The values of $x_{\text{uncor}}(\text{M})$ obtained from the data of Table VI using eq 2 are listed in Table VII along with those obtained for the MCl_6^{3-} and MBr_6^{3-} complexes from ref 4. It is interesting to note that there is a slight increase in all cases in the measured value of $x_{\text{uncor}}(\text{M})$ for a given lanthanide as one goes from hexachlorides through hexabromides to hexaiodides. A similar effect of about the same degree occurs for tetravalent actinide hexahalides and uranyl tetrahalides[8] and for uranium(V) hexahalides.[18]

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[18] J. L. Ryan, unpublished data presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1–5, 1968.

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Weak or Unstable Iodo Complexes. II. Iodo Complexes of Titanium(IV), Iron(III), and Gold(III)[1]

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Salts of iodo complexes of several d group metal ions which are strongly oxidizing toward the iodide ion were prepared by reaction of the corresponding chloro complexes with liquid anhydrous hydrogen iodide. These unstable complexes are TiI_6^{2-}, FeI_4^-, and AuI_4^-. An attempt to prepare CuI_4^{2-} by this method was unsuccessful. Of these, only FeI_4^- has any stability at all in solution at 25°, and it decomposes with a half-life of a few minutes. The absorption spectra of these complexes are compared with the spectra of the corresponding chloro and bromo complexes. Evidence is presented for the lack of higher halide complexes of Au(III) than AuX_4^-.

Introduction

The preceding paper[2] discusses the preparation of very weak iodo complexes of the trivalent lanthanides by condensing liquid anhydrous HI on the corresponding salts of the chloro complexes. The driving force for the reaction is the higher free energy of formation of HCl than of HI and to a lesser extent the greater volatility of HCl. Partly because of the low temperatures involved, this technique is also very useful in the preparation of relatively stable salts of halide complexes where the reducing power of the halide is such that the particular metal valence state cannot be maintained in solution in the presence of the halide. Thus salts of $CeBr_6^{2-}$ have been prepared by a similar method.[2,3] This paper discusses the preparation and absorption spectra of salts of the TiI_6^{2-} complex which can be expected to be both very weak and also unstable to autoreduction of the central metal and of the FeI_4^- and AuI_4^- complexes which are expected to be unstable to autoreduction. It appears from preliminary work that it will be possible to prepare salts of chloro complexes of very strongly oxidizing metal ions by treating the fluoro complexes with $SiCl_4$ or BCl_3 in liquid HCl at low temperatures.

Experimental Section

Salts of the iodo complexes were prepared and the absorption spectra of these solid salts obtained by the methods used for the lanthanide complexes.[2] The absorption spectrum of $(C_2H_5)_4NFeI_4$ was also obtained in solution in $CaSO_4$-dried acetone and nitromethane. Molar extinction coefficients of FeI_4^- were obtained by dissolving a weighed sample of the salt in a known volume of acetone at −78°. This solution was then added to a 0.1-cm cell and the spectrum was scanned rapidly immediately after the transfer. Small corrections were made for decomposition based on the rate observed at a constant wavelength on another sample of the solution. All spectra were obtained using a Cary Model 14 recording spectrophotometer.

Preparation of Complexes

Ti(IV) is considered to be one of the most typical A group acceptors[4] and thus iodo complexes, if such exist, are expected to be very weak. The absorption spectra (due to electron transfer) of $TiCl_6^{2-}$ and $TiBr_6^{2-}$ have been recently measured.[5,6] From these and the variation of optical electronegativity of the halide,[7] it can be predicted that TiI_6^{2-} will be black and relatively unstable to decomposition to Ti(III) and iodine. When $[(C_2H_5)_4N]_2TiCl_6$ is treated with liquid HI, a pure black solid resembling carbon black results. This material is very unstable to air and is changed to the dark red-brown of I_3^- in the time required to pour it quickly from one container to another in laboratory air. In this regard it is less stable than the lanthanide MI_6^{3-} salts.[2] It is not stable in solvents such as acetonitrile or nitromethane at 25° with or without excess I^-. If anhydrous HI is added to a partially frozen (about −46°) acetonitrile solution of $(C_4H_9)_4NI$ containing a small amount of $[(C_2H_5)_4N]_2TiCl_6$, an intense black solution results. The intense black color is completely replaced in a few seconds by the much less intense reddish brown color of I_3^-. (In the absence of the Ti salt only a white precipitate similar

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[1] This paper is based on work performed under Contract No. AT-(45-1)-1830 for the U. S. Atomic Energy Commission.

[2] J. L. Ryan, *Inorg. Chem.*, **8**, 2053 (1969).

[3] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, **70**, 2845 (1966).

[4] S. Ahrland, *Struct. Bonding* (Berlin), **1**, 207 (1966).

[5] J. L. Ryan, unpublished results quoted by C. K. Jørgensen.

[6] B. J. Brisdon, T. E. Lester, and R. A. Walton, *Spectrochim. Acta*, **23A**, 1969 (1967).

[7] C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963.

to that formed with HBr[3] forms when HI is added at the freezing point of the solvent, but at 25° some I_3^- forms due to HI reaction with the solvent.) It thus appears that TiI_6^{2-} is a sufficiently strong complex to be prepared in an acetonitrile solution containing excess iodide and anhydrous HI but that it is very unstable toward reduction of the Ti(IV). The TiI_6^{2-} complex then appears to be stronger than the lanthanide MI_6^{3-} complexes[2] which are not obtained at all under these conditions.

It should be noted that a pyridinium salt of TiI_6^{2-} has been previously reported as a "dark brown" solid isolated from concentrated aqueous HI.[8] When C_5H_5NHI in concentrated HI is added to the dark reddish brown solution obtained by dissolving hydrated TiO_2 in concentrated HI, a dark brown solid is isolated having the reported properties. It is not appreciably soluble in water but is soluble in acetone indicating that it is $C_5H_5NHI_3$. When black $[(C_2H_5)_4N]_2TiI_6$ is treated with cold, I_2-free, aqueous, concentrated HI, it is immediately converted to a dark brown solid which again is not water soluble but is acetone soluble and apparently is $(C_2H_5)_4NI_3$. From this and the observed air sensitivity of the $[(C_2H_5)_4N]_2TiI_6$ prepared in this manner, there is little doubt that the previous report[8] of a TiI_6^{2-} salt is in error. It appears that Ti(IV) is not stable in concentrated aqueous HI.

In order to demonstrate further the utility of this method for the preparation of iodo complexes of moderately strongly oxidizing metal ions, the iron(III) system was chosen. Pure Fe(III) iodide compounds are unknown and it has been stated that "iron(III) is too strong an oxidizing agent to coexist with a good reducing agent like I^-."[9] Although Fe(III) is considered to be an A group acceptor,[4] its chemistry (stable complexes with thiocyanate, etc.) indicates that it is certainly not as strongly A group in character as trivalent lanthanides and Ti(IV). Because of this and since $FeBr_4^-$ salts are readily prepared even from aqueous HBr solutions, there is no reason to believe that FeI_4^- would not be a moderately strong complex. Thus there is every reason to believe that barring oxidation state stability problems, if the chlorides of an $FeCl_4^-$ salt were replaced by iodides, the resulting material would be a salt of FeI_4^-. When $(C_2H_5)_4NFeCl_4$ is treated with liquid anhydrous HBr, it is completely converted to $(C_2H_5)_4NFeBr_4$ as determined by the identity of the absorption spectrum of the product to that of $(C_2H_5)_4NFeBr_4$ prepared from aqueous HBr.

The electron-transfer spectra of $FeCl_4^-$ and $FeBr_4^-$ have been published.[10] From these it can be predicted that the lowest molar extinction coefficient for FeI_4^- in the visible region would be about 4000 and thus salts of FeI_4^- would be black. When $(C_2H_5)_4NFeCl_4$ is treated with anhydrous liquid HI, a black crystalline solid is obtained. This material is considerably more stable than the Ti(IV) or lanthanide(III) hexaiodo complexes and appears to be stable in dry air. It can be handled for very short periods in laboratory air but is decomposed completely in a few hours by atmospheric moisture. It can be dissolved in dry acetone, acetonitrile, or nitromethane to produce an intensely purplish black solution. At 25° the Fe(III) is reduced with a half-life of a few minutes in these solvents, and this rate is greatly accelerated by excess I^-. The decomposition rate is decreased markedly by decrease in temperature and the half-life is at least several hours in acetone at −78°. Similar purplish black solutions of FeI_4^- can be obtained by adding anhydrous HI directly to acetonitrile solutions of $(C_2H_5)_4NFeCl_4$ at the freezing point of the solvent or to acetone solutions at −78°. The color of these solutions is not affected by addition of excess I^- as $(C_4H_9)_4NI$.

Au(III) is a very typical Chatt–Ahrland B group acceptor[4] and as such should form very strong iodo complexes. Several 19th century references to gold(III) iodide and iodoaurates exist.[11] All of these involve evaporation of aqueous iodide solutions thought to contain Au(III). It is now known that Au(III) is not stable in aqueous iodide solutions,[12–14] and in fact the quantitative liberation of iodine by Au(III) in aqueous iodide solutions has been used as an analytical procedure for gold.[14] The products obtained in these 19th century references probably consisted of mixtures of gold (I) iodide or complex iodides and salts of I_3^-. When $(C_2H_5)_4NAuCl_4$ (composition checked by analysis) is treated with liquid anhydrous HI, a crystalline black solid (resembling graphite) is obtained. Analysis for total gold content indicates complete conversion to $(C_2H_5)_4NAuI_4$, and qualitative turbidimetric Cl^- analysis indicated only a trace of residual Cl^-. The salt is moderately stable to laboratory air apparently because of its extreme water insolubility. This insolubility is related to the expected strength of the AuI_4^- complex and its lack of tendency to hydrolyze (B group behavior) and to the inherent low solubility of quaternary ammonium salts of AuX_4^- complexes (see also the extremely high distribution coefficient of $AuCl_4^-$ onto quaternary ammonium anion exchangers[15]). The salt dissolves with immediate decomposition in nonaqueous solvents such as acetone, acetonitrile, and nitromethane. At −78° the salt dissolves to a very slight extent in acetone and to a greater extent in propylene carbonate to produce violet solutions which change to brown in a few minutes indicating that AuI_4^- is very unstable in solution. The solid is also violet when streaked on porcelain.

Several insoluble "double auric iodides" have been reported as having been prepared from aqueous solution

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(8) H. J. Emeleus and G. S. Rao, *J. Chem. Soc.*, 4245 (1958).

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1966, p 857.

(10) P. Day and C. K. Jørgensen, *J. Chem. Soc.*, 6226 (1964).

(11) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., New York, N. Y., 1946, pp 609–610.

(12) A. K. Gangopadhayay and A. Chakrovorty, *J. Chem. Phys.*, **35**, 2207 (1961).

(13) Reference 9, p 1048.

(14) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," 3rd ed, The Macmillan Co., New York, N. Y., 1951, p 127.

(15) K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 113 (1956).

TABLE I

ELECTRON-TRANSFER SPECTRA OF TiX_6^{2-} [a]

$TiCl_6^{2-}$	(25.0)	[~1300],	(29.6)	[~17,000],	31.8	[22,000],			43.8	[30,000]
$TiBr_6^{2-}$	(17.7)	[~700],	(21.7)	[~8000],	24.9	[16,000],	(27)	[~12,000],	36.1	[20,000]
$[(C_2H_5)_4N]_2TiI_6$	(9.5)	[0.3],	12.1	[0.65],	14.3	[0.65],	(18.7)	[0.8],	23.2	[1.0]

[a] Wave numbers in kilokaisers with shoulders in parentheses. For $TiCl_6^{2-}$ and $TiBr_6^{2-}$ values in brackets are molar extinction coefficients and for $[(C_2H_5)_4N]_2TiI_6$ values are intensities relative to the strongest listed transition taken equal to 1.0.

by adding auric chloride to the appropriate iodide solutions.[16] If halogen exchange and precipitation are fast enough relative to reduction of Au(III) and the precipitate is sufficiently insoluble, this method might work. It should be noted though that the same cations which give insoluble salts with AuI_4^- can be expected to give insoluble I_3^- salts and the resulting mixture of insoluble AuI and MI_3 will appear analytically to be a salt of AuI_4^-. The reported preparation of $CsAuI_4$[16] was repeated and the black precipitate first formed was found to begin to turn brown immediately and this continued during filtering and drying. A similar preparation was carried out using triethylmethylammonium iodide in which case the solubility and formation of I_3^- appeared to be much less. Three preparations all contained Au(III) iodo complexes as determined by the absorption spectra. The spectra varied and only one was close to that of $(C_2H_5)_4NAuI_4$ prepared as discussed above. These preparations from aqueous solution all contained more residual chloride than the $(C_2H_5)_4NAuI_4$ prepared by reaction of the chloro complex with HI. This is not surprising in view of the fact that such salts of both $AuCl_4^-$ and AuI_4^- have very low solubility, and in this aqueous method iodide will be removed from the mixing zone more rapidly than the quaternary ammonium ion. Thus the aqueous method cannot be expected to yield pure salts of AuI_4^- but instead will give mixed chloro–iodo complexes generally contaminated with I_3^- and AuI or salts of AuI_2^-.

An attempt was made to prepare a salt of the hypothetical ion CuI_4^{2-} by treating a salt of $CuCl_4^{2-}$ with liquid HI. Salts of this complex, if such exist, would be black. When HI was condensed onto $[(C_2H_5)_4N]_2CuCl_4$, the color immediately became that of I_3^- indicating reduction of the Cu(II).

Absorption Spectra

The absorption spectra (due to electron transfer) of $TiCl_6^{2-}$ and $TiBr_6^{2-}$ have been measured by this author as well as by Brisdon, *et al.*,[6] who along with Jørgensen,[17,18] using the data of ref 5, have discussed the spectra in detail. Band assignments have been proposed by Jørgensen.[17,18] Since TiI_6^{2-} is not sufficiently stable in any of the nonaqueous solvents tried, only the spectrum of solid $[(C_2H_5)_4N]_2TiI_6$ was obtained. Because of the very high molar extinction coefficients of the TiX_6^{2-} (in contrast to the much lower values for the electron-transfer spectra of the lanthanide MX_6^{3-} complexes[2,3]), the spectrum of $[(C_2H_5)_4N]_2TiI_6$ was difficult to obtain. In order to obtain good mull spectra of this highly absorbing substance, very thin mulls with very fine particle sizes were required. Unlike the case of the AuI_4^- salt discussed later, the instability of the compound made preparation of such mulls difficult. As a result of this and the uncertainty in the base line due to possible mismatch of light scatter of sample and reference, the accuracy of the positions of the transitions and to an even greater degree the relative intensities for the transitions (particularly the shoulders) of $[(C_2H_5)_4N]_2TiI_6$ in Table I is not so great as those for $TiCl_6^{2-}$ and $TiBr_6^{2-}$. The $TiCl_6^{2-}$ and $TiBr_6^{2-}$ data are for acetonitrile solutions containing excess of the respective halide along with a small amount of the respective hydrogen halide to dehydrate[19] the solutions and prevent hydrolysis.

The values in Table I are listed in such a way that the values for $TiBr_6^{2-}$ occur directly below those for the corresponding transitions for $TiCl_6^{2-}$ (the $TiCl_6^{2-}$ and $TiBr_6^{2-}$ spectra are almost identical in appearance except for energy shift). The data for $[(C_2H_5)_4N]_2TiI_6$ are listed under what would appear to be the corresponding transitions for $TiBr_6^{2-}$ and $TiCl_6^{2-}$ based on the energy differences expected due to differences in electronegativities of the halides. Since the 25.0-kK shoulder for $TiCl_6^{2-}$ and the 17.7-kK shoulder for $TiBr_6^{2-}$ are, relatively, too weak to be observed with certainty in a mull spectrum, it may be that a similar very weak shoulder might have been missed for $[(C_2H_5)_4N]_2TiI_6$ and the 9.5-kK shoulder observed for this solid might correspond instead to the 29.6- and 21.7-kK shoulders for $TiCl_6^{2-}$ and $TiBr_6^{2-}$, respectively. The data of Brisdon, *et al.*,[6] indicate a considerable difference in the relative intensities of the transitions between the solution and solid spectra of $TiCl_6^{2-}$ and $TiBr_6^{2-}$ and even an appreciable difference between the relative intensities of the transitions between two different salts of the same TiX_6^{2-}. Because of this an exact comparison is not possible and it is probable that the transitions match as shown in Table I. Considering such difference in relative intensities of transitions between ions in solutions and in the solids, the data for $[(C_2H_5)_4N]_2TiI_6$ in Table I are quite consistent with what is expected for the TiI_6^{2-} ion.

As discussed in the preceding section, the FeI_4^- ion is considerably more stable than the other iodo complexes discussed here, and the absorption spectrum of this ion was obtained in both acetone and nitromethane in which there was no difference. The absorption spectrum (although more difficult to obtain because of

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(16) S. K. Gupta, *J. Am. Chem. Soc.*, **36**, 747 (1914).

(17) C. K. Jørgensen in "Halogen Chemistry," V. Gutman, Ed., Academic Press, London, 1967, pp 265–401.

(18) C. K. Jørgensen in "Chemical Applications of Spectroscopy," B. G. Wybourne, Ed., Interscience Publishers, New York, N. Y., in press.

(19) J. L. Ryan in "Progress in Coordination Chemistry" (Proceedings of the 11th International Conference on Coordination Chemistry), M. Cais, Ed., Elsevier Publishing Co., New York, N. Y., 1968, paper D16, p 220.

the shorter life of the FeI_4^-) also appears to be identical in all respects when a large excess of I^- as $(C_4H_9)_4NI$ and a small amount of anhydrous HI is present in the acetone solution. This indicates that the FeI_4^- complex does not dissociate in dry acetone or nitromethane. $FeCl_4^-$ and $FeBr_4^-$ both show relatively weak and narrow internal d transitions at energies just below the start of the intense electron-transfer bands. At low temperature nine of these transitions are observed for $FeCl_4^-$ and eight are observed for $FeBr_4^-$ with the bands for $FeBr_4^-$ at 2 kK lower energy than for the chloride.[20] The complete assignment of these bands is not firmly established since more bands are observed than are expected for t_d symmetry.[17] Three similar bands are observed for FeI_4^- at 9.615, 10.300, and 11.000 kK having molar extinction coefficients approximately 60, 80, and 200, respectively, with others presumably hidden under the first electron-transfer band. This gives an average shift for the first three bands of 2.3 kK to lower energy for FeI_4^- *vs.* $FeBr_4^-$ due to increased covalency. It is interesting to note that the molar extinction coefficients of these transitions increase markedly with increase in halide mass. About a 30-fold average increase is observed[21] in going from $FeCl_4^-$ to $FeBr_4^-$, and the transitions for FeI_4^- are about 5–10 times as intense as the corresponding transitions for $FeBr_4^-$. Assuming that these are spin-forbidden bands (as suggested by Jørgensen[17]), the increased covalency in going from the chloride to the iodide might be expected to cause relaxation of the forbiddenness and increase the observed intensities.

Day and Jørgensen[10] have measured the electron-transfer spectra of several 3d group tetrahalides including $FeCl_4^-$ and $FeBr_4^-$ and have discussed these in some detail. The electron-transfer spectra of FeX_4^- are compared in Table II where the results for $FeCl_4^-$ and $FeBr_4^-$ are from ref 10. The trend toward lower molar extinction coefficients and increased structure with increase in halide mass observed by Day and Jørgensen[10] apparently continues with FeI_4^-. The change in energy of the electron-transfer bands in going from $FeBr_4^-$ to FeI_4^- agrees very well with what would be expected from the difference between $FeCl_4^-$ and $FeBr_4^-$ and the difference in electronegativities of the halides.

TABLE II

ELECTRON-TRANSFER SPECTRA OF FeX_4^- [a]

$FeCl_4^-$	27.45 [7350], 31.8 [7600], (36.8), 41.2 [11,900]
$FeBr_4^-$	21.20 [5800], (23.6), 25.50 [5960], (31.5), 35.65 [10,500]
FeI_4^-	14.3 [4800], 17.1 [5100], 19.0 [5300], 21.2 [6400], 24.6 [9900]

[a] Wave numbers in kilokaisers with shoulders in parentheses and molar extinction coefficients in brackets. FeI_4^- is in acetone.

The absorption spectra of the solid $(C_2H_5)_4N^+$ salts of $AuCl_4^-$, $AuBr_4^-$, and AuI_4^- are shown in Figure 1.

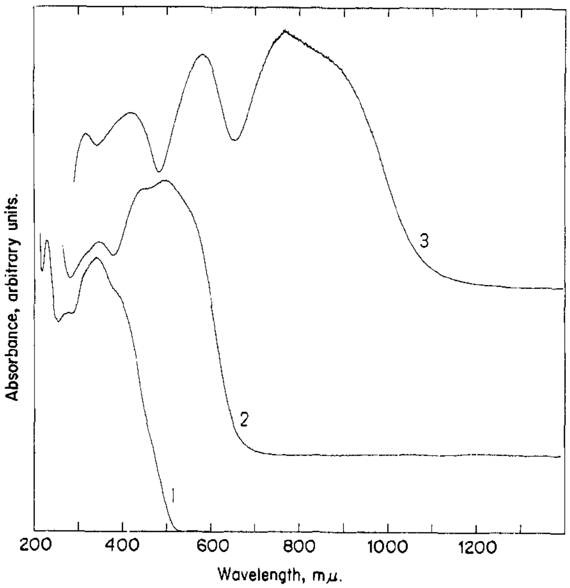

Figure 1.—Absorption spectra of solid gold(III) tetrahalides: (1) $(C_2H_5)_4NAuCl_4$; (2) $(C_2H_5)_4NAuBr_4$; (3) $(C_2H_5)_4NAuI_4$. Spectra 2 and 3 are displaced vertically.

The absorption spectrum of solid $(C_2H_5)_4NAuI_4$ is very similar to those of the chloro and bromo salts with energy shifts of the order of magnitude expected from change of electronegativity of the halide. It is interesting to note the rather marked difference in appearance of the solution spectra[12] and solid spectra of the chloro and bromo complexes (also observed for $CsAuCl_4$[22]). It appears that this difference is due almost entirely to differences in relative intensities as indicated in Table III where the spectra of solid salts are compared with those of their solutions in acetonitrile. The acetonitrile spectra are essentially the same as those reported by Gangopadhayay and Chakrovorty[12] except for the 18.2-kk shoulder for $AuBr_4^-$ which was apparently overlooked by them. Table III is arranged in such a way that the transitions in a given column correspond most closely in shape and appearance in the solid spectra. The $AuCl_4^-$ and $AuBr_4^-$ solution spectra correspond to each other similarly and are matched to the solid spectra closest in energy.

TABLE III

ABSORPTION SPECTRA OF AuX_4^- [a]

$AuCl_4^-$ (CH_3CN soln)	(25.7),		31.1,		43.8
$(C_2H_5)_4NAuCl_4$	(25.0),	29.8,	(31.3),	37.0,	43.5
$AuBr_4^-$ (CH_3CN soln)	(18.2),	(21.1),	25.3,		39.1
$(C_2H_5)_4NAuBr_4$	(17.7),	19.6,	(23.0),	28.2,	~38
$(C_2H_5)_4NAuI_4$	(10.8),	12.7,		17.0,	23.2

[a] Notation as in Table I.

In the solid spectra, relatively strong transitions are observed which correspond to weak shoulders or transitions not resolved at all in the solution spectra. It has been proposed that these shoulders might be crystal field transitions within the d shell.[12] If this were the case, the apparent increase in intensity might be expected if distortion of the square-planar AuX_4^- in the

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[20] A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963).

[21] N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

[22] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 424 1956).

crystal lattice destroyed the center of inversion. Such an explanation is not reasonable since not nearly so large an energy shift with change of halide would be expected for internal d transitions (less than 2-kK shift between successive halides is observed for internal d transitions of isoelectronic PtX_4^{2-}).[17] Thus all of the transitions of Table III appear to be electron-transfer transitions as also concluded by Jørgensen.[17]

It should be noted that the weak shoulders in the spectra of $AuCl_4^-$ and $AuBr_4^-$ in solution are not due to complexes other than AuX_4^-. The absorption spectra are the same in various solvents except for very small energy shifts. Addition of excess Cl^- (up to saturated $(C_2H_5)_4NCl$) to an acetonitrile solution of $(C_2H_5)_4NAuCl_4$ causes no change in absorption spectrum. Harris and Reece[23] found that addition of Br^- to a nitromethane solution of $AuBr_4^-$ markedly lowers its absorption in the visible region and attributed this to formation of $AuBr_6^{3-}$. A similar effect was observed by this author except that the reported[23] shift in the rather broad absorption peak from 394 to 379 mμ was not observed. The nitromethane cutoff occurs in this region and any reference mismatch may cause an apparent shift in a broad peak. When the experiment is done in acetonitrile, the spectrum can be measured to lower wavelength. In freshly prepared $(C_4H_9)_4NBr$-saturated solution the 394-mμ peak is reduced to less than 10% of its value in the absence of excess Br^-, and a strong band develops at 273 mμ. This band has exactly the same position and shape as Br_3^- in this solvent, and the molar extinction coefficient is that of Br_3^- assuming 1 mol of Br_3^- produced per mole of $AuBr_4^-$ disappearing. This 273-mμ peak decays slowly with time as does that of Br_3^- due to slow reaction with the solvent. The conclusion is that Au(III) is reduced in such solutions in qualitative agreement with results obtained in aqueous solutions,[24,25] and there is no evidence for gold(III) halide complexes beyond AuX_4^-.

(23) C. M. Harris and I. H. Reece, *Nature*, **182**, 1665 (1958).

(24) B. I. Peschevitski, V. P. Kazakov, and A. M. Erenburg, *Russ. J. Inorg. Chem.*, **8**, 437 (1963).

(25) V. P. Kazakov and M. V. Konovalova, *ibid.*, **13**, 231 (1968).

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Study of the Pentacyanonitrosylchromate Ion. III. Aquation

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Aquation of $Cr(CN)_5NO^{3-}$ in mildly acidic solutions yields $Cr(CN)_2(H_2O)_3NO$ which is inert to further aquation. In solutions of pH less than 2, further loss of CN^- occurs. The Cr–NO grouping remains intact until loss of CN^- is complete. The slow step in the initial aquation is the loss of the first CN^-. This step is first order in substrate with a rate constant $k = k'K[H^+]/(1 + K[H^+])$, where K is $9 \times 10^2\ M^{-1}$ and k' is $7 \times 10^{-3}\ sec^{-1}$ at 17.5° in 1 M NaCl. For k', $\Delta H^{\ddagger}$ is 19 kcal/mol.

Several studies of the pentacyanonitrosylchromate ion, $Cr(CN)_5NO^{3-}$, have led to the conclusion that this ion may be considered to contain Cr(I).[1] Although the ion is stable in basic or neutral solutions, it undergoes aquation in acidic solution. The ultimate products of this process are familiar Cr(III) species. We have studied the kinetics of the multistep aquation and the nature of intermediates in order to observe the chemical properties of the Cr–NO grouping.

Experimental Section

Reagents and Instruments.—$K_3Cr(CN)_5NO$ was prepared by reduction of K_2CrO_4 by NH_2OH in the presence of KCN[1] and recrystallized three times from water. $NaClO_4$ was prepared by neutralization of $HClO_4$, water was triply distilled from quartz, and other reagents were reagent grade used without further purification.

Spectrophotometric measurements were made using a Cary 14 spectrophotometer and 1- and 5-cm cells. A Sargent XV polarograph and a V-301-Zbrojovka, Brno, polarograph (sensitivity of galvanometer used 3.33×10^{-10} A/mm m) were used for polarographic studies. The capillary employed had a drop time of 3.4 sec and flow rate of 2.05 mg/sec (in short circuit with sce and 64-cm Hg column). A modified Kalousek polarographic cell was used for measurements. No maximum suppressor was used. Ionic strength for polarographic measurements was generally maintained at 1 M. Potentials were measured and are reported *vs.* the sce.

A Metrohm E-336A potentiograph and Sargent combination electrode were used for pH titrations. A Sargent pH stat with combination electrode was used for kinetic measurements.

Results

Kinetics of Primary Aquation.—Solutions of $Cr(CN)_5NO^{3-}$, containing NaCl as inert electrolyte, were allowed to undergo aquation at various temperatures and at hydrogen ion concentrations controlled by the pH stat. In the course of aquation, 3.00 ± 0.05 hydrogen ions were absorbed per ion. Below pH 2.0 a slower, further absorption of hydrogen ions occurred. Figure 1 shows a logarithmic plot of a typical run. There is definite deviation from linearity at the beginning of the reaction. Similar deviations during the first third of the reaction were present in all runs.

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(1) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 872 (1959).