

CONTRIBUTION FROM PACIFIC NORTHWEST LABORATORIES,
BATTELLE MEMORIAL INSTITUTE, RICHLAND, WASHINGTON 99352**Weak or Unstable Iodo Complexes. I. Hexaiodo Complexes of the Lanthanides¹**

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The extremely weak hexaiodo complexes of the trivalent lanthanides can be prepared as triphenylphosphonium or pyridinium salts by the reaction of the corresponding hexachloro salts with liquid anhydrous hydrogen iodide. These complexes dissociate in nonaqueous solvents even in the presence of excess iodide, and the solid salts are attacked by atmospheric moisture and oxygen. The internal transitions in the 4f shell are very similar to those of the corresponding hexachloro and hexabromo complexes. The metal-halogen frequencies in the vibronic and far-infrared spectra decrease by the amount expected with increase in halide mass. The electron-transfer spectra of hexaiodo complexes of Sm, Eu, Tm, and Yb are discussed and compared with those of the hexachloro and hexabromo complexes.

Introduction

The octahedral symmetry of the hexahalide, MX_6^{+m-6} , complexes is very desirable for the interpretation of absorption spectra, and a large amount of effort has been expended in the preparation and study of such complexes. Of particular emphasis has been the detailed study of electron-transfer spectra of the hexahalide complex.^{2,3} Since the positions of electron-transfer spectra and the magnitudes of optical electronegativities calculated therefrom are known to be affected by the symmetry and bond distance in halide complexes,²⁻⁷ it is desirable to compare data obtained with various metals in complexes of constant symmetry, and the octahedral hexahalide arrangement is probably the most universally attainable. The hexaiodo complexes would be expected (barring chemical stability problems) to be the most useful of the hexahalide complexes of a given metal for study of the electron-transfer spectra. This is because the electron-transfer transitions will be at much lower energy and thus more easily measured for the hexaiodo species than for the other hexahalides. Thus it was possible to measure electron-transfer spectra for UI_6^{2-} , whereas UCl_6^{2-} and UBr_6^{2-} electron-transfer spectra were not observed because of overlap with stronger and narrower $5f \rightarrow 6d$ transitions.⁸

The hexachloro and hexabromo complexes of the trivalent lanthanides⁴ and of some of the trivalent actinides⁹ have recently been prepared in solid salts and in nitrile solutions. Previous attempts to prepare hexaiodo complexes of the trivalent lanthanides were unsuccessful.⁴ The lanthanide hexachloro and hexabromo complexes are weak; and since the lanthanides show pronounced Chatt-Ahrlund A group behavior, the

hexaiodo complexes were expected to be very weak indeed. The complex $CeBr_6^{2-}$ has been prepared both in nitrile or nitromethane solutions and as the $(C_2H_5)_4N^+$ salt by treating the $CeCl_6^{2-}$ complex in solution or as the $(C_2H_5)_4N^+$ salt with anhydrous HBr.⁴ This technique has now been extended to iodide complexes. There is roughly a 20-kcal difference between the free energies of formation of HCl and HI favoring the reaction $MCl_6^{+m-6} + HI \rightarrow MI_6^{+m-6} + HCl$. A corresponding free energy difference of about 10 kcal favors the conversion of chloro complexes to bromo complexes. Thus, even with metals showing pronounced A group behavior resulting in markedly decreasing complex stability in going from chlorides to iodides, this equilibrium may be well to the right. If the conversion of solid salts from chlorides to bromides or iodides is carried out with liquid HBr or HI, the much higher volatility of HCl further promotes the conversion. This work discusses the use of this technique to prepare the hexaiodo complexes of the trivalent lanthanides. The absorption spectra of these complexes are discussed.

Experimental Section

Preparation of Compounds.— $[(C_2H_5)_4N]_2CeBr_6$ was made earlier by the reaction of solid $[(C_2H_5)_4N]_2CeCl_6$ with HBr gas.⁴ Further experiments indicated that the reaction proceeded more rapidly and was more easily performed if liquid anhydrous HBr was condensed onto the chloride salt and allowed to evaporate slowly in a stream of dry air. The conversion appears to be rapid and complete based on bromide analysis of the product and on the far-infrared spectrum which shows frequencies expected for $CeBr_6^{2-}$ with no residual trace of Ce-Cl vibrational frequencies.¹⁰ $[(C_6H_5)_3PH]_2CeCl_6$ is also readily converted quantitatively to the $CeBr_6^{2-}$ salt by this method, but Cs_2CeCl_6 gives only a trace of surface conversion. In order to study further the technique with systems giving products whose properties were already known, various salts of the UCl_6^{2-} ion were converted to the corresponding UBr_6^{2-} salts. The completeness of the reaction was checked by absorption spectra of the products, the spectrum of UBr_6^{2-} being well known.^{8,11} Again the Cs^+ salt showed only partial conversion, but tetraphenylarsonium and triphenylphosphonium salts were completely converted. This lack of conversion of the more dense cesium salts may be due to slow kinetics or may also be related to a lower stability of the UBr_6^{2-} salt with the smaller cesium ion. The conversion of quaternary ammonium salts of $UO_2Cl_4^{2-}$ to $UO_2Br_4^{2-}$ salts was

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

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

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(7) C. K. Jørgensen, "Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964," Publishing House of the Hungarian Academy of Sciences, Budapest, 1965.

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(10) J. L. Ryan and W. E. Keder, unpublished results.

(11) C. K. Jørgensen, *Acta Chem. Scand.*, **17**, 251 (1963).

found to be rapid and complete by comparison of the absorption spectra of acetonitrile solutions of the product and of the tetramethylammonium salt⁸ prepared from mixed ethanol-aqueous HBr solution.

In order to test the feasibility of this method for the preparation of iodo complexes, the U(IV) system was studied since the absorption spectrum of UI_6^{2-} is known⁸ and salts of this anion have been prepared.¹² Both $[(C_6H_5)_4As]_2UBr_6$ and $[(C_6H_5)_3PH]_2UBr_6$ were found to be converted to the corresponding orange-red UI_6^{2-} salts (based on the absorption spectra of the solid products) when liquid HI was condensed onto the bromo salts and allowed to evaporate off in a stream of dry N_2 and the procedure was repeated a couple of times. In order to prevent oxidation, air must be excluded and the final salts appear to be oxidized (although slowly) by dry air. The reaction appears to go faster with the UCl_6^{2-} salts and appears to be a very rapid method of preparing salts of UI_6^{2-} . The reaction did not proceed to an appreciable extent with Cs_2UCl_6 and was incomplete with the $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ salts. The reaction is complete with the $(C_6H_5)_3PH^+$ and $(C_6H_5)_4As^+$ salts giving in each case reddish orange products. A trace of chloride (<1%) can be detected by a qualitative turbidimetric method, but the absorption spectra of the salts in both the region of the internal f-electron transitions and in the far-infrared region show no trace of UCl_6^{2-} remaining. This trace of residual chloride can be reduced but not entirely eliminated by more extensive treatment with liquid HI. A similar treatment of a salt assumed to be $[(C_6H_5)_3PH]_2ThCl_6$ (and prepared in the same manner as the hexachloro salts of the trivalent lanthanides⁴) produced a pure white iodide-containing product again containing only a faint trace of Cl^- . ThI_6^{2-} would be expected to be white. It is probable that the yellow color of ThI_6^{2-} reported by Bagnall, *et al.*,¹² for salts of ThI_6^{2-} is due to traces of I_3^- which would be very difficult to avoid by their method of preparation. These experiments indicate the usefulness of this rather simple technique for preparing iodo complexes which are otherwise difficult to prepare free of I_3^- . The technique was then tried on the trivalent lanthanides for which iodo complexes were not previously known.

Both hexabromo and hexachloro salts of the lanthanides prepared as before^{4,13} were treated with anhydrous HI. The hexaiodo complexes of Sm, Eu, and Yb were expected to be strongly colored, and it was found that when the triphenylphosphonium salts of $SmBr_6^{3-}$ and $EuBr_6^{3-}$ were treated with liquid anhydrous HI, bright lemon yellow and dark green compounds were formed, respectively. The reaction appeared to be relatively slow, and after evaporation of the HI a second treatment with liquid HI appeared to intensify the color. Similar treatment of the off-white $YbBr_6^{3-}$ salt resulted in only slight reddish discoloration. Treatment of the corresponding chloro salts with liquid HI results in immediate conversion to bright yellow for Sm, dark green for Eu, and wine red for Yb. No change in color with further treatment with HI occurs. The completeness of the conversion was checked by condensing liquid HI onto the Nd and Yb salts until the liquid covered the solids, allowing the HI to evaporate rapidly (within 5 min) and analyzing for Cl^- in the products by X-ray fluorescence. The Cl^- was below the detection limit or less than 1% of that initially present. A trace of Cl^- was detected qualitatively by a turbidimetric method. Since the Nd and Yb salts are essentially completely converted and since they are close to opposite ends of the lanthanide series, it can be safely assumed that conversion of the other lanthanide salts under the same conditions is as complete. The iodo complexes of La, Pr, Nd, Sm, Eu, Gd, Ho, Er, Tm, and Yb were actually prepared. Further analysis of the product would not be

meaningful with this method of preparation, and spectral evidence showing that these are indeed triphenylphosphonium salts of the MI_6^{3-} ions will be presented in the section on absorption spectra. The pyridinium salts of MCl_6^{3-} also are rapidly converted to the iodides.

The lanthanide MI_6^{3-} complexes are very weak and are decomposed rapidly by moisture. They are also oxidized rapidly by oxygen, forming strongly colored I_3^- . For this reason the salts were handled entirely in dry N_2 . Even with these precautions a trace of I_3^- was usually present, and warming the salts of the lighter lanthanides with a heat lamp or illuminating with a bright light in a N_2 atmosphere increased this considerably, indicating instability even in an inert atmosphere. The stability of these lanthanide hexaiodo complexes, particularly toward decomposition or oxidation to form I_3^- , seemed (not surprisingly) to increase considerably with increasing atomic number (decreasing ionic radius) of the lanthanide. Thus the red Yb salt could be kept for over 1 year in a tightly capped bottle without color change, whereas the Sm and Eu salts changed from yellow and green, respectively, to brown in a few weeks under the same conditions.

An attempt was made to prepare salts of the hypothetical ion CeI_6^{2-} by treating the corresponding chloro salts with liquid HI. Salts of CeI_6^{2-} would be black. There appeared to be a black surface color formed as the first HI condensed onto salts of $CeCl_6^{2-}$ which had been precooled to -78° , but this was immediately (~ 1 sec) replaced by the red-brown color of I_3^- . Thus, as expected, the CeI_6^{2-} ion is extremely unstable.

Technique.—The procedure for preparation of the iodo salts was to condense an excess of solid HI onto the chloride salt at Dry Ice temperature, allow the HI to melt, then evaporate slowly while the system was being swept slowly with dry N_2 or He, and finally sweep the system thoroughly with dry N_2 or He to remove the last trace of excess HI. No more than a few hundred milligrams was prepared at a time to facilitate removal of the last of the HI. All contact with O_2 was avoided and the system including the line to the HI tank was thoroughly flushed with dry N_2 or He before the HI was admitted. The apparatus was made of glass, Monel, and Saran plastic with use of materials such as polyethylene which react rapidly with HI being avoided. The inert gas flush was added immediately downstream from the Monel HI inlet needle valve to remove any O_2 from the inlet line and to minimize the length of contact of HI with this line. Even with these precautions, a trace of I_3^- was always formed as evidenced by very faint yellow color for the La and Gd salts. The LaI_6^{3-} and GdI_6^{3-} salts were pure white when the last of the HI evaporated; but after thorough inert gas sweeping at 25° , a very slight yellowish off-white color was observed. Warming of the compounds with a heat lamp caused considerably more I_3^- formation indicating some instability of the LnI_6^{3-} salts even in an inert atmosphere.

Absorption spectra of the salts were obtained in mulls in Kel-F brand chlorofluorocarbon grease between fused-silica plates *vs.* a reference of $CaCO_3$ in Kel-F grease. The I_3^- ion has a very broad absorption band of $\epsilon \sim 25,000$ at $362\text{ m}\mu$.¹⁴ The LnI_6^{3-} salts were found to be very sensitive to air oxidation; and if mulls were prepared rapidly (~ 30 sec) in air, sufficient I_3^- formed to cause interference with spectra of the relatively intense electron-transfer bands of the MI_6^{3-} and prevent measurement of the weak internal f-electron transitions below about $500\text{ m}\mu$. For this reason all handling of the compounds including mull preparation was done in a dry nitrogen or dry helium atmosphere. The samples in grease between silica plates are protected from air except for slow diffusion of O_2 and H_2O in from the edges. All spectra were run immediately after preparation of the samples. The LnI_6^{3-} salts produced by this method have a very small crystal size and scatter light badly at the shorter wavelengths. This, along with a small amount of I_3^- contamination present even when samples were handled in dry N_2 , produced a steep base line in the spectra of the very weak (ϵ generally

(12) K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, 350 (1965).

(13) Previous attempts⁴ at preparation of both the triphenylphosphonium and pyridinium hexabromo salts of the heavier lanthanides had been unsuccessful. It has now been found that this was due to insufficient decomposition of the hydrated bromide prior to its dissolution in HBr-ethanol. If the hydrated bromides are decomposed at about 350° , the residue dissolves slowly in HBr-ethanol, and the hexabromo salts can be precipitated from the resulting solutions.

(14) A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, **77**, 3724 (1955).

<1) internal f-electron transitions below about 500 $m\mu$; and these transitions could not be measured below about 420 $m\mu$ at all. The I_3^- peak at 362 $m\mu$ could be detected as a shoulder on the rising base line for samples of LnI_6^{3-} salts such as GdI_6^{3-} not expected to have strong absorption bands of their own in this region. It is felt that this I_3^- contamination was not sufficient to interfere seriously with measurement of the stronger electron-transfer spectra in this region, but bands in the electron-transfer spectra in the 350–375- $m\mu$ region are obviously more questionable because of these problems. All spectra were obtained using a Cary Model 14 recording spectrophotometer, and the spectra in the figures are reproduced photographically from the originals.

Absorption Spectra

Since the iodo complexes reported here are prepared by replacement of chloride (or bromide) by iodide with HI, elemental analysis on the products is of value in establishing their identity only to the extent that it shows the chloride (or bromide) to be essentially completely replaced by iodide, and the product must of necessity have the same halogen to metal ratio as the starting material. Thus, although the over-all stoichiometry is $[(C_6H_5)_3PH]_3MI_6$, the compounds might not contain MI_6^{3-} complexes but might possibly instead be mixtures of MI_3 and $(C_6H_5)_3PHI$. Absorption spectra in the region of the internal 4f transitions and the electron-transfer transitions and the far-infrared region of metal-halogen vibration can be compared with that expected from the known data for the corresponding chloro and bromo complexes to establish the identity of these complexes.

Internal 4f Transitions.—The absorption bands of the lanthanide hexachloro and hexabromo complexes due to the internal 4f transitions are generally some 5–30 times weaker than the corresponding bands for the aquo ions except for those due to the hypersensitive transitions which are quite pronounced.⁴ This is due to the octahedral or near-octahedral symmetry of these hexahalides. The hexachloro and hexabromo complexes were found⁴ to have *hypersensitive pseudoquadrupolar*¹⁵ transitions about as strong as or in some cases stronger than the corresponding transitions in the aquo ions. This means that these hypersensitive transitions are 10–30 times more intense than other transitions in the hexachloro and hexabromo complexes whereas they are of about the same intensity in the aquo ions.

Three factors combine to make the internal f-electron-transition spectra of the lanthanide hexaiodo complexes difficult to measure. These are the very low molar extinction coefficients and the formation of I_3^- and light-scattering problems discussed in the Experimental Section. Despite these problems, at least part of the internal f-electron-transition spectra of the hexaiodo salts were obtained for the Pr, Nd, Ho, and Er compounds. The spectra were very similar in all respects, including the relative intensities of the various transitions, to those of the corresponding hexachloro and hexabromo complexes. The hypersensitive transitions are about as strong relative to other transitions as in the hexachloro and hexabromo complexes. Since the

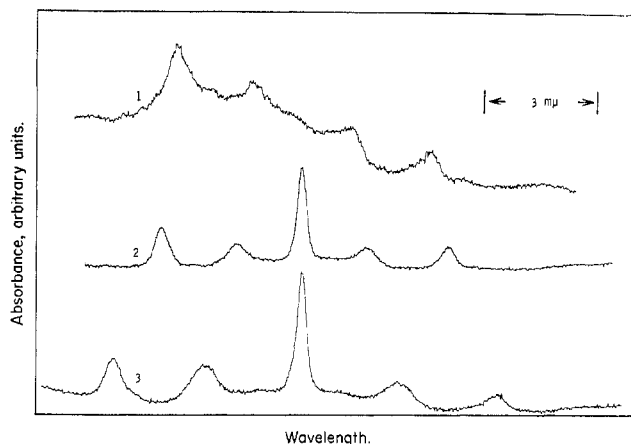


Figure 1.—The $^3H_4 \rightarrow ^3P_0$ transition of solid praseodymium(III) hexahalide salts: (1) $[(C_6H_5)_3PH]_3PrI_6$; (2) $[(C_6H_5)_3PH]_3PrBr_6 \cdot (C_6H_5)_3PHBr$; (3) $[(C_6H_5)_3PH]_3PrCl_6$. Spectra are displaced individually along the wavelength scale sufficiently to match the center (pure electronic) transitions. See Table I for exact positions (slit width 0.02 mm).

hexaiodo complexes are not stable in any solvent, only the spectra of the solid salts could be obtained. Because of this the absolute intensities could not be measured, but they appear to be about the same both from the color of the compounds and from the amount of sample required in the light beam as the hexachloro and hexabromo salts.

The $^3H_4 \rightarrow ^3P_0$ transition for praseodymium(III) hexahalides is shown in Figure 1. The structure of this transition has been interpreted in the case of the hexachloro and hexabromo complexes as being due to the pure electronic transition with vibronic transitions equally spaced at higher and lower energies.⁴ The two stronger pairs of these vibronic transitions were interpreted as due to bending and stretching normal modes of the octahedral hexahalide,⁴ and this interpretation is borne out by far-infrared measurements¹¹ as shown below. The absorption spectrum of $[(C_6H_5)_3PH]_3PrI_6$ is very similar to that of the salts of $PrCl_6^{3-}$ and $PrBr_6^{3-}$. The one pronounced difference is the marked decrease in relative intensity of the center band (interpreted here as the electronic line) in $[(C_6H_5)_3PH]_3PrI_6$ vs. the case of the $PrCl_6^{3-}$ and $PrBr_6^{3-}$ salts. Since this band is forbidden (except as possibly an extremely weak magnetic dipole transition) in an ion of exact octahedral symmetry, the presence of this band in $PrCl_6^{3-}$ and $PrBr_6^{3-}$ was interpreted as evidence of very slight distortion.⁴ This indicates that there is less distortion in the PrI_6^{3-} ion than in $PrCl_6^{3-}$ and $PrBr_6^{3-}$ and that the PrI_6^{3-} ion is very close to exact octahedral symmetry. This is not surprising in view of the fact that the coordination number of trivalent lanthanides is normally greater than 6 and it would be expected that octahedral symmetry would be more favored with the large iodide ion than with chloride or bromide.

The values in cm^{-1} of the lines in the $^3H_4 \rightarrow ^3P_0$ transition for $[(C_6H_5)_3PH]_3PrI_6$ along with those for the hexachloro and hexabromo salts from ref 3 are

listed in Table I. The vibrational wave number differences in cm^{-1} from the data in Table I are listed in Table II along with values of the metal-halogen frequencies obtained by far-infrared measurements¹⁰ on the Pr and Yb salts. These values decrease in the expected manner with increasing halide mass. For all of these salts the far-infrared spectra show only two absorption bands in the energy region of metal-halogen frequencies as expected for octahedral complexes.

TABLE I
WAVE NUMBERS OF THE ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$ TRANSITION
FOR PRASEODYMIUM(III) HEXAHALIDE SALTS^a

[[C ₆ H ₅] ₃ PH] ₃ PrCl ₆ , 300°K				
20,384	20,492	20,600	20,708	20,820
[[C ₆ H ₅] ₃ PH] ₃ PtBr ₆ ·(C ₆ H ₅) ₃ PHBr, 300°K				
20,350	20,442	20,509	20,584	20,661
[[C ₆ H ₅] ₃ PH] ₃ PrI ₆ , 300°K				
20,179	20,266	20,318	20,373	20,457

^a Values are in cm^{-1} .

TABLE II
VIBRATIONAL FREQUENCIES
FOR LANTHANIDE(III) HEXAHALIDE SALTS^a

[[C ₆ H ₅] ₃ PH] ₃ PrCl ₆		[[C ₆ H ₅] ₃ PH] ₃ PrBr ₆ · (C ₆ H ₅) ₃ PHBr		[[C ₆ H ₅] ₃ PH] ₃ PrI ₆
218	(210)	155	(154)	139
108	(110)	70	(73)	53
[[C ₆ H ₅] ₃ PH] ₃ YbCl ₆		[[C ₆ H ₅] ₃ PH] ₃ YbBr ₆ · (C ₆ H ₅) ₃ PHBr	[[C ₆ H ₅] ₃ PH] ₃ YbI ₆	
(218)	(126)	(143)	(124)	(60)
		(72)		

^a Values (in cm^{-1}) not in parentheses are obtained from the data of Table I. Those in parentheses are from far-infrared measurements.

Tables III–V compare the baricenters of excited J levels of the MI_6^{3-} salts with those of the hexachloro and hexabromo salts, the aquo ions, and the oxides. The difference, $d\beta$, between the nephelauxetic ratio of the hexaiodide salts and that of the aquo ions can be evaluated from the relationship

$$\sigma_{\text{iodo complex}} - \sigma_{\text{aquo}} = d\sigma - (d\beta)\sigma_{\text{aquo}} \quad (1)$$

where $\sigma_{\text{iodo complex}}$ and σ_{aquo} are the wave numbers of the baricenters of the band groups corresponding to excited J levels and where $d\sigma$ represents the stabilization of the lowest sublevel of the ground J level of the iodo complex minus the similar stabilization of the aquo ion.¹⁶ The data of Table III give values of $d\beta = 2.4\%$ and $d\sigma = +40 \text{ cm}^{-1}$ for NdI_6^{3-} . Thus the hexaiodo salt exhibits a nephelauxetic effect of the same order of magnitude as those of NdCl_6^{3-} and NdBr_6^{3-} which in turn are large compared to most other Nd complexes.⁴ The values of $d\beta$ were not calculated for $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{HoI}_6$ and $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{ErI}_6$ because of the limited number of transitions measured and the moderately large scatter of points from the linear relation in (1). They do appear though to show at least as large a nephelauxetic effect as the hexachloro and hexabromo complexes, and the effect may be as large as that in the oxides.

(16) C. K. Jørgensen, R. Pappalardo, and E. Rittershaus, *Z. Naturforsch.*, **20a**, 54 (1965).

TABLE III
WAVE NUMBERS OF INTERNAL $4f^8$ TRANSITIONS
IN NEODYMIUM(III) COMPLEXES^a

	NdCl_6^{3-}	NdBr_6^{3-}	[[C ₆ H ₅] ₃ - PH] ₃ NdI ₆	$\text{Nd}(\text{H}_2\text{O})_9^{3+}$	A-Nd ₂ O ₃
${}^4\text{F}_{3/2}$	11.35	11.39	11.31	11.58	11.19
${}^4\text{F}_{5/2}$	12.38	12.45	12.36	12.62	12.27
${}^4\text{F}_{7/2}$	13.39	13.37	13.28	13.58	13.25
${}^4\text{F}_{9/2}$	14.58	14.56	14.53	14.84	14.47
${}^4\text{G}_{5/2}$	16.95	17.04	16.81	17.40	16.72
${}^4\text{G}_{7/2}$	18.73	18.76	18.66	19.18	18.60
${}^4\text{G}_{9/2}$	19.34	19.23	19.27	19.63	19.17

^a Wave numbers are in kK of the baricenter of the band group corresponding to the excited J level indicated. Values other than those for the iodo complexes are from ref 4.

TABLE IV
WAVE NUMBERS OF INTERNAL $4f^{10}$ TRANSITIONS
IN HOLMIUM(III) COMPLEXES^a

	HoCl_6^{3-}	HoI_6	$\text{Ho}(\text{H}_2\text{O})_9^{3+}$	C-Ho ₂ O ₃
${}^5\text{F}_5$	15.43	15.38	15.42	15.50
${}^5\text{S}_2, {}^5\text{F}_4$	18.45	18.42	18.45	18.55
${}^5\text{F}_3$	20.49	20.45	20.56	20.53
${}^3\text{K}_6$	22.03	21.88	22.25	22.22
${}^3\text{G}_5$	23.75	23.64	24.03	23.92

^a Notation as in Table III.

TABLE V
WAVE NUMBERS OF INTERNAL $4f^{11}$ TRANSITIONS
IN ERBIUM(III) COMPLEXES^a

	ErCl_6^{3-}	[[C ₆ H ₅] ₃ - PH] ₃ - ErBr ₆ · (C ₆ H ₅) ₃ - PHBr	[[C ₆ H ₅] ₃ - PH] ₃ - ErI ₆	$\text{Er}(\text{H}_2\text{O})_9^{3+}$	C-Er ₂ O ₃
${}^4\text{I}_{9/2}$ (${}^4\text{F}_{9/2}$)	15.23	15.17	15.16	15.35	15.29
${}^4\text{S}_{7/2}$	18.21	18.21	18.18	18.48	18.21
${}^2\text{H}_{11/2}$	19.09	19.05	18.98	19.23	19.09
${}^4\text{F}_{7/2}$	20.40	20.40	20.33	20.60	20.37
${}^4\text{F}_{5/2}$	21.69	21.62	21.60	22.27	22.03
${}^4\text{F}_{3/2}$	22.03	22.03	22.03	22.61	22.43

^a Notation as in Table III.

The very close similarity of the absorption spectra of the iodo complexes discussed here to the absorption spectra of the hexachloro and hexabromo complexes prepared earlier⁴ leaves little doubt that they are indeed the hexaiodo complexes, MI_6^{3-} . This close similarity includes the apparent vibronic nature of the internal 4f transitions with appropriate shifts in vibrational frequency, the similar relative intensities of the transitions including the hypersensitive transitions, the similarity in nephelauxetic effect, the similarity with the predicted energy shifts in the far-infrared region, and the similarity of the electron-transfer spectra with the expected energy shifts as discussed in the next section. One further experiment supporting this conclusion involves treating $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{PrCl}_6$ with liquid anhydrous HBr to convert it to the bromide. The triphenylphosphonium salts of the bromo complexes contain an extra mole of $(\text{C}_6\text{H}_5)_3\text{PHBr}$ of crystallization.⁴ When the chloro salt is converted, there is a deficiency of $(\text{C}_6\text{H}_5)_3\text{PHBr}$ and the resulting preparation is a mixture of $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{PrBr}_6$, $(\text{C}_6\text{H}_5)_3\text{PHBr}$ and

a nonoctahedral praseodymium bromo complex (possibly PrBr_3). The visible absorption spectrum of this product is very different from that of the hexabromo complex. Although the hexabromo lines can be detected in the spectrum, the much more intense spectrum of the nonoctahedral Pr(III) dominates. The over-all intensity of the spectrum appears to be much greater than that of $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{PrBr}_6 \cdot (\text{C}_6\text{H}_5)_3\text{PHBr}$ also. If the iodo complexes discussed here were not MI_6^{3-} , their spectra should also be quite different from those of the MCl_6^{3-} and MBr_6^{3-} complexes.

Electron-Transfer Spectra.—The absorption spectra of the hexiodo complexes of the more reducible trivalent lanthanides are dominated by broad, strong electron-transfer bands. The theory of electron-transfer spectra of halide complexes has been reviewed in detail by Jørgensen,^{2,3} and the electron-transfer spectra of lanthanide hexachloro and hexabromo complexes have been discussed.⁴ The variation of position of the first electron-transfer band with halogen may be estimated from

$$\sigma_{\text{obsd}} = [x_{\text{opt}}(\text{X}) - x_{\text{uncor}}(\text{M})]30 \text{ kK} \quad (2)$$

where σ_{obsd} is the wave number in kK ($=1000 \text{ cm}^{-1}$) of the first electron-transfer band, $x_{\text{opt}}(\text{X})$ is the optical electronegativity of the ligand, and $x_{\text{uncor}}(\text{M})$ is the optical electronegativity of the central metal ion in a definite oxidation state uncorrected for spin-pairing energy and other forms of electronic repulsion or relativistic effects.^{2-4,8,17} For this purpose values of $x_{\text{opt}}(\text{X})$ are: F, 3.9; Cl, 3.0; Br, 2.8; I, 2.5. From this it can be seen that the first electron-transfer bands of the MI_6^{3-} complexes will be at roughly 9 kK lower energy than those of the corresponding MBr_6^{3-} complexes and therefore the MI_6^{3-} complexes of the more reducible M(III) will be intensely colored. Thus EuI_6^{3-} is intense olive green, YbI_6^{3-} is bright wine red, SmI_6^{3-} is bright yellow, and TmI_6^{3-} is cream to pale tan.

Figure 2 compares the absorption spectra (due to electron transfer) of EuCl_6^{3-} , EuBr_6^{3-} , and $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{EuI}_6$. It can be seen that the electron-transfer spectrum of EuI_6^{3-} is very similar to those of EuCl_6^{3-} and EuBr_6^{3-} except for the predicted energy shift. The positions of the electron-transfer transitions for the MI_6^{3-} are listed in Table VI. In general it was felt that the electron-transfer spectra of the MI_6^{3-} below about 320–330 $\text{m}\mu$ could not be obtained in this way due to absorption by the $(\text{C}_6\text{H}_5)_3\text{PH}^+$ ion. In the case of SmI_6^{3-} though, the first electron-transfer band would be expected to have $\epsilon \sim 1000$ by comparison with the hexachloro and hexabromo complexes,⁴ and the second transition would be expected to be stronger. Since all samples of $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{SmI}_6$ showed a distinct peak at 308 $\text{m}\mu$ and the $(\text{C}_6\text{H}_5)_3\text{PH}^+$ ion has ϵ of only 190 at this point and 500 at 300 $\text{m}\mu$, it is felt that this transition is real for the SmI_6^{3-} ion. As discussed in the Experimental Section, the I_3^- ion was a problem having $\epsilon \sim 25,000$ at 362 $\text{m}\mu$. Because the peaks listed in the

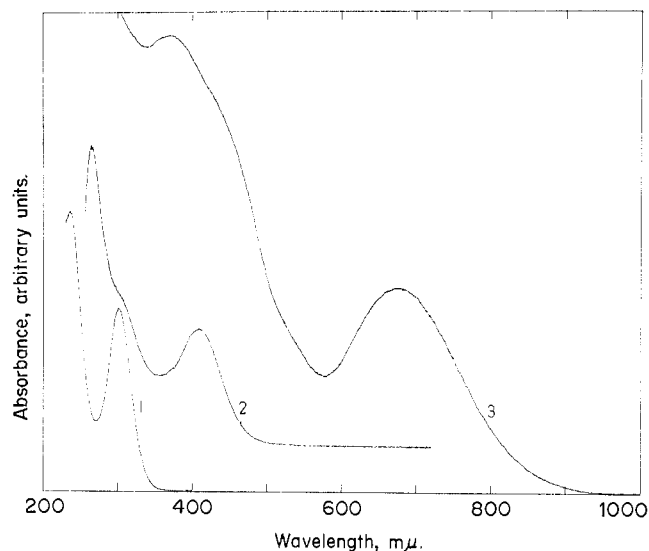


Figure 2.—Electron-transfer spectra of europium(III) hexahalides: (1) EuCl_6^{3-} in acetonitrile; (2) EuBr_6^{3-} in acetonitrile (spectrum displaced vertically); (3) solid $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{EuI}_6$.

350–375- $\text{m}\mu$ region in Table VI were reproducible in regard to position and relative intensity and were not found in other MI_6^{3-} salts such as the Sm salt, it is felt that they are not due to I_3^- impurity. This is particularly true of the more stable Tm and Yb salts. An attempt was made to measure an electron-transfer spectrum of $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{NdI}_6$, but because of the problems with light scatter, I_3^- contamination, and $(\text{C}_6\text{H}_5)_3\text{PH}^+$ interference no conclusive results were obtained.

TABLE VI
ELECTRON-TRANSFER SPECTRA OF
LANTHANIDE HEXAIODIDES^a

	λ	σ
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{SmI}_6$	402	24.9
	308	32.8
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{EuI}_6$	675	14.8
	(450)	(22.2)
	375	26.7
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{TmI}_6$	356	28.0
	560	17.85
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{YbI}_6$	(445)	(22.4)
	370	27.0

^a The wavelengths λ are in $\text{m}\mu$; wave numbers σ are in kK with shoulders in parentheses.

TABLE VII
OPTICAL ELECTRONEGATIVITIES

	$x_{\text{opt}}(\text{X})$	$x_{\text{uncor}}(\text{M})$
SmCl_6^{3-}	3.0	1.56
SmBr_6^{3-}	2.8	1.63
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{SmI}_6$	2.5	1.67
EuCl_6^{3-}	3.0	1.89
EuBr_6^{3-}	2.8	1.98
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{EuI}_6$	2.5	2.01
TmBr_6^{3-}	2.8	1.51
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{TmI}_6$	2.5	1.56
YbCl_6^{3-}	3.0	1.78
YbBr_6^{3-}	2.8	1.83
$[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{YbI}_6$	2.5	1.90

The values of $\alpha_{\text{uncoord}}(M)$ 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 $\alpha_{\text{uncoord}}(M)$ 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 tetrahalides⁸ and for uranium(V) hexahalides.¹⁸

(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 paper² 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 $(C_2H_5)_4NI \cdot FeI_4$ 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 vol-

ume 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 acceptors⁴ 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

(4) S. Ahlrand, *Struct. Bonding* (Berlin), **1**, 207 (1966).

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

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