

SELECTED MIXED HALIDE PHASES
OF EUROPIUM AND YTTERBIUM

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ABSTRACT

SELECTED MIXED HALIDE PHASES OF EUROPIUM AND YTTERBIUM

By

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Two mixed halide phases of europium have been prepared. They are $\text{EuCl}_{(0.46 \pm 0.02)}\text{Br}_{(1.56 \pm 0.07)}$ and $\text{EuCl}_{(0.16 \pm 0.04)}\text{Br}_{(1.85 \pm 0.04)}$. A single crystal of the first phase was prepared. The unit cell was determined to be orthorhombic with lattice parameters: $a = 7.879_7 \pm 0.003_5$, $b = 9.197_7 \pm 0.004_3$, and $c = 4.611_1 \pm 0.002_0$ Å. An attempt was made to solve the structure based on the least squares refinement of the atomic coordinates of EuCl_2 (PbCl_2 structure type) with various concentrations of bromide ion substituted for chloride ion.

An ytterbium mixed halide ammine complex of the empirical formula $\text{YbCl}_{(0.31 \pm 0.03)}\text{Br}_{(2.07 \pm 0.09)}(\text{NH}_3)_{(2.51 \pm 0.43)}$ is believed to have been prepared.

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CHAPTER I

INTRODUCTION

Lanthanides and their compounds are used for cracking oil, as additives to increase the ductility of iron and steel, as mischmetal-iron lighter flints, mixed oxide polishing compounds and liners for military shells, as hosts and activators in phosphors, as magnetic and electronic materials, optical devices, alloy additives, carbon arcs, and as control rod materials or diluents in nuclear fuels.¹ The anhydrous lanthanide chlorides are of particular importance because they are widely used for the production of metals and for starting materials from which many other anhydrous compounds are prepared.

For theoretical reasons there has been interest in the thermodynamic properties of the lanthanide halides. The structure types of several of these halides have been determined and methods of preparation have been described in the literature. The "simple" compounds (MX_2 and MX_3) of this series of elements have been shown to have both ionic and covalent character.

Insight into the thermodynamics and the bonding involved with 4f shell elements would be gained by an analysis of the thermodynamic and structural data available plus a careful study of some lanthanide mixed halide phases. Stability relationships of the transition from MX_3 to MY_3 and MX_2 to MY_2 (X and Y are nonidentical halide ions), metal-halogen bond strengths and the effect of anion size on packing may be

established by such studies.

It was, therefore, the intent of this work to prepare various lanthanide mixed halides and to study their structural relationship to the pure halide analogue.

The europium and ytterbium systems were selected because they are known to exist in both the trivalent and divalent oxidation states, and as such allow the study of both MY_2 and MY_3 systems for the same metal. Europium and ytterbium halides are also representative of the different structure types which have been found for the lanthanide halides. Thermodynamic data are known for $EuCl_2$, $EuBr_2$, and to a lesser extent for $YbCl_2$ and $YbBr_2$. For this reason, the chloride ion and bromide ion were selected as the halide ions, X and Y.

CHAPTER II

BACKGROUND AND THEORETICAL CONSIDERATIONS

A. Preparation of Anhydrous Lanthanide Halides

Preparative methods have been reviewed by Taylor.² Johnson and Mackenzie have compared many of these methods based on the purity of the product obtained.³

Taylor and Carter have described a general method for the preparation of anhydrous lanthanide trihalides in which the trihalide hydrates are dehydrated in the presence of an appropriate ammonium halide.⁴ The preparation of the europium bromides and hydrated bromides has been described by Haschke and Eick.⁵ Carter and Murray have also presented a method for the preparation of anhydrous rare earth trihalides. This method involves the reaction of excess mercuric halide with the rare earth metal.⁶

Preparation or the growth of single crystals of anhydrous lanthanide halides has been described by Mroczkowski⁷ and Cox and Fong.⁸

Synthesis of the dichlorides of samarium, europium, and ytterbium from the anhydrous lanthanide trichlorides with zinc as the reducing agent in a zinc chloride melt has been described by DeKock and Radtke.⁹ Tanguy, Pezat, Fontenit, and Fouassier have prepared the mixed halide EuFCl by mixing the pure dihalides in stoichiometric amounts.¹⁰

A study of the reduced halides of most of the rare earth elements has been detailed by Corbett.¹¹

B. Structural Information

1. Lanthanide Trichlorides and Tribromides

Structural data for the anhydrous lanthanide trichlorides and bromides is summarized in Table 2-1.

Of particular importance to this study is the structure of EuCl_3 which is isostructural with the lanthanide trichlorides included in the group La-Gd. Typical of the $\text{Y}(\text{OH})_3$ or UCl_3 structure type, the metal ion is nine coordinated and is surrounded by six chloride ions which define a trigonal prism. Three other chloride ions lie in the same mirror plane as the metal ion, approximately perpendicular to the rectangular faces of the prism. The single crystal structure determination of EuCl_3 and other lanthanide chlorides has been reported by Morosen.¹³

2. Lanthanide Dichlorides and Dibromides

Structural information for the known lanthanide dichlorides and dibromides is summarized in Table 2-2.

Baernighausen has reported the single crystal structure of EuCl_2 .¹⁷ The coordination sphere of the Eu is similar in its basic shape to that of the trichloride. The chloride ions may be classified according to the types of holes they occupy. The first type may be described as a chloride ion surrounded by four europium metal ions forming a tetrahedron while the second as a chloride ion centered in a square pyramid of metal ions. In contrast to the metal ion coordination sphere in EuCl_2 , its coordination sphere in EuBr_2 is believed to be only eight coordinate.

Table 2-1. Structural information on the lanthanide trichlorides and tribromides.

Species	Structure Type	Lattice Parameters				Ref.
		a (Å)	b (Å)	c (Å)	α, β	
LaCl ₃	Y(OH) ₃ ^a	7.4779		4.3745		13
LaBr ₃	Y(OH) ₃	7.967		3.54		12
CeCl ₃	Y(OH) ₃	7.451		4.313		12
CeBr ₃	Y(OH) ₃	7.952		4.444		12
PrCl ₃	Y(OH) ₃	7.42		4.26		12
PrBr ₃	Y(OH) ₃	7.93		4.39		12
NdCl ₃	Y(OH) ₃	7.3988		4.2423		13
NdBr ₃	PuBr ₃ ^b	12.65	4.11	9.16		12
PmCl ₃	Y(OH) ₃	7.397		4.211		15
SmCl ₃	Y(OH) ₃	7.378		4.171		12
SmBr ₃	PuBr ₃	12.63	4.04	9.07		12
EuCl ₃	Y(OH) ₃	7.3746		4.1323		13
EuBr ₃	PuBr ₃	9.12	12.66	4.013		5
GdCl ₃	Y(OH) ₃	7.3663		4.1059		13
GdBr ₃	FeCl ₃ ^c	7.633			56.400°	14
TbCl ₃	PuBr ₃	3.86	11.71	8.48		15
TbBr ₃	FeCl ₃	7.608			56.133	14
DyCl ₃	YCl ₃ ^d	6.91	11.97	6.40	111.2	12
DyBr ₃	FeCl ₃	7.592			55.834	14
HoCl ₃	YCl ₃	6.85	11.85	6.39	110.80	12
HoBr ₃	FeCl ₃	7.576			55.666	14

Table 2-1 (cont'd).

Species	Structure Type	Lattice Parameters				Ref.
		a (Å)	b (Å)	c (Å)	α, β	
ErCl ₃	YCl ₃	6.80	11.79	6.39	110.70°	12
ErBr ₃	FeCl ₃	7.568			55.466	14
TmCl ₃	YCl ₃	6.75	11.73	6.39	110.60	12
TmBr ₃	FeCl ₃	7.544			55.333	14
YbCl ₃	YCl ₃	6.73	11.65	6.38	110.40	12
YbBr ₃	FeCl ₃	7.540			55.166	14
LuCl ₃	YCl ₃	6.72	11.60	6.39	110.40	12
LuBr ₃	FeCl ₃	7.527			55.000	14

- a. Y(OH)₃ is isostructural with UCl₃, of hexagonal symmetry and belongs to the space group P6₃/m.
- b. PuBr₃ is of orthorhombic symmetry and belongs to the space group Cmm.
- c. FeCl₃ is of rhombohedral symmetry and belongs to the space group R $\bar{3}$.
- d. YCl₃ is isostructural with AlCl₃, of monoclinic symmetry and belongs to the space group C2/m.

Table 2-2. Structural information for the lanthanide dihalides.

Species	Structure Type	Lattice Parameters			Ref.
		a (Å)	b (Å)	c (Å)	
NdCl ₂	PbCl ₂ ^a	9.06	7.59	4.50	18
SmCl ₂	PbCl ₂	8.99	7.55	4.51	16
EuCl ₂	PbCl ₂	8.965(2)	7.538(1)	4.511(1)	17
EuBr ₂	SrBr ₂ ^b	11.574		7.098	5
EuFCl	PbFCl ^c	4.1181(3)		6.972(1)	23
DyCl ₂	SrI ₂ ^d	13.38	7.06	6.76	19
TmCl ₂	SrI ₂	13.10(4)	6.93(2)	6.68(2)	20
YbCl ₂	SrI ₂	13.150	6.942	6.693	21
YbBr ₂	CaCl ₂ ^e	6.63(2)	6.93(2)	4.37(2)	22

a. PbCl₂ is of orthorhombic symmetry and belongs to space group Pbnm.

b. SrBr₂ is of tetragonal symmetry and belongs to space group P4/n.

c. PbFCl is of tetragonal symmetry and belongs to space group P4/nmm.

d. SrI₂ is of orthorhombic symmetry and belongs to space group Pbca.

e. CaCl₂ is of orthorhombic symmetry and belongs to space group Pnnm.

3. Lanthanide Trichloride and Tribromide Hexahydrates

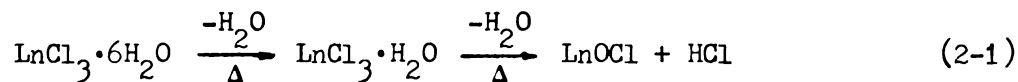
Structural information for the lanthanide trichloride and tribromide hexahydrates is tabulated in Table 2-3.

The lanthanide trichloride and tribromide hexahydrates are isostructural with monoclinic symmetry and belong to the space group $P2_1/n$.

C. Thermal Decomposition Studies

1. Lanthanide Trichloride Hydrates

Wendlandt and Bear²⁵⁻²⁷, Powell and Burkholder²⁸, and Haeseler and Matthes²⁹ have studied the thermal decomposition of the lanthanide(III) chloride hydrates in air. They disagree over the composition of the intermediate hydrates in the decomposition process, however, they do agree that the lanthanide oxidechloride is the principle final product. A mole of HCl is evolved in favor of the last mole of water, (2-1).



The thermal decomposition of the lanthanide trichloride hydrates in nitrogen was investigated by Ashcroft and Mortimer.³⁰ Using a differential scanning calorimeter, they defined three stable hydrate intermediates for the LaCl_3 - EuCl_3 hydrates with the exception of SmCl_3 hydrate. The intermediate complexes contain three, two, and one water of hydration, (Table 2-4). The stable intermediates found for ErCl_3 - LuCl_3 hydrates contain four, two, and one water of hydration. In all cases, anhydrous lanthanide trichloride is reported as the principle final product. Other investigators, using similar experimental conditions, have found significant contamination of the anhydrous lanthanide

Table 2-3. Structural information on the lanthanide trichloride and triiodide hexahydrates.

Species	Space Group	Symmetry	Lattice Parameters				Ref.
			a (Å)	b (Å)	c (Å)	β	
NdBr ₃	P2/n	monoclinic	10.074	6.785	8.212	93.51°	14
SmCl ₃	P2/n	monoclinic	9.67	6.55	7.96	93.67	24
EuCl ₃	P2/n	monoclinic	9.68	6.53	7.96	93.67	24
GdCl ₃	P2/n	monoclinic	9.64	6.53	7.93	93.67	24
GdBr ₃	P2/n	monoclinic	10.014	6.753	8.149	93.43	14
TbCl ₃	P2/n	monoclinic	9.63	6.51	7.89	93.67	24
TbBr ₃	P2/n	monoclinic	10.000	6.744	8.139	93.35	14
DyCl ₃	P2/n	monoclinic	9.61	6.49	7.87	93.67	24
DyBr ₃	P2/n	monoclinic	9.969	6.733	8.102	93.50	14
HoCl ₃	P2/n	monoclinic	9.58	6.47	7.84	93.67	24
HoBr ₃	P2/n	monoclinic	9.937	6.717	8.085	93.53	14
ErCl ₃	P2/n	monoclinic	9.57	6.47	7.84	93.67	24
ErBr ₃	P2/n	monoclinic	9.925	6.700	8.073	93.54	14
TmCl ₃	P2/n	monoclinic	9.55	6.45	7.82	93.67	24
TmBr ₃	P2/n	monoclinic	9.920	6.698	8.056	93.73	14
YbBr ₃	P2/n	monoclinic	9.920	6.693	8.046	93.72	14
LuBr ₃	P2/n	monoclinic	9.902	6.678	8.024	93.73	14

Table 2-4. Temperatures ($^{\circ}\text{C}$) at which the intermediate hydrates were stable in the thermal decomposition of the hydrated lanthanide chlorides. (ref. 30)

Element	$7\text{H}_2\text{O}$	$6\text{H}_2\text{O}$	$5\text{H}_2\text{O}$	$4\text{H}_2\text{O}$	$3\text{H}_2\text{O}$	$2\text{H}_2\text{O}$	$1\text{H}_2\text{O}$	LnCl_3
La	40				90	100	130	180
Ce		30			95	115	140	220
Pr		55			115	140	160	225
Nd		40			105	125	160	225
Sm		40		120		140	165	250
Eu		50			110	130	145	230
Gd		60			120	130	160	245
Tb	70			115		135	150	250
Dy	70				130		180	275
Ho	70					150	180	260
Er	60			135		155	185	250
Tm	70			140		165	185	240
Yb	70			135		160	180	240
Lu	70			135		160	180	220

trichloride product by the oxidechloride and dichloride.

Il'in, Krenev, and Evdokimov have carried out a similar thermal decomposition study of selected rare earth halide hexahydrates in vacuum.³¹ There is a significant difference between the intermediate hydrated phases which they found and those which Ashcroft and Mortimer found³⁰, (Table 2-5). They find the final phase of decomposition consists of a mixture of the anhydrous trihalide, the dichloride, and the oxidechloride. The proportion of oxidechloride found in the final product for the three systems increases in the order Yb-Eu-Sm.

2. Lanthanide Trichloride Ammine Complexes

Ephraim and Bloch³², Beck and Gasse³³, and Hüttig and Dauschan³⁴ have investigated the ammine complexes of selected lanthanide trichlorides. The results of their thermal decomposition studies are summarized in Table 2-6.

It is uncertain from the data listed whether the phases are stable and pure at the temperature given. It appears from a comparison of the data on the ammine complexes to that tabulated on the hydrates that the ammine complexes are stable to decomposition at higher temperatures.

Ammoniation energies for europium and ytterbium ammoniate ions $[M(NH_3)_6]^{++}$ have been reported by Frisbee and Senozan.³⁵ Gaseous ammoniation energies are -260 kcal/mol for Eu^{++} and -281 kcal/mol for Yb^{++} , (2-2).

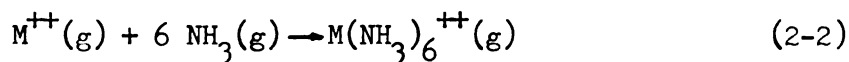


Table 2-5. Temperatures^a (°C) at which the intermediate hydrates were stable in the thermal decomposition of the lanthanide trichloride hexahydrates. (ref. 31)

Element	6H ₂ O	5H ₂ O	4H ₂ O	3H ₂ O	2H ₂ O	1H ₂ O	Final Product
Sm	50	65	100	180		300	400
Eu	40	60			110	120	280
Yb	35		75		100		280

a. Initial plateau temperatures.

Table 2-6. Temperatures (°C) at which the intermediate ammine complexes were found during the thermal decomposition study of LnCl₃·8NH₃. (refs. 32 and 33)

Element	8NH ₃	7NH ₃	6NH ₃	5NH ₃	4NH ₃	3NH ₃	2NH ₃	1NH ₃	0NH ₃
La	68			70		86	147	183	>265
Ce	64			70		102	135	244	>281
Pr	67			71			149	220	>310
Nd	49			71			209	283	>293
Gd	18	37	63		100	160	216		
Er	70			100		197	259	>360	
Y	25			90		180	335		

D. Amperometric Determination of the Chloride and Bromide Ion

Electroanalytical techniques normally give erroneous results due to mixed-crystal formation when the bromide and chloride ion are successively titrated. However, both the total halide and the individual halide content can be determined quite precisely and accurately by amperometric titration with silver nitrate at a rotating platinum electrode.

Amperometric titrations are performed by observing changes in the current between two electrodes as the titration is carried out. The principle of such titrations is inherent in current-applied emf curves or polarograms, (Figure 2-1). If one applies an increasing voltage to an polarized electrode immersed in a solution of substance to be examined, the current between the polarized electrode and reference electrode remains essentially zero until the reduction potential of the substance to be determined is reached (A). At this point the current rises rapidly as the emf is increased (B) until a maximum known as the limiting current is reached (C). Once the limiting current is reached, further increases in the emf cause little or no change in the current. The limiting current is proportional to the concentration of the reducible substance in solution. Indifferent electrolytes in the solution suppress current which would be due to the migration of an ion being examined.

When titrating, one applies to the polarized electrode a voltage which is sufficient to reduce either one or both of the species involved in the solution. In the silver nitrate-halide titration performed in this work, an emf which was sufficient to reduce the silver ion in solution was applied to the polarized electrode. Essentially zero current should flow until an excess of silver nitrate is present in the solution.

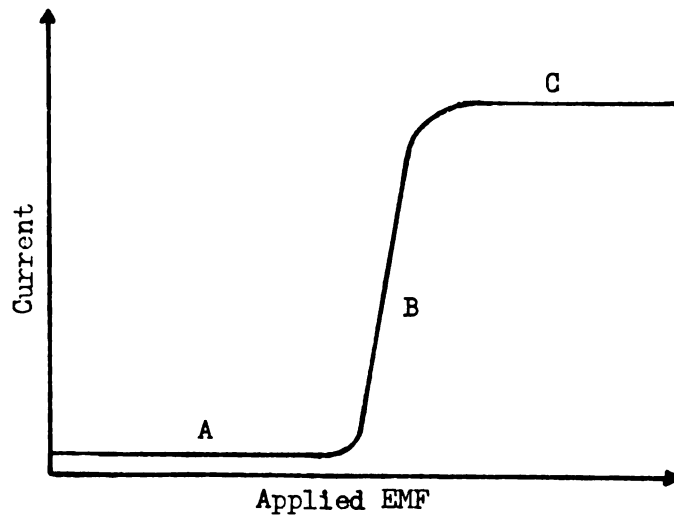


Figure 2-1. Current-applied EMF curve.

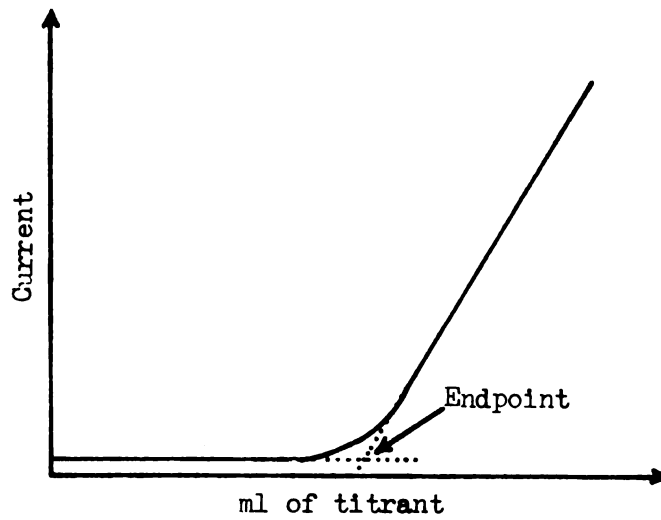
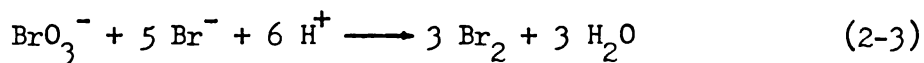


Figure 2-2. Reversed L amperometric titration curve.

The current should then increase linearly with the concentration of the silver ion. Because the solubility of the silver halide formed is significant compared to the amount of excess silver nitrate present through the end point region, one must titrate to 80-100 % excess of silver nitrate and extrapolate back to find the true end point³⁶, (Figure 2-2).

The use of amperometric titrations for the determination of chloride, bromide, and iodide was first developed by Laitinen, Jennings, and Parks.³⁷ Kolthoff and Kuroda later extended the method for more dilute solutions.³⁸ Stock and Sienkowski apply amperometric titrations to the analysis of bromide-chloride mixtures.³⁹ For completeness, it also should be noted that Rashbrook and Woodger use a dead-stop end-point titration (biamperometric titration) to determine trace amounts of chloride in sodium bromide.⁴⁰

The analyses performed here are based on Stock's work.³⁹ Stock first titrates the total halide amperometrically with silver nitrate. By using a second sample, the bromide ion is selectively oxidized with NaBrO_3 and nitric acid according to (2-3).



The chloride content is then analysed amperometrically.

A rotating platinum electrode serves as the polarized electrode. Rotating platinum electrodes are known to have high sensitivity, and are easily constructed and maintained. The hydrogen overpotential is smaller with this electrode than with a dropping mercury electrode, and an emf of up to 1 volt may be applied to the platinum electrode before it is subject to oxidative attack.

A saturated calomel electrode (SCE) serves as the reference electrode. Large non-polarizable electrodes are usually selected as reference electrodes. The SCE electrode has the advantage that the potential difference between it and the platinum indicator electrode is sufficient to reduce the silver ion.

E. X-Ray Diffraction Analysis

The phenomenon known as X-ray diffraction may be represented as a "reflection" of X-rays by successive planes of atoms in a crystal. More precisely, the diffraction pattern arises from the constructive interference of waves scattered from adjacent parallel lattice planes. The path difference between waves must be an integral number of wavelengths according to the Bragg equation, (2-4).

$$n\lambda = 2d \sin \theta \quad (2-4)$$

where λ is the wavelength of radiation, and θ , the angle of incidence. The symmetry and size of a unit cell determines the angles at which constructive interference of the diffracted X-rays will occur, while the relative intensities of these reflections depend on the arrangement of the atoms or ions within this cell.

X-Ray diffraction patterns are described more easily in terms of reciprocal than real space. The reciprocal lattice may be related to the real lattice of a crystal by erecting normals to the two dimensional planes in the crystal. Given a common origin, the length of the normal is a distance $1/d_{hkl}$ from the origin. The reciprocal lattice points are then the points at the end of the normals. They are indexed according to the plane to which they are normal.

Indexing is done by integers (hkl), the Miller indices. The plane with Miller indices h, k, and l makes intercepts a/h, b/k, and c/l with the unit cell axes a, b, and c.

Because the electrons in a crystal are responsible for the scattering of X-rays, it is realistic to think of a crystal as a continuous distribution of electron density, $\rho(x,y,z)$. The electron density is a function with the periodicity of the lattice and, therefore, can be written as a Fourier series in three dimensions as in equation (2-5).

$$\rho(x,y,z) = 1/V \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz - \alpha_{hkl})] \quad (2-5)$$

V is the volume of the unit cell, $F(h\ k\ l)$ is the structure factor, and α_{hkl} is the phase angle (2-6).

$$\alpha_{hkl} = \arctan \left[\frac{\sum_+ \sin 2\pi (hx + ky + lz)}{\sum_+ \cos 2\pi (hx + ky + lz)} \right] \quad (2-6)$$

The relationship between the electron density and the structure factors is that one is the Fourier transform of the other. The summation is carried out over all values of h, k, and l, in order that there is one term for each set of planes (hkl) and for each diffracted spot.

The intensity of scattered radiation is proportional to the square of the amplitude, $|F(hkl)|^2$. One cannot calculate the structure factors directly from intensity data because the phase angle is not known and cannot be measured. The lack of information regarding the phase angle is often referred to as the phase problem. To determine the spatial arrangement of atoms, one may propose a structure by assigning spatial coordinates to all atoms, and compare the calculated structure factors, (F_c) , to those observed (F_o) , or one may generate from $|F(hkl)|^2$ a Patterson synthesis which has peaks corresponding to all

the interatomic vectors in the cell. From a knowledge of the interatomic vectors and the known symmetry of the cell, one may infer an initial set of atomic coordinates. One may also use a direct method to obtain initial values for the atomic coordinates. This initial set of atomic coordinates may be refined by least squares techniques.

The R function (reliability or residual factor), as defined in equation (2-7), is used to evaluate the preciseness of the structure.

$$R = \frac{||F_o| - |F_c||}{|F_o|} \quad (2-7)$$

The least squares refinement procedure consists of systematically varying the atomic parameters to minimize the R function.

Intensity data are corrected for the following: (a) background, (b) absorption of the X-rays by the ions in the crystal, (c) polarization due to the monochromator, (d) different sweep rates of the reciprocal lattice points through the sphere boundary (Lorentz factor), and (e) the efficiency of the reflection of the X-ray beam (polarization factor). Anomalous dispersion corrections for phase changes due to the electronic nature of the electron are applied to the scattering factors.

Atoms are known to vibrate at their lattice points; therefore, the "electron cloud" describing the atom is considered as dispersed over a volume of space. The correction term to the scattering factor for this effect is defined by B, the thermal parameter. One may define the electron cloud isotropically in terms of a sphere or anisotropically in terms of an ellipse.

CHAPTER III

EXPERIMENTAL MATERIALS, EQUIPMENT, AND PROCEDURES

A. Chemicals and Materials

Chemicals and materials used were: (a) ytterbium and europium oxide, 99.9 %, Michigan Chemical Corp, St. Louis, MI; (b) argon and helium, Air Reduction Co. Inc., New York, NY; (c) nitrogen, technical prepurified, Air Reduction Co. Inc., New York, NY; (d) silver nitrate, 99.9 %, J.T. Baker Chemical Co., Phillipsburg, NJ; (e) mercury, hydrochloric acid, and nitric acid, analytical reagent, Mallinckrodt, St. Louis MO; (f) gelatin, practical, Eastman Kodak Co., Rochester, NY; (g) potassium nitrate and ammonium bromide, reagent grade, Matheson Coleman and Bell, Norwood, Ohio; (h) potassium chloride and ammonium chloride, certified A.C.S., Fisher Scientific Co., Fair Lawn, NJ; (i) sodium bromate, reagent grade, Baker and Adamson, Allied Chemical, New York, NY; (j) vitreous carbon boats and crucibles, Beckwith Carbon Corp., Van Nuys, CA; and (k) quartz tubing, Englehard Industries, Inc., Hillsdale, NJ.

B. Handling Procedures

The storage and handling of air and moisture-sensitive materials such as EuCl_2 , YbCl_3 and the mixed halide phases were made in the recirculating argon atmosphere glove box. The glove box has been described in detail by Hariharan.⁴¹ Because of the difficulty encountered

in adjusting the internal pressure of the box, exact weighings of samples were generally done by difference outside of it. Care was taken to pour the argon atmosphere out of the weighing bottle prior to weighing. Weighings were made in less than 1 minute. Weight gains due to the hydration of the sample were not noticeable within this time period.

Crystalline samples could be viewed under paraffin oil or in the single crystal mounting apparatus described later.

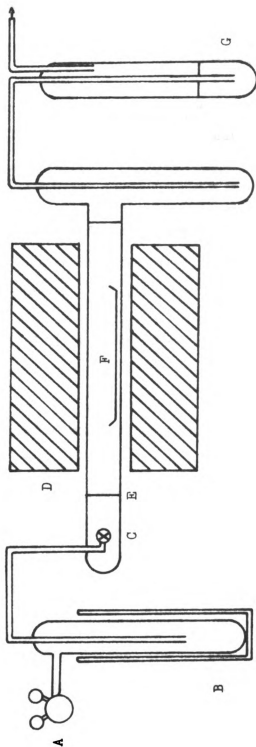
C. Preparative Procedures

1. Anhydrous Lanthanide Trichlorides

Both europium and ytterbium trichloride were prepared according to the method of Taylor and Carter⁴ as modified by Hariharan.⁴¹

Two grams of M_2O_3 ($M = Eu, Yb$) were added to 30 ml of 6 N HCl. The solution was heated on a hot plate and stirred until it became clear. Ammonium chloride was then added in a 6:1 molar ratio of ammonium chloride to lanthanide ion along with 50 ml of concentrated HCl. The solution was returned to the hot plate, stirred, and allowed to evaporate to a thick slurry, which was subsequently transferred to a carbon boat and placed in the apparatus as shown in Figure 3-1.

The sample was heated at 200 °C under a stream of deoxygenated helium for several hours ($\approx 16h$) until excess water and water of hydration appeared to have evaporated. The temperature was then increased to 350 °C until all the ammonium chloride has evolved ($\approx 7h$). The carbon boat was shifted to the transfer tube; the transfer tube separated from the Vycor tube under a high helium flow, and capped.



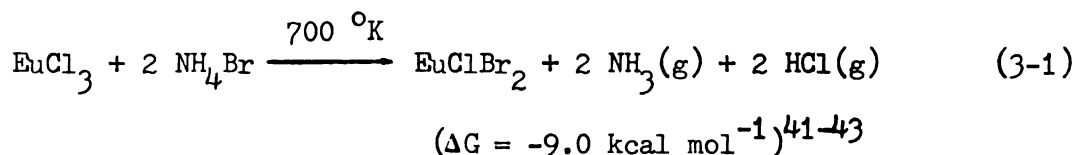
- A. Gas entry
- B. Liquid nitrogen trap
- C. Transfer tube
- D. Furnace
- E. Vycor tube
- F. Carbon boat
- G. Paraffin oil trap

Figure 3-1. Halide preparation system.

The tube was evacuated and transferred to a dry box, where the sample was stored in a screw capped vial, which was then sealed in plastic under a dry argon atmosphere.

2. Anhydrous Lanthanide Chloride Bromide Phases

Based on the known thermodynamics for the europium trichloride and tribromide systems, and thermodynamic functions for a mixed halide phase assumed to lie linearly between those of the pure phases, methods that use $\text{Cl}_2(\text{g})$ or $\text{Br}_2(\text{g})$ to chlorinate or brominate the desired lanthanide trihalide are unfavorable for the preparation of pure mixed halide phases. However, the reaction (3-1) involving ammonium bromide and europium trichloride seemed favorable.



The sealed bomb preparation was based on these calculations.

The acidic nature of ammonium halide is believed to prevent hydrolysis of the lanthanide trihalide in the Taylor-Carter preparation.⁴ It is my belief that there is an exchange of halide ion between the ammonium halide and the intermediate phase, but no investigation presently available defines this reaction pathway. The pseudo Taylor-Carter preparation of the mixed halide is based on the assumption of a halide ion exchange between the ammonium halide and the europium halide hydrate or other decomposition intermediate.

a. Sealed Bomb Preparation

A 1:1.25 mole ratio of anhydrous europium trichloride to dried ammonium bromide was heated in an outgassed quartz tube under vacuum at 395 °C for four days. (The quartz tube is flamed under vacuum until it is nearly white hot to remove absorbed water. Lanthanide halides in the presence of quartz and water are known to form silicates.¹¹) The sealed bomb was cooled over a period of $\approx$ 6h, transferred to the glove box, opened, and the contents removed. The various colored phases were separated according to color and stored in screw-capped vials sealed in plastic.

An attempt was made to remove the excess ammonium halide by heating the sample in vacuum over a temperature range of 170-200 °C for a period of $\approx$ 24h. A setup similar to that described in Figure 3-1 was used. A fore pump and a mercury diffusion pump replaced the paraffin oil trap; an argon inlet valve was located between the system and the pumps. The system, excluding the transfer tube, was repeatedly evacuated and filled with argon. Under a strong flow of argon, the transfer tube containing the sample was attached, its stopcock closed, and the system evacuated. a liquid nitrogen trap was placed between the Vycor tube and the pumps before heating, to trap the ammonium halide. The sample was removed under a strong flow of argon and transferred as described for the anhydrous lanthanide trichlorides.

b. Pseudo Taylor-Carter Preparation

This preparatory method is similar to that described earlier for the anhydrous lanthanide trichlorides. The anhydrous lanthanide trichloride and ammonium bromide, in a 1:6 mole ratio, were mixed in

aqueous solution which was subsequently evaporated to dryness. The lanthanide trihalide hydrate-ammonium bromide matrix was transferred to a carbon boat and heated under a deoxygenated helium stream at 200 °C (or 250 °C) for $\approx$ 16h, (Figure 3-1). Once excess water appeared to have evaporated, the temperature was raised to 370 °C and heating continued ($\approx$ 4h) until the orange phase had completely decomposed into a light grey powder. The sample was cooled and treated as described earlier.

3. Single Crystal Preparation

Single crystals of mixed halides (obtained from the pseudo Taylor-Carter preparation) were crystallized from the liquid melt by slow cooling.

The mulled sample was sealed in an outgassed quartz tube under vacuum (10^{-6} torr), heated to a liquid melt ($\approx$ 660 °C), and then cooled to a temperature of 300 °C over a period of several days at $\approx$ 20 °C/8h. The sample was cooled rapidly from 300 °C and transferred to the glove box in the sealed quartz tube.

D. Elemental Analyses

1. Metal Analysis

The metal content was measured gravimetrically. Samples were weighed directly into constant weight platinum crucibles and ignited to the sesquioxide at 950 °C in a muffle furnace.⁴⁴

2. Halide Analyses

a. Total Halide Analysis

The titration assembly is shown in Figure 3-2. Electrical measurements were made with a Hewlett Packard DC vacuum tube multimeter (model 412A). The platinum microelectrode (E.H. Sargent and Co., Chicago, Ill.) was rotated at 600 rpm by a Sargent synchronous rotator. The sensitivity of the microelectrode at 25 °C was $120 \mu\text{A}/10^{-3}\text{M Ag}^+$ in 0.3 % nitric acid containing 0.0625 % gelatin.

The electrode was initially prepared according to the standard procedure outlined by Stock.³⁶ The electrode is washed with concentrated HCl and soaked for several hours in 10 % sodium cyanide solution. Soaking is continued until the electrode gives a residual current in 0.1 N KNO_3 - 0.1 N HNO_3 of the order $0.1 \mu\text{A}$ at 0.2 V versus SCE.

Between titrations, the electrode is stored in 10 M nitric acid. The nitric acid will remove deposited silver. Washing with ammoniacal sulfite solution prior to titrating is necessary to remove deposited silver chloride. A final rinse with distilled water completes the cleaning process.

To titrate, an appropriate amount of the unknown is added to the titration vessel. The final concentration of halide should be between $3 \times 10^{-4}\text{N}$ and $6 \times 10^{-4}\text{N}$. To the unknown is added 5 ml of 6 % nitric acid, 1 ml of 2.5 % gelatin solution, and enough water to bring the total volume to 40 ml. Nitrogen gas is bubbled through the solution until the rate of current drop is less than 3 namp/min. (The current was found to drop below $0.1 \mu\text{A}$ for these experimental conditions.) During current measurements, N_2 is blown over the solution to prevent

- A. Synchronous motor
 B. Copper wire
 C. Terminal
 D. μ ammeter
 E. Mercury connection
 F. Rubber bung
 G. Nitrogen inlet
 H. Two-way stopcock
 I. Titration vessel
 J. Platinum electrode
 K. Buret inlet
 L. Glass frit
 M. KNO_3 bridge
 N. KNO_3 (sat.) solution
 O. KCl bridge
 P. Mercury
 Q. Hg_2Cl_2
 R. KCl (sat.) solution

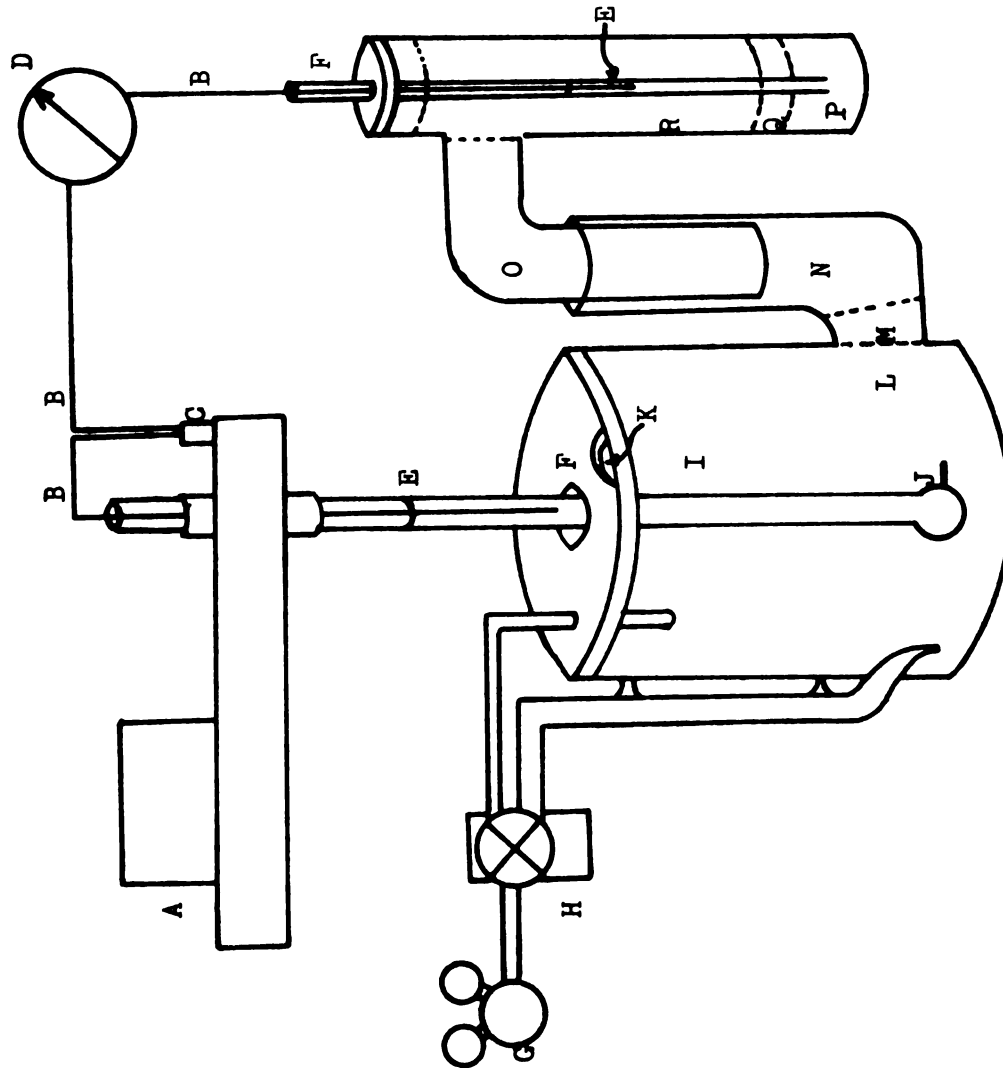


Figure 3-2. Halide titration vessel.

O₂ diffusion into the solution. A large initial surge of current occurs when the electrode is initially rotated, and to protect the meter, the circuit across it is short-circuited (or the meter set to a high range). Aliquots of silver nitrate cannot be added while in a current measuring mode, with the electrode rotating.

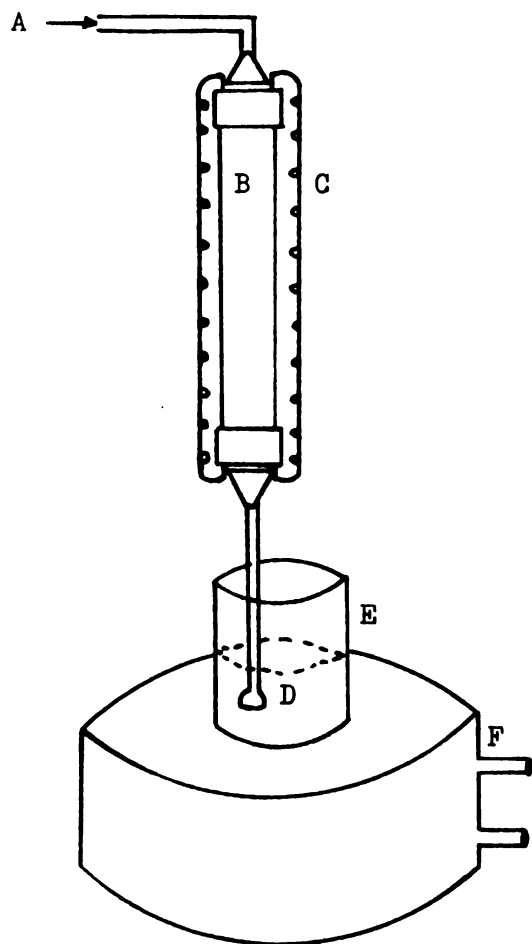
The total halide is titrated at zero applied potential (potential difference between the rotating platinum electrode and the SCE) until the excess of 0.01 N silver nitrate is 100 %.

Stock solutions of unknown were made 0.01 N in halide concentration and diluted to working solutions of 0.002 N in halide. Blanks comprised of the supporting electrolyte diluted to volume with distilled water and standard KCl solution were run with each set of titrations.

b. Chloride Analysis

An aliquot containing 0.12-0.24 μmol of chloride is measured into a 150 ml beaker. Five ml of 6 % nitric acid and an appropriate volume of 0.45 % sodium bromate solution is added. (An appropriate volume is 1.0 ml per 0.01 mmol of bromide, plus an excess of 1.4 ml.) The solution is heated on a steam bath for twenty minutes while dust free air is bubbled through it, (Figure 3-3). The solution is allowed to cool to room temperature, then transferred quantitatively to the titration vessel. One ml of gelatin solution and enough distilled water to bring the volume to 40 ml is added. The solution is then titrated as described for the total halide analysis. (Base currents of 0.2-5.0 μA were obtained under these experimental conditions.)

Blanks and standards were treated as the unknowns with 1.4 ml of 0.45 % sodium bromide added.



- A. Air inlet
- B. Glass wool column
- C. Springs
- D. Glass sinter
- E. Beaker (150 ml)
- F. Steam bath

Figure 3-3. Bromine oxidation setup.

3. Data Reduction

The titration endpoint was determined by the intersection of the base line and the line formed by the set of points where the current is directly proportional to the silver ion concentration (80-100 % excess Ag^+). A linear least squares technique was used to determine the slope and intercept of each line. With each line mathematically described, the two equations were solved for their intersection. The value of X, ml of AgNO_3 (Figure 2-2), at this intersection was taken to be the endpoint. Because the current rises rapidly for the blank, the base current before titrating was assumed to be constant and this value was used in place of a set of base line points. Care was taken not to use any points within the region where the concentration of Ag^+ changes significantly as a result of the solubility of AgCl .

To calculate the concentration, the endpoints of the blanks were averaged and the average was used to correct the sample endpoints as described in equation 3-2, in which X is the ml of AgNO_3 at the endpoint of sample i.

$$X_i(\text{corr}) = X_i - (\sum_1^n X_{\text{bk}})/n \quad (3-2)$$

By knowing the corrected values of X and using the normality of the KCl standard solution, the normality of the silver nitrate solution was calculated. These values were averaged and it was the average value (N) which was used to calculate the millimoles of halide per milligram of sample (H) according to equation 3-3.

$$H = \frac{NX_i(\text{corr})}{CS} \quad (3-3)$$

where C is the concentration of the sample solution used in mg/ml and S is the sample size in ml. At least three samples of each unknown were titrated. The average value of H is reported along with its standard deviation.

The metal analysis results are also reported in terms of moles of metal per gram of sample. Three samples were analyzed for each unknown. The average value and the standard deviation are reported.

The empirical formula was calculated using the results of the metal, total halide and chloride analyses.

E. X-Ray Diffraction Analyses

1. Powder Diffraction Analysis

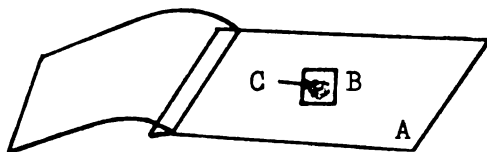
a. Sample Preparation

Water and air sensitive samples were prepared by placing a small piece of transparent tape, the size of the mounting disk hole, on a portion of PVC bag, (Figure 3-4). The sample and internal standard, Pt, were placed on the gum side of the tape. With the two flaps of the PVC bag held together with forceps, the sample was sealed with heat in plastic. The sample could then be removed and mounted on the disk.

General sample preparation, film measurement, and Guinier techniques have been detailed by Stezowski.⁴⁵

b. Equipment

Diffraction patterns of powdered samples were obtained with a Haegg Type Guinier forward focussing camera (radius 80 mm) and Cu $K\alpha_1$ radiation, Pt internal standard ($a_0 = 3.9231 \text{ \AA}$), $t = 24 \pm 2 \text{ }^\circ\text{C}$. The X-ray



- A. PVC bag
- B. Transparent tape
- C. Sample

Figure 3-4. Powder pattern sample preparation.

source was a fine focus tube powered by a Picker 809B generator.

c. Data Reduction

With platinum powder as the internal standard, the diffraction data were reduced with the least squares regression program of Lindqvist and Wengelin.⁴⁶

2. Single Crystal X-Ray Diffraction Analysis

a. Crystal Mounting

Crystals were transferred to a special capped transfer tube (Figure 3-5) in the glove box. Under a strong flow of argon, the transfer tube was uncapped and attached to the mounting apparatus. The entire apparatus was alternately evacuated and filled with argon. The last evacuation period was for a minimum of thirty minutes. The tube was then filled with argon and a crystal selected through the viewing tube. Under a heavy flow of argon the closing tube was removed and a

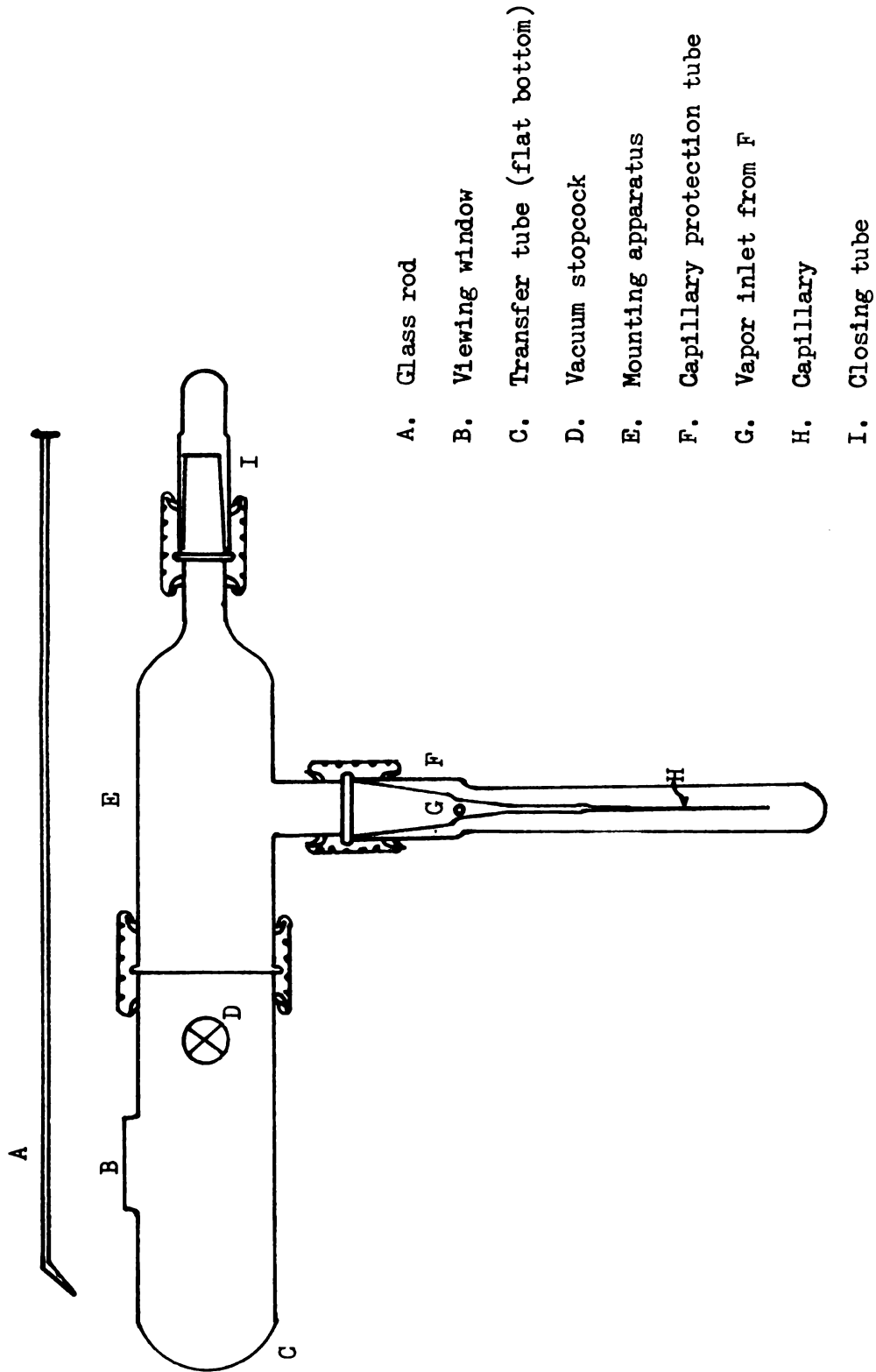


Figure 3-5. Single crystal mounting apparatus.

bent glass rod inserted in order that more crystals could be moved into the viewing field. An attempt was made to select a crystal which was clear, colorless, of uniform shape and lacking signs of fracture. Once a crystal was selected and somewhat isolated by using a glass rod, it was transferred to the entrance of the capillary. A strong tap on the glass rod caused the crystal to fall into the capillary tube. The system was then closed and evacuated once again. Under argon flow the capillary protection tube was removed. The capillary was sealed with a small gas and oxygen flame. It was necessary to seal the capillary as close to the crystal as possible in order that it would be locked in place. The tube was then mounted in clay on the goniometer head.

b. Equipment and Parameters

Lattice parameters and intensity data measurements were made at a temperature of 23 ± 3 °C with a computer-controlled, four circle, Picker goniostat with Mo K α radiation ($\lambda = 0.7093$ Å), and a graphite monochromator mounted adjacent to the X-ray tube.

The ω -scan technique was used for data collection with a scan range of 1.5° and a scan rate of $1.0^\circ/\text{min}$. Both the hkl and $\bar{h}\bar{k}l$ octants were collected.

Cell constants were obtained from a least squares refinement of 12 reflections which were hand-centered on the goniostat. Reflections from the $\bar{h}\bar{k}l$ and hkl octants were centered.

PKCORR, an adaption of NUFACS written by Ibers⁴⁷, was used to correct the intensity measurements for background. An empirical absorption correction around the phi curve was applied using EMPASS. Lorentz and polarization corrections were effected with the program INCOR provided

by A. Zalkin. This program had been modified to include a correction for the graphite monochromator. The least squares refinement program was also provided by Zalkin.

Table 3-1. Crystal Data for $\text{EuCl}_{0.46(2)}\text{Br}_{1.56(7)}$

$$\text{EuCl}_{0.46(2)}\text{Br}_{1.56(7)}, \underline{M} = 239(6) \text{ g mol}^{-1}$$

$$\underline{a} = 7.8797(35), \underline{b} = 4.611(2), \underline{c} = 9.198(4) \text{ \AA}$$

Systematic Absences: $0kl, k + l = 2n + 1; hk0, h = 2n + 1$

Space Group: $Pnma$, No. 62

$$\underline{Z} = 4, F(000) = 502(11) \text{ e}, \underline{V} = 334.2(3) \text{ \AA}^3$$

$$\mu = 387.1 \text{ cm}^{-1} (\text{Mo K}\alpha)$$

$$D = 4.75 \text{ g cm}^{-3}$$

$$\lambda(\text{Mo K}\alpha, \text{graphite monochromator}) = 0.7093 \text{ \AA}$$

CHAPTER IV

RESULTS

A. Europium Mixed Halides

1. Phase 1

a. Elemental Analyses

The pseudo Taylor-Carter preparation in which the initial heating period was at a temperature less than 200 °C yielded a white hydroscopic powder. Halide and metal analysis showed the product to be $\text{EuCl}_{0.46}\text{Br}_{1.56}$. Results of the analysis are listed in Table 4-1.

Table 4-1. Analysis of Phase 1 ($\text{EuCl}_x\text{Br}_{2-x}$).

Species	moles/gram of sample	moles of halide/mole of Eu ion
Total Halide	$7.1_2 \pm 0.27 \times 10^{-3}$	2.02 ± 0.07
Chloride	$1.6_2 \pm 0.07 \times 10^{-3}$	0.46 ± 0.02
Bromide	$5.4_9 \pm 0.28 \times 10^{-3}$	1.56 ± 0.07
Eu ion	$3.51_2 \pm 0.005 \times 10^{-3}$	

b. X-Ray Diffraction Analyses(1) Powder Diffraction

The powder pattern is compared to that calculated from single crystal data in Appendices IA and IB. Close correlation between the two can be seen.

(2) Single Crystal X-Ray Diffraction Analysis

From precession measurements and intensity data collected by use of a four circle goniostat, the unit cell was determined to be orthorhombic with lattice parameters: $a = 7.879_7 \pm 0.003_5$, $b = 9.197_7 \pm 0.004_3$, and $c = 4.611_1 \pm 0.002_0$ Å. Because of the close similarity between the unit cell and extinctions observed in the intensity data of the mixed halide phase and that of EuCl_2 ($a = 7.51$, $b = 8.93$, $c = 4.50$ Å)⁴¹, an attempt was made to solve the structure based on least squares refinement of the atomic coordinates of EuCl_2 (PbCl_2 structure type) with various concentrations of bromide ion substituted for chloride ion.

The positions used for the calculations were those of the space group Pbnm , no. 62, as given by Baernighausen¹⁷ with x and y being interchanged according to the choice of the principle axes. In this setting all atoms are in special positions defined by the symmetry relationships:

$$x, y, z \quad (4-1)$$

$$1/2 - x, 1/2 + y, 1/2 + z \quad (4-2)$$

$$1/2 + x, 1/2 - y, z \quad (4-3)$$

$$-x, -y, 1/2 + z \quad (4-4)$$

The chloride ions have two different points of symmetry. Negative

thermal parameters arose when a chloride ion was refined in position two, an indication that the electron density was too low. A bromide ion was substituted for the chloride ion in this position. The electron density was then increased further by progressively replacing the chloride ion scattering curve with that of a bromide ion until the R factor was minimized (and thermal parameters maximized). By plotting R as a function of the mole % Bromide of the total halide and finding the best least squares parabola to fit the data (4-5), one finds the minimum at 75.1 % Bromide, which corresponds to an empirical formula of $\text{EuCl}_{0.498}\text{Br}_{1.502}$, (Figure 4-1).

$$y = 70.9 - 1.76x + 0.0117x^2 \quad (4-5)$$

c. Reaction Pathway

Samples were taken at various stages of the heating period. The samples were divided according to color. Sample (a) was an air-dried portion of the initial thick slurry which was transferred to the carbon boat; (b) a light orange phase which developed first on heating; (c) a dark orange phase which became bright orange on cooling; and (d) the light grey phase which appears after heating at 370 °C. Each sample was examined by powder X-ray diffraction.

The powder pattern of sample (a) corresponds to a mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and NH_4Br (Appendices IB, IC, and ID) and that of (d) to what is normally obtained for Phase 1. However, the powder patterns of (b) and (c) could not be indexed successfully and no known phase was identifiable.

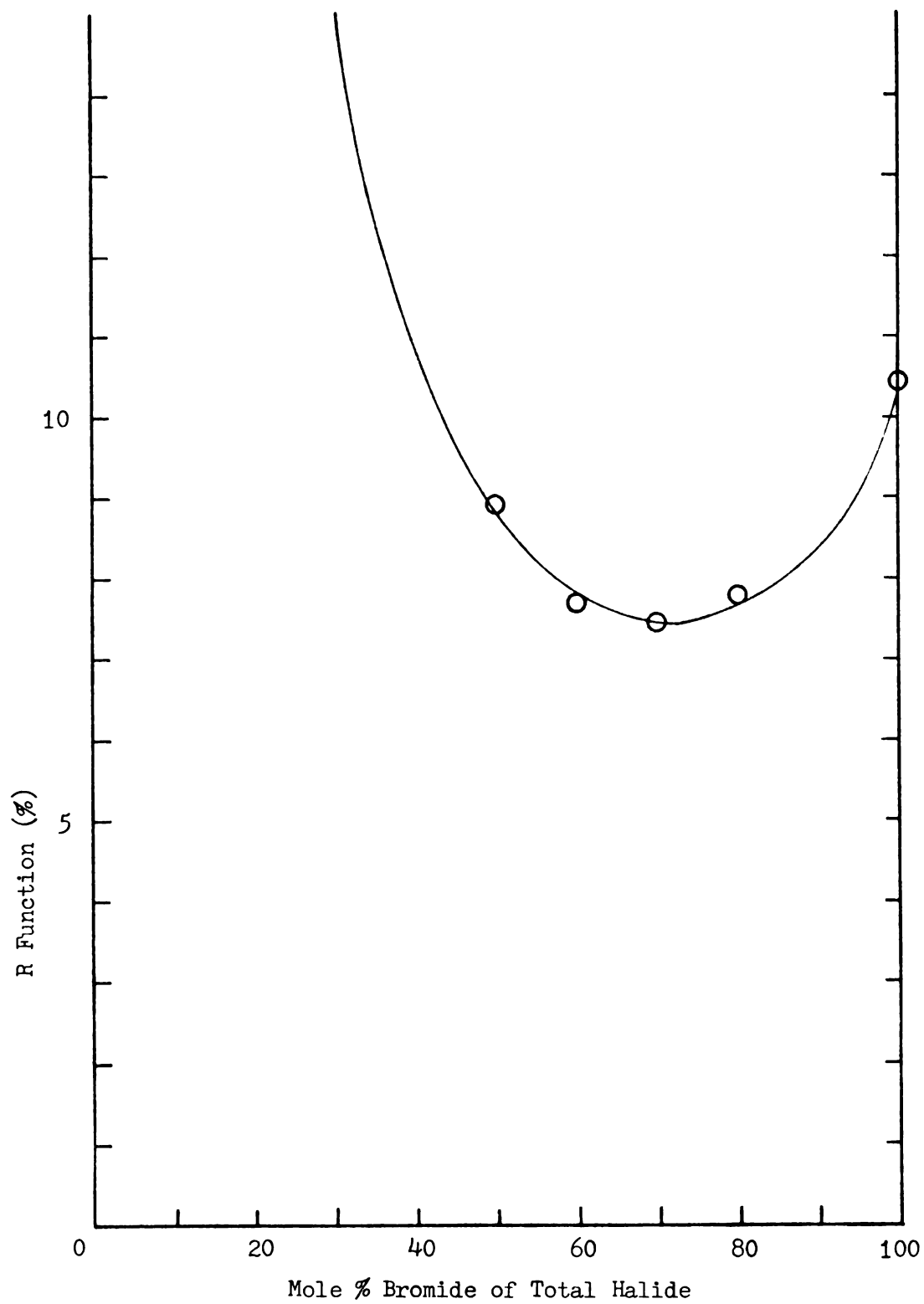


Figure 4-1. R as a function of bromide concentration in Phase 1.

2. Phase 2

a. Elemental Analyses

The white hygroscopic powder obtained from the pseudo Taylor-Carter preparation (initial heating temperature greater than 250 °C) had the empirical formula $\text{EuCl}_{0.16}\text{Br}_{1.85}$. Results of the metal and halide analyses are listed in Table 4-2.

Table 4-2. Analysis of Phase 2 ($\text{EuCl}_x\text{Br}_{2-x}$).

Species	moles/gram of sample	moles of halide/mole of Eu ion
Total Halide	$6.6_3 \pm 0.50 \times 10^{-3}$	2.01 ± 0.04
Chloride	$5.3_0 \pm 1.3 \times 10^{-4}$	0.16 ± 0.04
Bromide	$6.1_0 \pm 0.51 \times 10^{-3}$	1.85 ± 0.04
Eu ion	$3.3_0 \pm 0.08_3 \times 10^{-3}$	

b. X-Ray Diffraction Analysis

The powder pattern of Phase 2 is characteristic of an orthorhombic cell similar to that of Phase 1 with increased lattice parameters.

3. Sealed Bomb

Four colored phases including a dark yellow powder, a light yellow powder, a dark grey powder and dark grey crystals were found present in the quartz tube upon cooling.

The dark yellow and dark grey phases which were heated under

vacuum to remove excess ammonium halide decomposed into a dark grey phase. The X-ray powder pattern of the final dark grey phase was similar to that of Phase 1 and Phase 2, characteristic of an orthorhombic cell with lattice parameters smaller than that of Phase 1.

B. Ytterbium Mixed Halide

A white hygroscopic powder was obtained from the pseudo Taylor-Carter preparation. The results of the elemental analyses are tabulated in Table 4-3. The results indicate that the bromide, chloride and ytterbium ion are not the sole constituents of the ytterbium mixed halide phase. Because thermal decomposition studies of ytterbium trichloride hydrates have shown the possible existence of a hydrate to be minimal at the experimental temperatures used; and because the presence of elements which have a molecular weight of 67 ± 7 (which may be calculated from the results of the elemental analyses, assuming the Yb ion to be in a +3 oxidation state) cannot be justified, it seems likely that the remaining constituent of the system is ammonia. When the remaining fraction is considered to be ammonia, the empirical formula for the ytterbium mixed halide phase is

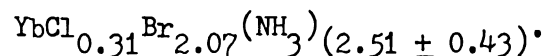


Table 4-3. Analysis of the ytterbium mixed halide phase.

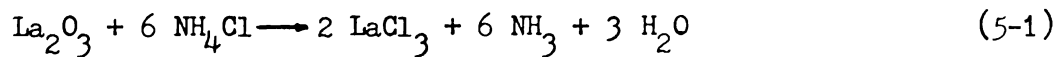
Species	moles/gram of sample	moles of halide/mole of Yb ion
Total Halide	$6.07 \pm 0.21 \times 10^{-3}$	$2.38 \pm 0.08_3$
Chloride	$7.88 \pm 0.80 \times 10^{-4}$	$0.31 \pm 0.03_1$
Bromide	$5.28_9 \pm 0.23 \times 10^{-3}$	$2.07 \pm 0.08_9$
Yb ion	$2.55_2 \pm 0.0067 \times 10^{-3}$	

CHAPTER V

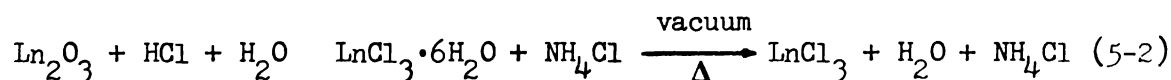
DISCUSSION

As described earlier, there have been many methods reported for the preparation of anhydrous lanthanide halides. Many investigators, however, have experienced difficulty in preparing these compounds in pure form. Very few of the reaction pathways of the systems used have been investigated. The known methods generally involve either converting the oxide to the halide with a suitable halogenating reagent or dehydrating the wet halide.

Reed, Hopkins and Audrieth⁴⁸ prepared anhydrous rare earth halides by the action of fused and solid "onium" salts in the lanthanide oxides, (5-1).



They believe the ammonium salts are acting as acids according to the Brönsted definition. Because of its acidic nature, the excess ammonium chloride is believed to prevent hydrolysis of the lanthanum trichloride. Taylor and Carter⁴ also used an ammonium halide to prevent hydrolysis of the rare earth halide they had prepared by dehydration of the lanthanide hexahydrate, (5-2).



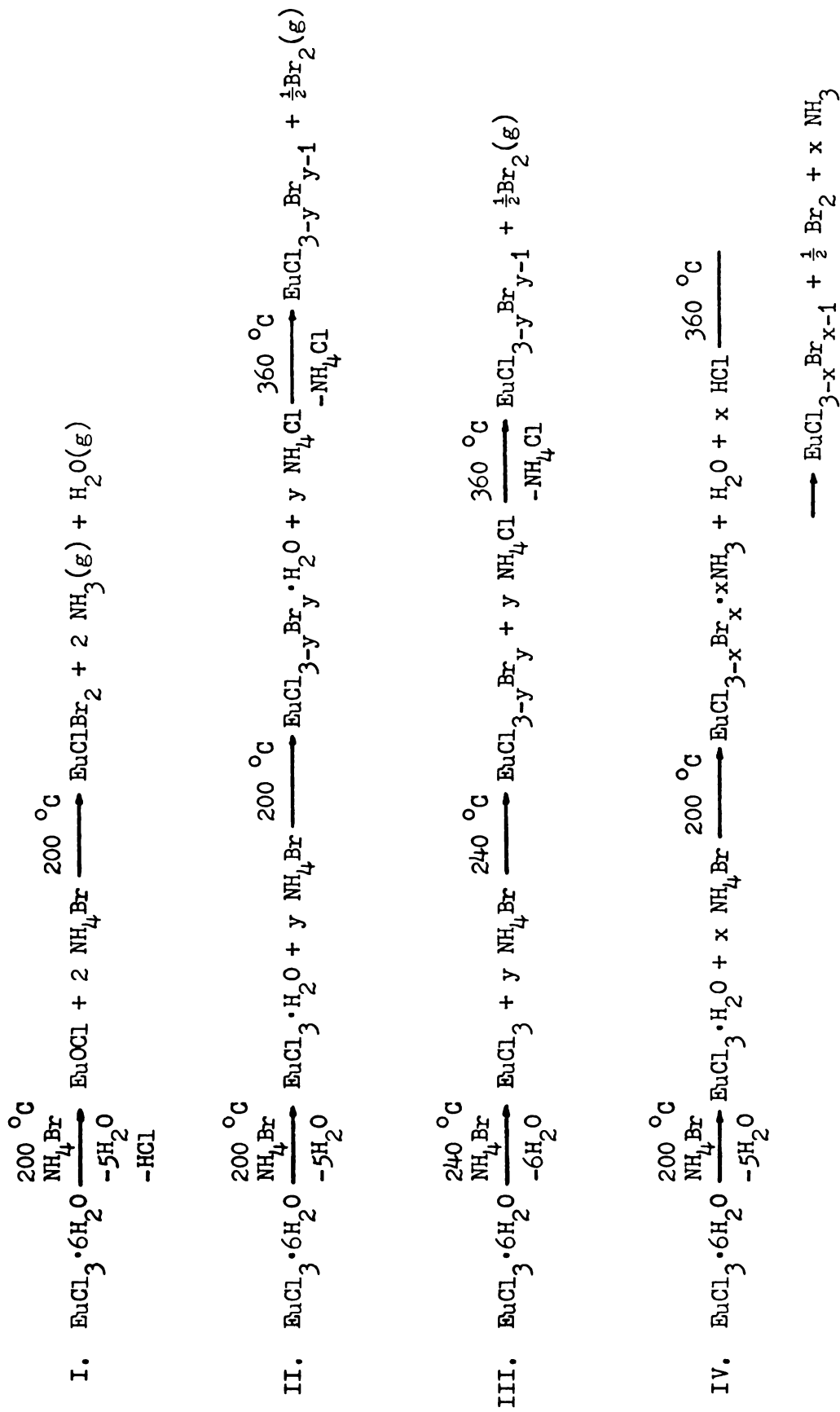
The results of the thermal decomposition studies of the lanthanide halide hydrates have been outlined in Chapter II. Although the authors differ on which intermediate hydrate phases are formed, they both agreed that $\text{EuCl}_3 \cdot \text{H}_2\text{O}$ exists at 200 °C and the principle phase at 250 °C is EuCl_3 .

The results of thermal decomposition studies of the lanthanide trichloride ammine complexes have also been summarized in Chapter II. Ammine complexes appear to be more stable to decomposition at higher temperatures than the hydrates.

With these facts in mind, one might propose several reaction pathways for the pseudo Taylor-Carter preparations used in this work, (Table 5-1). Reaction pathway I is probably the easiest to eliminate. Neither Ascroft and Mortimer³⁰ nor Il'in, Krenev and Evdokimov³¹ found the oxidechloride to be the principle product when the lanthanide trichloride hydrates are dehydrated in a deoxygenated system. Because the bromide ion is the stronger reducing agent, we would expect the final product to contain a 1:1 ratio of bromide ion to chloride ion rather than the 3.4 and 12 ratio which was found for the europium mixed halide system.

The only difference in the experimental conditions for the preparation of Phase 1 and Phase 2 is the temperature of the initial heating period. Phase 1 was obtained when the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O} \cdot \text{NH}_4\text{Br}$ matrix was initially dehydrated at a temperature of 200 °C, and Phase 2 when the initial temperature was greater than 250 °C. It has already been determined from the thermal decomposition studies, that $\text{EuCl}_3 \cdot \text{H}_2\text{O}$ should be the principle phase during this period at 200 °C and EuCl_3 , the principle phase at a temperature greater than 250 °C provided that

Table 5-1. Proposed reaction pathways.



there is no interaction with the ammonium halide. Pathway II might then be suitable to describe the preparation of Phase 1 and pathway III for the preparation of Phase 2.

Very little is known concerning the crystal structure of the lanthanide trihalide monohydrate. Crystal data for the monohydrate of europium tribromide is given by Haschke and Eick.⁵ Although the hexahydrates of the lanthanide trichlorides and tribromides are isomorphic, the anhydrous lanthanide trichloride and tribromide belong to different structure types, (Chapter II). The anion: cation ratio is more significant for the close packing of the anhydrous compounds than for the hexahydrates. Therefore, correlations drawn between the monohydrate of europium tribromide and that of europium trichloride would be nebulous, and it is difficult to draw any further conclusions concerning the correctness of pathway II.

A single crystal structure determination of EuCl_3 was done by Morosin¹³, (Chapter II). Four of the chloride ions in the metal ion coordination sphere have metal-chloride bond distances of $4.492 \text{ \AA}$, two have bond distances of $2.835 \text{ \AA}$, and there is one with a M-Cl bond distance of $2.919 \text{ \AA}$. The ionic radius of Eu(III) is $0.950 \text{ \AA}$ ¹⁵, while Pauling lists the ionic radius of bromide ion as $1.95 \text{ \AA}$. The sum of the ionic radii is $2.90 \text{ \AA}$. A bromide could easily substitute for the four chloride ions with bond distances of $4.492 \text{ \AA}$. The empirical formula for such a compound would be $\text{EuCl}_{1.28}\text{Br}_{1.72}$. There is the possibility of further substitution of a bromide ion for the chloride ion with a metal bond distance of $2.919 \text{ \AA}$. The empirical formula of this compound would be $\text{EuCl}_{0.86}\text{Br}_{2.14}$. In either case, we would expect the bromide ion to be the reducing ion, and the final divalent halide, from

the decomposition of these trivalent europium mixed halide phases, to be richer in chloride than either phase prepared, which does not support pathway III.

A similar study of the EuCl_2 structure shows one metal-chloride bond each of $3.046 \text{ \AA}$, $2.994 \text{ \AA}$, and $2.916 \text{ \AA}$ and two metal-chloride bonds of $3.440 \text{ \AA}$ and $2.925 \text{ \AA}$. The ionic radius of Eu^{+2} is reported to be between 1.21 and $1.29 \text{ \AA}$ depending on the anion.¹⁷ In this structure 56 % of the chloride ions lie in the center of a square pyramid of metal ions and 44 % lie in a tetrahedral hole. As would be expected, the M-Cl bond distances greater than $3.0 \text{ \AA}$ are for those chloride ions in the tetrahedral holes. If a bromide ion were substituted for seven of the nine chloride ions in the coordination sphere, the empirical formula for such a compound would be $\text{EuCl}_{0.44}\text{Br}_{1.56}$. The R function in the single crystal analysis of Phase 1 was minimized for a compound with the empirical formula $\text{EuCl}_{0.5}\text{Br}_{1.5}$ with bromide ion substituted entirely for the chloride ion in position two. The elemental analyses showed Phase 1 to be $\text{EuCl}_{(0.46 \pm 0.02)}\text{Br}_{(1.56 \pm 0.07)}$. For bromide ions in eight of the nine positions, the empirical formula of such a compound would be $\text{EuCl}_{0.22}\text{Br}_{1.78}$, analogous to Phase 2, $\text{EuCl}_{(0.16 \pm 0.04)}\text{Br}_{(1.85 \pm 0.04)}$.

The reduction of the anhydrous europium trichloride to the dichloride is not known to be significant under the experimental conditions used in this work. One would not expect EuCl_2 to be a major intermediate, yet the structure may be used to account for the particular phases obtained. It is interesting to note that even with the high concentration of bromide ion, the unit cell appears to retain its orthorhombic symmetry.

The final proposed pathway, IV, is through an ammonia complex, but not necessarily the one given in IV. The structural chemistry of YbCl_3 is isomorphic with that of YCl_3 , while the structure of EuCl_3 is isomorphic with that of NdCl_3 and GdCl_3 , (Table 2-1). The thermal decomposition temperatures of ammine complexes of NdCl_3 , GdCl_3 and YCl_3 probably are similar to those of EuCl_3 and YbCl_3 respectively. From the data tabulated in Table 2-6, an ammine complex of europium trichloride would not exist above 360°C (the final temperature used in the Taylor-Carter preparation), but a ytterbium mixed halide ammine complex may exist. The results of the ytterbium mixed halide preparation supports this contention.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

One may conclude from this work that the substitution of the bromide ion for the chloride ion was selective rather than random as originally thought. This conclusion suggests that the space group used for the least squares refinement of the atomic parameters was of too high symmetry. Redefining the data in terms of a lower space group may increase the refinement. Further refinement was not attempted previously because it was believed that the empirical absorption correction, which was applied because of the irregular shape of the crystal was not representative of the real absorption problem. The intermediate phase then, should also require selective substitution of the chloride ion.

An ammine complex of the lanthanide trihalide is a likely candidate for an intermediate phase. If an ammine complex could stabilize the trihalide during dehydration, by using other complexing agents, various anhydrous compounds may be prepared by a more direct route. A Mössbauer study of the reaction intermediates or a detailed analysis of the structure of the ammine complexes and the monohydrates of the lanthanide trichlorides could better define the reaction pathway.

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APPENDICES

Appendix I: Observed and Calculated $\sin^2\theta$ ($\lambda = 1.54051 \text{ \AA}$) and Interplanar d-Values

Appendix IA: $\text{EuCl}_{0.46(2)}\text{Br}_{1.56(7)}$ (Observed)

Relative Intensity	$\sin^2\theta$	d value ($\text{\AA}$)	Relative Intensity	$\sin^2\theta$	d value ($\text{\AA}$)
m	0.0371	4.000	vvw	0.2074	1.692
w	.0378	3.962	vvw	.2112	1.676
m	.0439	3.684	vw	.2215	1.636
m	.0648	3.027	w	.2243	1.626
w	.0655	3.009	vw	.2392	1.555
s	.0725	2.861	vw	.2592	1.513
m	.0900	2.567	vw	.2634	1.501
w	.0924	2.534	vvw	.2650	1.494
m	.0995	2.440	vw	.2724	1.476
m	.1107	2.315	vw	.2869	1.438
mw	.1132	2.289	vw	.2942	1.420
w	.1201	2.223	vvw	.3213	1.359
vw	.1485	1.999	vvw	.3281	1.345
vvw	.1523	1.974	vvw	.3348	1.331
vvw	.1761	1.836	vvw	.3410	1.319
vvw	.1800	1.815	vw	.3496	1.303
vvw	.1828	1.802	vvw	.3770	1.255
vvw	.2032	1.709			

Appendix IB: $\text{EuCl}_{0.46(2)}\text{Br}_{1.56(7)}$ (Calculated)

hkl	$\sin^2\theta$	d value ($\text{\AA}$)	hkl	$\sin^2\theta$	d value ($\text{\AA}$)
101	0.0375	3.980	151	0.2128	1.670
120	.0376	3.972	042	.2238	1.628
111	.0445	3.653	322	.2257	1.621
030	.0631	3.066	142	.2415	1.568
121	.0655	3.009	500	.2389	1.576
130	.0727	2.857	332	.2607	1.509
031	.0910	2.553	013	.2582	1.516
310	.0930	2.526	402	.2645	1.498
131	.1006	2.429	440	.2651	1.496
002	.1116	2.306	412	.2715	1.478
040	.1122	2.299	511	.2738	1.472
301	.1139	2.282	053	.2869	1.438
311	.1209	2.215	123	.2887	1.433
330	.1491	1.995	521	.2948	1.419
400	.1529	1.970	133	.3238	1.354
331	.1770	1.831	432	.3256	1.346
401	.1808	1.812	450	.3282	1.345
420	.1809	1.811	303	.3371	1.327
132	.1843	1.794	360	.3385	1.324
051	.2032	1.709	502	.3505	1.301
421	.2088	1.686	442	.3767	1.255

Appendix IC: $\text{EuCl}_3 \cdot 6\text{H}_2\text{O} \cdot \text{NH}_4\text{Br}$ Matrix

Relative Intensity	hkl	$\sin^2\theta$	d value ($\text{\AA}$)	Relative Intensity	hkl	$\sin^2\theta$	d value ($\text{\AA}$)
mw		0.0146	6.375	s		0.0731	2.850
mw		.0164	6.009	vvw		.0956	2.492
w		.0228	5.097	vvw		.1053	2.374
w		.0252	4.853	mw		.1094	2.329
w		.0282	4.589	vw		.1112	2.310
w		.0302	4.435	mw		.1461	2.015
ms		.0365	4.033	mw		.1826	1.803
mw		.0460	3.591	mw		.2191	1.646
mw		.0501	3.443	vvw		.2917	1.426
w		.0613	3.111	vw		.3288	1.343
vvw		.0643	3.037	vw		.3648	1.275

Appendix ID: Cubic $\text{NH}_4\text{Br}^{50}$ ($a = 6.91 \text{ \AA}$)

110	.0248	3.989	222	.1491	1.995
111	.0373	3.990	322	.2112	1.676
200	.0497	3.455	422	.2982	1.410
211	.0746	2.821	510	.3231	1.355
220	.0994	2.443	520	.3603	1.283
300	.1183	2.303			

Appendix IE: Monoclinic $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}^{24}$

hkl	$\sin^2\theta$	d value ($\text{\AA}$)	hkl	$\sin^2\theta$	d value ($\text{\AA}$)
-101	0.0148	6.338	-203	0.1041	2.387
101	.0168	5.952	113	.1079	2.345
011	.0233	5.044	320	.1129	2.293
200	.0254	4.830	-313	.1469	2.010
-111	.0287	4.548	330	.1824	1.803
111	.0307	4.399	-521	.2191	1.646
-211	.0468	3.562	424	.2920	1.426
211	.0507	3.420	701	.3279	1.345
120	.0620	3.093	-711	.3279	1.345
021	.0651	3.020	504	.3292	1.343
-212	.0730	2.851	151	.3646	1.276
-122	.0976	2.465	116	.3647	1.276
103	.0939	2.513			

Appendix IF: $\text{EuCl}_{0.16(4)}\text{Br}_{1.85(4)}$ (Observed)

Rela- tive Inten- sity	$\sin^2\theta$	d value ($\text{\AA}$)	Rela- tive Inten- sity	$\sin^2\theta$	d value ($\text{\AA}$)
vw	0.0329	4.247	w	0.1251	2.178
w	.0337	4.193	vw	.1294	2.141
w	.0359	4.066	vvw	.1412	2.050
w	.0371	3.998	vvw	.1450	2.023
w	.0564	3.245	vvw	.1506	1.985
w	.0628	3.073	vvw	.1721	1.857
w	.0642	3.040	vw	.1773	1.829
w	.0697	2.919	vvw	.2153	1.660
m	.0710	2.891	vw	.2188	1.647
m	.0875	2.604	vvw	.2516	1.536
w	.0889	2.584	vvw	.2584	1.515
w	.0911	2.552	vvw	.2619	1.505
w	.0921	2.538	vw	.2687	1.486
vvw	.1006	2.429	vw	.2795	1.457
w	.1070	2.355	vw	.2849	1.443
w	.1114	2.307	vvw	.3382	1.324
vw	.1179	2.243			

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