the SERC Interactive Computing Facility or the modified version of the Rietveld program[10] on the Oxford University ICL 2988 computer. Neutron scattering lengths were taken from Bacon.[11] Since chlorine has a large mass absorption coefficient, an absorption correction was applied to the thermal parameters. An "effective" overall temperature factor due to absorption was calculated[12] and kept fixed during refinement while the individual isotropic temperature factors of all the atoms were refined independently.

Results

Cubic Salts. The simplest powder neutron diffraction profiles were obtained from the compounds $Rb_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ (M = Tl, In, Fe, Rh) and $Cs_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ (M = In, Fe) at 4.7 K. The small number of very sharp peaks indicates the high symmetry of the structure. Further, the background was flat and the signal-to-noise ratio excellent. A systematic investigation near the background level confirmed the absence of weak superlattice peaks, and all the reflections present in the profiles can be accounted for by the space group *Fm*3*m*. The difference between the $A_2M^{III}{}_{0.5}Sb^{V}{}_{0.5}Cl_6$ salts and the $A_2M^{IV}Cl_6$ antifluorite crystals is that the former contain two different octahedral units MCl_6^{3-} and $SbCl_6^-$ with M^{III} and Sb^{V} having different neutron scattering lengths, *b*. To perform the Rietveld refinement,[10] a random

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