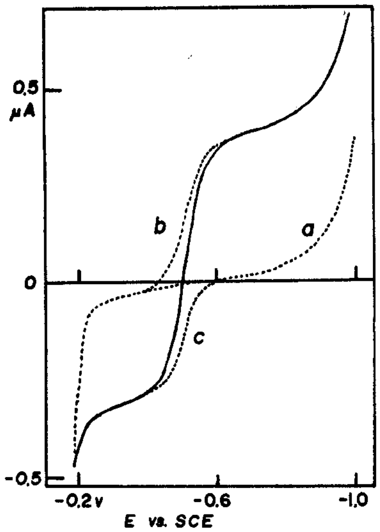

Figure 3.—Current–potential curves for Cr^{2+} and $CrBr^{2+}$ in 2 M HBr: curve a, residual current; curve b, 0.2 mM $CrBr^{2+}$; curve c, 0.2 mM Cr^{2+}; solid line, 0.2 mM Cr^{2+} and 0.2 mM $CrBr^{2+}$.

Figure 3 shows an example of the polarograms when equal amounts of $CrBr^{2+}$ and Cr^{2+} are present. In considering these results we conclude that the reduction of $CrBr^{2+}$ at a dropping mercury electrode is reversible if bromide ion is present. Therefore the mechanism of the electrode reaction will be

$$(H_2O)_5CrBr^{2+} \rightleftharpoons (H_2O)_5\text{-Cr-Br—Hg electrode}$$
$$\rightleftharpoons Cr^{2+} + Br^-$$

The most reasonable explanation of the electrode reaction seems to be that the halide ions act as bridging ligands in the case of the electron-transfer reaction between halogenochromium(III) complexes and Cr^{2+} [7,8] and that electrolytic oxidation of Cr^{2+} at the mercury pool electrode in the presence of halide ion produces the halogenopentaaquochromium(III) complex.[9]

One can therefore explain the dependence of the half-wave potential for $CrBr^{2+}$ on the concentration of bromide ion using the Nernst equation

$$E = E_0 - \frac{RT}{F}\ln\frac{(\mathrm{CrBr^+})}{(\mathrm{CrBr^{2+}})} = E_0 - \frac{RT}{F}\ln\frac{(\mathrm{Cr^{2+}})}{(\mathrm{CrBr^{2+}})}K(\mathrm{Br^-})$$

where E_0 is the equilibrium potential for the $CrBr^+$–$CrBr^{2+}$ couple, and K is defined as

$$K = \frac{(\mathrm{CrBr^+})}{(\mathrm{Cr^{2+}})(\mathrm{Br^-})}$$

At the half-wave potential, $(\mathrm{Cr^{2+}}) = (\mathrm{CrBr^{2+}})$ if $K \ll 1$, and

$$E_{1/2} = E_0 - \frac{RT}{F}\ln K - \frac{RT}{F}\ln(\mathrm{Br^-})$$

This equation is in accordance with the experimental result shown in Figure 1. Because the reduction potential for $CrCl^{2+}$ is far more negative than the oxidation potential for Cr^{2+} in bromide ion solution, the half-wave potential for $CrCl^{2+}$ observed did not vary with the concentration of bromide ions (Figure 2).

In the further experiments, chloride ion also caused the negative shift of the half-wave potential for $CrBr^{2+}$; however, the reduction wave in chloride ion solution was not a reversible one. It is impossible at the reduction potential for $CrBr^{2+}$ to reduce the product of the reverse reaction

$$Cr^{2+} + Cl^- \xrightarrow{-e^-} CrCl^{2+}$$

Experimental Section

Polarography.—All measurements were made in 2 M hydrogen ion solution with no maximum suppressor at 25.0 ± 0.1°. The polarograph used for all measurements was a Yanagimoto Model PA-102. The dropping mercury electrode had the following characteristics: m = 1.628 mg/sec, t = 4.01 sec/drop in 1 M perchloric acid at a potential of −0.6 V.

Materials.—$[CrBr_2(H_2O)_4]Br \cdot 2H_2O$ was obtained from Mitsuwa Chemical Co., Osaka, Japan, as $CrBr_3 \cdot 6H_2O$ and was recrystallized twice from hydrobromic acid. A solution containing only bromopentaaquochromium(III) ion in perchloric acid was obtained by the use of a cation-exchange resin, Dowex 50W-X8, after the aquation of $CrBr_2^+$ to $CrBr^{2+}$. The procedure used for purification with the resin was quite similar to that described by Guthrie and King.[10] Chloropentaaquochromium(III) solution was prepared in the same way. Chromium(II) perchlorate solution was prepared by electrolytic reduction of chromium(III) perchlorate at a mercury pool electrode. Other reagents used were of Guaranteed Reagent grade.

Analyses.—Chromium content was determined spectrophotometrically as chromate ion after oxidation with peroxide in alkaline solution. Chloride and bromide ion were analyzed by amperometric titration with silver nitrate after neutralization of the solutions. Analyses of bromo- and chlorochromium(III) solutions gave ratios of Br:Cr = 1.01 and Cl:Cr = 0.998, respectively. Amperometric titration was also used to determine the content of chromium(II) with cerium(IV) standard solution.

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Tetraphenylarsonium Hydrogen Dihalide Hydrates[1]

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We have found,[2] in contrast to an earlier report,[3] that the infrared spectrum of the hydrogen dibromide ion in a series of anhydrous tetraalkylammonium hydrogen dibromides is strongly affected by cation environment; similar observations have recently been independently reported by Evans and Lo.[4]

In continuing these studies we wished to examine the hydrogen dihalide salts of the large, delocalized tetraphenylarsonium cation. "Tetraphenylarsonium chloride hydrochloride" is a familiar compound; its prepara-

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(1) Work supported by the Petroleum Research Fund and the National Science Foundation.

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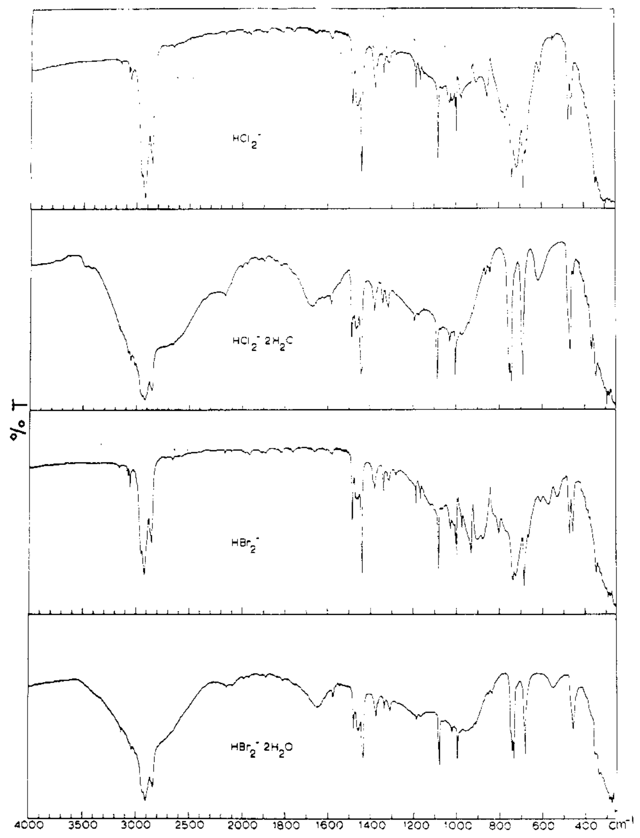

Figure 1.—Infrared spectra of anhydrous and hydrated tetraphenylarsonium hydrogen dihalides.

tion is given in ref 5, and it can be purchased from several commercial sources. On the assumption that this material was a hydrogen dihalide salt, we prepared a sample by recrystallization of tetraphenylarsonium chloride from concentrated hydrochloric acid, as reported,[5,6] and prepared an analogous "tetraphenylarsonium bromide hydrobromide" by recrystallization of the bromide from concentrated hydrobromic acid. The infrared spectra of these salts are nearly identical (Figure 1) and closely resemble the spectra of "wet" tetraalkylammonium hydrogen dibromides;[2-4] this, coupled with the observation that aqueous hydrohalic acid was evolved when either "tetraphenylarsonium halide hydrohalide" was heated *in vacuo*, caused us to doubt the assigned formulation of these materials. Subsequent careful analyses have shown both compounds to be stoichiometric dihydrates.[7,8] Anhydrous tetraphenylarsonium hydrogen dihalides were prepared by solution of halide salt in liquid hydrogen halide and evaporation of excess solvent, after the method of Waddington.[9] The infrared spectra of the anhydrous salts (Figure 1) show anion absorptions [hydrogen dichloride, 700 and 1000 cm^{-1} (broad); hydrogen dibromide, about 800 cm^{-1} (very broad)] as would be expected for hydrogen dihalide salts of a large cation;[2,4,10] in addition, there are no absorptions in the O–H region.

Experimental Section

Materials.—Baker and Adamson reagent grade 37% hydrochloric acid and Matheson anhydrous hydrogen chloride and hydrogen bromide were used without further treatment. Baker and Adamson reagent grade 48% hydrobromic acid was distilled before use; Baker and Adamson reagent grade anhydrous acetone was stored over Linde 4A Molecular Sieves. City Chemical Co. tetraphenylarsonium chloride was recrystallized from acetone and dried *in vacuo*.

Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer, using potassium bromide plates. The Nujol used for mulling was dried by solution in purified[11] pentane, treatment with Linde 4A Molecular Sieves, and evaporation of pentane in the glove box. All mulls were prepared in a glove box under carefully dried nitrogen.

Tetraphenylarsonium Chloride Hydrochloride Dihydrate.—Tetraphenylarsonium chloride was recrystallized from hot 37% hydrochloric acid to yield a mass of white needles which were air dried for several days. *Anal.* Calcd for $C_{24}H_{25}AsCl_2O_2$: C, 58.70; H, 5.13; Cl, 14.44; loss on drying, 15.76; H_2O, 8.34. Found:[12] C, 58.70; H, 5.16; Cl, 14.24; loss on drying, 15.69; H_2O, 8.36.[13,14]

Tetraphenylarsonium Bromide Hydrobromide Dihydrate.—Tetraphenylarsonium bromide was prepared by recrystallization of the chloride three times from 48% hydrobromic acid, once from a hot aqueous solution which had been neutralized with sodium hydroxide to a pH of 8, and twice from acetone. A sample of this bromide was then recrystallized from oxygen-free 48% hydrobromic acid to yield white crystals which were air dried for several days. *Anal.* Calcd for $C_{24}H_{25}AsBr_2O_2$: C, 49.68; H, 4.34; Br, 27.54; loss on drying, 20.16; H_2O, 6.21. Found:[12] C, 50.55; H, 4.56; Br, 27.30; loss on drying, 20.34; H_2O, 6.52.[13,14]

Anhydrous Hydrogen Dihalides.—Each carefully recrystallized halide salt was dried for 1 week at 65° and 1 torr in a drying pistol with phosphorus pentoxide; infrared spectral analysis showed no trace of solvent or water in these salts. A Pyrex cell fitted with a high-vacuum stopcock was charged with a weighed sample of the halide salt in the glove box; the cell was then evacuated, removed from the glove box, and sealed to an all-glass vacuum system. The total system was evacuated, filled with dry nitrogen several times, evacuated again, and filled with anhydrous hydrogen halide. The cell was then opened to the system and sufficient hydrogen halide condensed on the sample by liquid nitrogen cooling to afford a clear solution. Excess solvent was then removed by pumping or expansion into an evacuated 5-l. bulb until the amount of hydrogen halide remaining was equal to or less than 1 mol/mol of halide salt. Both of the hydrogen dihalides were white, crystalline solids. *Anal.* Calcd for tetraphenylarsonium hydrogen dichloride: HCl, 8.01. Found: HCl, 7.86. Calcd for tetraphenylarsonium hydrogen dibromide: HBr, 14.87. Found: HBr, 14.57. After completion of this process, the sealed, evacuated cell was returned to the glove box for the preparation of infrared mulls.

Discussion

It is not surprising that the tetraphenylarsonium halide hydrohalides occur as hydrates, since examina-

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(7) The reported titration of Blicke and Monroe for "tetraphenylarsonium chloride hydrochloride"[6] is in better agreement with the dihydrate formula than with the formula assigned.

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(13) The amount of water is found by subtracting the amount of hydrogen halide, based on halide elemental analysis, from the total weight loss on drying. The gases lost on drying were condensed in a cold trap; at room temperature a liquid phase was present in the evacuated trap. Mass spectral analysis[14] of the vapor in the trap showed the presence of water and hydrogen halide only; infrared and qualitative chemical analysis of the liquid phase showed it to be aqueous hydrohalic acid.

(14) We are indebted to Stephen V. Filseth for the mass spectra.

tion of the literature shows that all other reported attempts to prepare hydrogen dihalides from aqueous solutions have also resulted in hydrated products. Curtis[15] examined *trans*-dichlorobis(ethylenediamine)-cobalt(III) chloride hydrochloride, prepared from aqueous hydrochloric acid, and its bromide analog; both compounds were dihydrates containing hydrated hydrogen ion and not hydrogen dihalide anion. West[16] reported the preparation of cesium hydrogen dichloride by passing hydrogen chloride into an aqueous solution of cesium chloride, but the product was later shown[17,18] to have a composition corresponding to $(CsCl)(H_3O^+)_{0.75}(Cl^-)_{0.75}$. Schroeder and Ibers[19] have found a second crystalline product in this reaction and have shown by crystallographic analysis that it is $(CsCl)(H_3O^+)_{0.33}(HCl_2^-)_{0.33}$.[20,21] Only in this last compound, where there is an excess of hydrogen halide over water, does a hydrogen dihalide ion appear to exist.

The nature of the hydrated proton is not the same in these salts; X-ray and neutron diffraction studies have shown that $(CsCl)(H_3O^+)_{0.33}(HCl_2^-)_{0.33}$ does contain the hydronium ion,[17,20] while *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride dihydrate and related compounds contain the diaquohydrogen ion, $H_5O_2^+$.[22–25] No structural information is available on West's compound.[15–17] The infrared spectra of the hydrated protons in the tetraphenylarsonium halide hydrohalide dihydrates more nearly resemble that of the diaquohydrogen ion in *trans*-dichlorobis(ethylenediamene)cobalt(III) chloride hydrochloride dihydrate[15] than they do the spectrum of hydronium ion;[26] however, the differences in these spectra are not large enough to allow positive identification by this means. The water in the arsonium hydrates is very tightly held and cannot be removed without concurrent removal of hydrogen halide,[27,28] and the O–H stretching frequencies of the hydrates appear low for a compound containing a molecule of water. This, coupled with the similarities of the stoichiometries of the arsonium and the complex cobalt dihydrates, leads us to suggest that the arsonium hydrates contain the diaquohydrogen ion; however, a final decision would require diffraction studies.

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(27) For example, when tetraphenylarsonium bromide hydrobromide dihydrate is heated above 60° in the vapor pressure apparatus,[28] a colorless liquid condenses in the side arm which has a vapor pressure at room temperature of 9.05 mm and which contains hydrogen halide.

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The Magnetic Circular Dichroism of $Ni(CN)_4^{2-}$

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The square-planar tetrahalide and cyanide complexes of d^8 transition metal ions show strong absorption bands in the visible–near-ultraviolet spectrum, in addition to the usual weak d → d bands. These have been attributed to intramolecular charge-transfer transitions and detailed assignments were made on the basis of molecular orbital calculations.[3] However, the interpretation is not always unambiguous, and further information on the excited states involved is to be desired. Polarized crystal spectra over a range of temperatures would greatly extend the present knowledge, yielding excited-state symmetries and distinguishing allowed and forbidden transitions. However, as yet, suitable crystals have not been obtained. An alternative tool, and one applicable to solutions, is magnetic circular dichroism (MCD). This likewise enables symmetries of excited states to be elicited; magnetic moments are also accessible and shed additional light on the excited-state wave functions.[4] We have studied the MCD of a variety of d^8 square-planar complexes and here report on $Ni(CN)_4^{2-}$.

A molecular orbital diagram for $Ni(CN)_4^{2-}$, the relevant portion of which is shown in Figure 1, was proposed by Gray and Ballhausen[5] and used to assign the aqueous solution spectrum (Figure 2). Bands 1 and 2 and 3–5 were attributed to d → d and $d \rightarrow \pi^*(a_{2u})$ transitions, respectively. The latter give three singlet states, $^1B_{1u}$, $^1A_{2u}$, and ^1E_u, arising in turn through excitation of d_{xy}, d_{z^2}, and d_{yz}, d_{xz} electrons. From the ground $^1A_{1g}$ state electric dipole transitions are allowed to $^1A_{2u}$ and ^1E_u. Band 3, being the weakest of bands 3–5, was therefore assigned to the forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$ transition. On the basis of the adopted d-orbital order d_{yz}, $d_{xz} < d_{z^2} < d_{xy}$, the upper states of bands 4 and 5 were then taken to be $^1A_{2u}$ and ^1E_u, respectively. More recently, Ballhausen and co-workers[6] have reported polarized crystal spectra for a variety of $Ni(CN)_4^{2-}$ salts below 30,000 cm^{-1}. The transitions observed were interpreted as d → d transitions to excited states greatly distorted from planarity.

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(1) University of Southern California.

(2) University of Virginia.

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