An investigation of highly reduced
halides of cerium, praseodymium, and neodymium

MASTER

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INTRODUCTION

The availability of pure lanthanide metals in the past 25 years has opened a vast area for scientific investigation. One area of investigation has been the apparent solubility of a metal in its corresponding halide salt. The phenomenon of metal solubility in one of its salts was first reported by Davy in 1807 for the solubility of potassium in KOH.¹ Extensive investigations of the phenomenon have been undertaken for alkali, alkaline, post transition, and transition metal solubility in their corresponding salts.² The extension of metal solubility investigations to the lanthanides produced, by thermal analysis, phase diagrams for most chloride and iodide systems along with part of the bromide systems.³ In many cases the metal solubility may be attributed to the formation of reduced species in the melt.

In addition to metal solubility, many reduced species, mostly dipositive, formed compounds from the melt, such as NdCl_2 ,⁴ $\text{PrCl}_{2.3}$,⁵ $\text{HoCl}_{2.2}$,⁶ etc. $\text{GdCl}_{1.5}$ ^{7,8} was the only phase found in a more reduced state than the dihalide.

The synthesis of highly reduced compounds ZrCl , ZrBr and other Group IVB monohalides^{9, 10, 11} provided the first examples of a new structure type involving double layers of metal atoms separated by a double layer of halogens. Two packing variations occur in the structure:

1) in ZrCl the halogens are in trigonal antiprismatic coordination and 2) in ZrBr the halogens are in trigonal prismatic coordination. The metal atoms are always antiprismatic. The ZrBr structure type allows interaction between the metal atoms and halogens two layers away, providing a more rigid structure. The Group IVB monohalides were initially synthesized by extended reduction of the tetrahalide with excess metal at moderately high temperatures, 750°C - 900°C .⁹

The existence of ScCl^{12} in the ZrBr structure was the first reported compound outside of Group IVB with the ZrX type double metal layer structure. The report of intermediate scandium chlorides between ScCl and $\text{ScCl}_{1.5}^{13,14}$ further showed a limitation in the previous thermal analysis work on this system where reactions are kinetically slow and only $\text{ScCl}_{1.5}$ was found. The existence of GdCl , TbCl , ErCl , and LuCl^{15} in the ZrCl structure, along with the synthesis of $\text{TbCl}_{1.5}^{15}$ indicated that many reduced species had been missed by the thermal analysis work on the M-MX_3 systems of the lanthanides because of the slow rates of formation of thin layers of reduced material which blocked further reaction of the metal. With the synthesis of monochlorides for the heavy lanthanides, a reinvestigation of the light lanthanide chlorides, cerium, praseodymium

and neodymium was considered very desirable and is the subject of this work.

A second type of novel reduced lanthanide compound is the double salt of CsCl and a lanthanide dichloride. The synthesis of CsScCl_3 ¹⁶ in an ABX_3 type structure was the first reported example for an element considered, in a very broad definition, as a rare earth. Phase diagrams are known for $\text{CsCl} - \text{CeCl}_3$ and $\text{CsCl} - \text{NdCl}_3$ ¹⁷ systems which comprise the starting materials for systems studied in this work, and these contain only the stable double salts $\text{Cs}_3(\text{RE})\text{Cl}_6$, $\text{RE}=\text{Ce}, \text{Nd}$. For the $\text{CsCl} - \text{PrCl}_3$ system, no phase diagram was available, but Cs_3PrCl_6 was assumed to be the only stable double salt in this system as well.

The three light lanthanide systems contrast with $\text{CsCl} - \text{ScCl}_3$ where the double salt $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ ¹⁶ forms ($\text{Cs}_3\text{Tl}_2\text{Cl}_9$ structure). $\text{Cs}_3\text{Sc}_2\text{Cl}_9$ is structurally related to CsScCl_3 by a vacancy in every third scandium metal site. For the three systems concerned in this study no relationship is thought to exist between the trivalent and the potential divalent structures.

EXPERIMENTAL

Preparation of the Trichlorides

High purity lanthanide metals were obtained from Ames Laboratory Metals Preparation group. The maximum non-lanthanide impurity levels in ppm atomic was 0581, N767, H697, F13.8, Ta8.6, Si, Cr, Cl, Cu < 3 all others < 1. Lanthanide impurities were < 10 maximum for any one metal, with an average level of < 2 for each metal. The metals were obtained in the desired form, turnings or 15 mil foil, and stored in sealed glass ampoules under high vacuum. The praseodymium and neodymium foils were electropolished before delivery. Cerium foil was not electropolished when XPS results were found to indicate a thin layer of oxide and carbonaceous material was produced by electropolishing.

The trichloride was prepared by the method of Druding,⁴ using commercial (Matheson) HCl, except that the -80° C trap in the gas train was deleted. The original purpose of this trap had been to remove moisture from the HCl gas produced from the reaction of KCl and H₂SO₄ used in earlier synthetic procedures. Rare earth metal turnings were placed in a molybdenum boat in the drybox and inserted into the preparation apparatus. The apparatus was removed from the drybox and connected to the gas train. A flush of helium was started and maintained while the temperature of the

apparatus was raised to 50°C above the melting point of the trichloride. At this temperature a slow flow of H_2 and HCl was started. After 1 to 2 minutes the flow of helium and hydrogen was stopped and the flow of HCl increased. Upon the appearance of MoCl_5 , usually after 30 to 40 minutes, the flow of hydrogen was restarted at a rate equal to 50% of that of the HCl . After 30 minutes the flow of HCl and H_2 was stopped and the system was flushed with helium. Helium flow was maintained until the apparatus cooled to room temperature.

Purification of the Trichlorides

The trichlorides were purified by vacuum sublimation in a tantalum lined fused silica tube. The fused silica tube was connected by a standard taper joint to a Pyrex top equipped with a stopcock and a flat end window. The tantalum liner was constructed in two sections from 1" diameter 20 mil. tubing. The lower section was capped at one end and swaged at the other end to allow overlap of sections. The need for a tantalum liner was suggested by the depression in melting point observed after reaction between lanthanide halides and SiO_2 had produced the oxyhalide.¹⁸

Sublimations were run under a dynamic vacuum of $<10^{-5}$ torr using temperatures in the range $900^{\circ} - 950^{\circ}\text{C}$. The sublimation temperature was adjusted to produce a

reasonable rate of sublimation, typically 15 grams in a 24 hour period.

A minimum of two sublimations was needed to produce pure trichlorides free of contamination from impurities in the commercial HCl used for synthesis. The final product was in the form of small 0.5 - 2.0 mm wide by 2 - 4 mm long crystals. The purified trichlorides were stored under high vacuum in sealed glass ampoules.

Purification of CsCl

Cesium chloride (Gallard-Schlesinger 99.9%) was used for all reactions. Purification was limited to fusing the salt under a dynamic vacuum to remove any occluded moisture.

Equipment

Drybox

A drybox filled with pre-purified nitrogen was used for all transfers. Atmospheric moisture was kept low by circulating the nitrogen through Molecular Sieve. An open dish of P_2O_5 also aided the process. During usage, moisture levels in the drybox varied from 6 ppm in the winter to 20 ppm in the summer. This variation was due to the greater permeability of the gloves at higher temperatures and humidity levels. The entry port was evacuated to 4×10^{-3} torr and filled with pre-purified nitrogen before entry.

X-ray

Powder x-ray diffraction films were obtained by Debye Scherrer and Guinier methods. The Debye Scherrer camera used was a Phillips 114.59 mm unit. Powder samples were loaded into 0.2 - 0.3 mm Lindemann glass capillaries and sealed off under nitrogen in the drybox. Nickel-filtered copper radiation was used for all exposures. Guinier films were obtained using an IRDAB model XDC-700 camera equipped with an evacuable case. A quartz monochromator was used to produce a clean copper K α x-ray beam from a long fine focus tube. NBS standard silicon was included as an internal reference. Samples were prepared by covering a disk-shaped area on a small piece of cellophane tape with sample and powdered silicon. This area was covered by a second piece of tape and mounted on a supporting washer. Transfer from the drybox to camera was in a sealed nitrogen filled bottle. The transfer of the sample from the bottle to the camera in air was of short duration, 10 to 15 seconds maximum. No decay of any sample from air exposure was noted. Line positions were measured using a Siemens coincidence scale of 300 mm length. The calibration and film shrinkage correction were accomplished using the silicon standard and a correction program for interpolation.

Furnaces

Two main types of furnaces were used: 1) small asbestos wrapped tube furnaces, 2) Marshall type tube furnaces. The small tube furnaces were used for reactions above 1050°C where the life expectancy of resistance furnaces becomes short. The burn out of a small inexpensive tube furnace was not considered a major loss. The tube furnaces were also used for reactions where large thermal gradients were desired. Any sample quenched from high temperatures was heated in the small tube furnaces because of the greater ease of tipping a small lightweight furnace. Marshall furnaces were used for long equilibrations, especially where little or no gradient was desired. A liner of inconel alloy along with asbestos cement radiation shields further reduced any gradient. The Marshall furnace had a second advantage in power consumption, as it required only 25% of the power needed to operate a tube furnace under similar conditions.

Temperature control

Two types of temperature controllers were used: 1) on-off types of various origins and 2) Honeywell series 15 continuous controllers. The on-off controls were used primarily with tube furnaces when the constancy of control ($\pm 2^{\circ}\text{C}$ minimum) was not critical. The series 15 controllers were capable of $\pm 0.5^{\circ}\text{C}$ or better and were used for any

reaction where extremely accurate control was needed, especially gradient reactions.

Thermal analysis apparatus

The thermal analysis apparatus described by Löchner¹⁹ consisted of a Thermac (Research Incorporated) controller equipped with temperature programmer, a Marshall furnace, and a Honeywell series 194 two channel recorder. A filled tantalum sample container, equipped with a thermocouple well, was placed in a fused silica tube. The tube was capped through a standard taper joint to a Pyrex top, which was equipped with a stopcock and vacuum thermocouple lead-throughs. Care had to be taken to insure that the thermocouple was secured to the exterior of the fused silica tube at the same level as the internal thermocouple. The entire apparatus was placed in the furnace and connected to the vacuum system. Pen 1 recorded sample temperature. Pen 2 recorded the difference between the thermocouples. The recorder was standardized using a Honeywell Rubicon potentiometer as a voltage source. Thermocouples were standardized against the melting point of NaI.

Reaction containers

Reactions were run in 6 and 9 mm OD tantalum tubing crimped at the ends and sealed by DC arc welding under helium. The tubing was cleaned with a $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-HF}$

solution before usage. A vise in the drybox was used to crimp the tubing after loading the sample. A glass sample container was used to transfer the reaction tube from the drybox. With minimum exposure to the air, the crimped tube was spotwelded and inserted into the arc welder. The welding chamber was evacuated and filled with a $2/3$ atmosphere of helium before welding. The reaction tubes were jacketed in HF-washed fused silica and sealed under high vacuum. The use of the HF solution slowed the devitrification of the fused silica permitting reaction periods of over three weeks at 1150°C .

RESULTS

Binary Systems

The reinvestigation of the RECl_3 -RE systems RE=Ce, Pr, Nd did not succeed in producing any monochlorides. The three systems were studied by the equilibration of the trichlorides with 15 mil metal foil or turnings under isothermal and gradient conditions. A typical isothermal reaction was equilibrated between 0.5 and 2.0 grams of trichloride with metal. The molar ratio of metal to halide varied from 1: 1 to 10: 1 or more. Duration of the equilibration varied from 7 to 60 days with temperatures spanning a range from 678° to 1150°C . See Table 1 for a more complete description of the reaction conditions used.

The products were identified by powder x-ray diffraction techniques. The amount of metal dissolved in the trihalide, for the CeCl_3 -Ce and the PrCl_3 -Pr reactions, was consistent with the previously determined phase diagrams for their respective systems. The synthesis of NdCl_2 as the apparent lowest phase for the NdCl_3 -Nd reactions was consistent with the previously determined phase diagram for the NdCl_3 -Nd system.⁴ At no time did a surface coating of a reduced phase occur that could block the metal surface. Equilibration of NdCl_2 with fresh metal showed no attack upon the metal surface and no metal was found in the dichloride after reaction.

Table 1. Reaction Conditions - Binary Systems
 CeCl_3 -Ce Reactions

$\text{CeCl}_3(\text{g})$	$\text{Ce}(\text{g})$	Temp. ($^{\circ}\text{C}$)	Time(days)
1.000	3.744(a)	678	28
1.000	1.137(a)	750	29
0.250	2.842(a)	750/800	29/27
1.000	1.137(b)	950/800	28/27
1.165	1.320(b)	855	28
0.250	3.332(a)	950	28
0.250	3.000(a)	1150	14

PrCl_3 -Pr Reactions

$\text{PrCl}_3(\text{g})$	$\text{Pr}(\text{g})$	Temp. ($^{\circ}\text{C}$)	Time(days)
1.673	1.908(a)	678	60
0.200	0.956(a)	800	60
0.200	0.502(b)	900/830	4/1
0.399	1.400(a)	900	49
1.000	1.140(b)	936	7
0.200**	0.536(b)	936	21
0.030	0.700(a)	936	35
0.200	1.000(b)	950	7
0.300	0.700(a)	970	39
0.200	0.502(b)	990	15
0.300	0.539(b)	990	15
0.200	0.300(a)	1100/800	14
0.200	(a)	1100	14
0.300	0.500(a)	1018/1150	14/14

NdCl_3 -Nd Reactions

$\text{NdCl}_3(\text{g})$	$\text{Nd}(\text{g})$	Temp. ($^{\circ}\text{C}$)	Time(days)
1.546	1.764(a)	678	30
0.200	0.460(a)	800	60
0.200*	0.500(b)	900	42
0.300	1.500(a)	900	49
0.030	0.700(b)	900	15

** - PrCl_3 + Pr mixture $\text{Pr}/\text{Cl} \approx \frac{1}{2}$.

* - NdCl_2 .

a=turnings.

b=15 mil foil.

Table 1. (Continued)

NdCl ₃ -Nd Reactions			
NdCl ₃ (g)	Nd(g)	Temp.(°C)	Time(days)
1.000	1.135(b)	936	7
0.200	0.409(a)	944	25
0.22	0.500(a)	950	7
0.030	0.700(b)	970	39
0.200	0.541(b)	990	15
0.300	0.481(a)	990	15
0		1100	14
0.500	3.000(a)	1018/1150	14/14
0.150	1.500(b)	850→1000	40

Attempted transport reactions in the NdCl_3 -Nd system showed no transport of reduced material and by implication the absence of a reduced gaseous species. Examination of reactions in the CeCl_3 -Ce and PrCl_3 -Pr systems where accidental gradients occurred, showed no transport of reduced material implying the absence of a reduced gaseous species.

Ternary Systems

The attempted synthesis of CsRECl_3 , RE=Ce, Pr, Nd by the reaction $3\text{CsCl} + 2\text{RECl}_3 + \text{RE} \rightarrow 3\text{CsRECl}_3$ produced a product that varied in coloration from light gray for cerium to almost black for praseodymium and neodymium. In no case was a new phase found. For a more complete description of reaction conditions see Table 2. Initial x-ray films by Debye-Scherrer techniques did not allow clear identification of the products because of poor resolution. The synthesis of the three trivalent compounds Cs_3RECl_6 for Guinier x-ray examination aided understanding the system. See Appendix 1 for a listing of the Cs_3RECl_6 patterns. The compounds Cs_3RECl_6 were confirmed by varying the molar ratio of CsCl to RECl_3 from Cs/RE ratios of 4/1 to 1/2 and examining the x-ray pattern of the products.

Guinier films showed the CsCeCl_3 composition to consist of a mixture of Cs_3CeCl_6 and CeCl_3 with the amount of finely divided metal produced below or very close to the limit of detection by x-ray techniques. The salt phase

Table 2. Reaction Conditions - Ternary Systems

CsCl-CeCl ₃ -Ce Reactions					
CsCl(g)	CeCl ₃ (g)	Ce(g)	Cs/Ce ratio	Temp.(°C)	Duration (days)
0.901	0.880	0.250	1/1	800	7
0.901	0.880	1.000	1/2	800	7
0.901	0.880	0.250	1/1	660	7
CsCl-PrCl ₃ -Pr Reactions					
CsCl(g)	PrCl ₃ (g)	Pr(g)	Cs/Pr ratio	Temp.(°C)	Duration (days)
0.200	0.294	0.500	1/4	700	7
0.010	0.015	1.000	1/120	1100	7
0.010	0.015	1.00	1/120	900	35
0.612	0.600	1.500	1/4	700	14
0.600	0.600	1.000	1/2.67	800	14
0.505	0.495	0.141	1/1	900/750	1/14
0.297	0.143	0.041	2/1	800	7
0.177	0.260	0.075	1/1.5	800	7
0.266	0.174	0.050	1.5/1	800	7
0.148	0.289	0.083	1/2	800	7
0.100	0.294	0.087	1/3	700	3
0.100	0.392	0.112	1/4	700	3
0.100	0.490	0.139	1/5	700	3

Table 2. (Continued)

CsCl-NdCl ₃ -Nd Reactions					
CsCl(g)	NdCl ₃ (g)	Nd(g)	Cs/Nd ratio	Temp.(°C)	Duration (days)
0.200	0.298	0.500	1/4	700	7
0.738	0.624	0.175	1.2/1	946	21
0.010	0.015	1.000	1/118	1100	7
0.010	0.015	1.000	1/118	900	21
0.010	0.015	1.000	1/118	700	14
0.156	0.200*		1/1	700	7
0.392	0.500*	2.000	1/7	800	7
0.505	0.501	0.144	1/1	800	21
0.112	0.288*		1/2	800	7
0.135	0.258*		1/1.5	800	7
0.202	0.172*		1.5/1	800	7
0.225	0.142*		2.0/1	800	7
2.000	1.746*		1.46/1	625	21

*Indicates -NdCl₂.

was noted to be light in color with bulk metal left after reaction. Changing the composition to more or less CsCl rich (i.e. Cs_2CeCl_4 , CsCe_2Cl_5 , etc.) only produced changes in the intensity of Cs_3CeCl_6 relative to CeCl_3 .

The CsPrCl_3 composition was identified as a mixture of Cs_3PrCl_6 , PrCl_3 and Pr. The solubility of praseodymium was great enough to produce praseodymium lines in the x-ray pattern and to yield a dark powder that reduced water. Varying the ratio of CsCl to the other components produced only intensity changes in Cs_3PrCl_6 relative to PrCl_3 and Pr.

The CsNdCl_3 composition was identified as a mixture of CsNdCl_3 , NdCl_2 and Nd consistent with $6\text{CsNdCl}_3 \rightarrow 2\text{Cs}_3\text{NdCl}_6 + 3\text{NdCl}_2 + \text{Nd}$. Varying the ratio of CsCl to NdCl_2 produced varying intensity for the Cs_3NdCl_6 lines relative to the NdCl_2 and Nd lines. The only other lines seen were oxychloride lines when using an old NdCl_2 sample that was slightly impure. For a listing of the CsRECl_3 patterns and assignments see Appendices 2, 3, and 4. The melting point of the CsNdCl_3 composition was found to be $595^\circ\text{C} \pm 2$.

DISCUSSION

Binary Systems

The ground states for the four M^+ ions known to form monochlorides are $Gd^+; 4f^7 5d^1 6s^1$, $Tb^+; 4f^9 6s^1$, $Er^+; 4f^{12} 6s^1$, and $Lu^+; 4f^{14} 6s^1$.²¹ Gd^+ and Lu^+ have two outer valence electrons. Tb^+ and Er^+ have only one valence electron. The first excited states for Tb^+ and Er^+ with two valence electrons are $Tb^+; 4f^9 6s^1 \rightarrow 4f^8 5d^1 6s^1$ 9.4 kcal./mole, and $Er^+; 4f^{12} 6s^1 \rightarrow 4f^{11} 6s^2$ 20 kcal./mole.²¹ Comparing the ground states above to those of $La^+; 5d^2$, $Ce^+; 4f^1 5d^2$, $Pr^+; 4f^3 6s^1$, and $Nd^+; 4f^4 6s^1$,²¹ only lanthanum and cerium have ground states with two valence electrons, which presumably would be necessary to form an analog of $ScCl$. The lowest excited states for praseodymium and neodymium with two valence electrons are $Pr^+; 4f^3 6s^1 \rightarrow 4f^2 5d^2$ 15.7 kcal./mole, and $Nd^+; 4f^4 6s^1 \rightarrow 4f^3 5d^2$ 26.38 kcal./mole.²¹ In both cases this is the second excited state. The stabilization of these states can only come from metal-metal interactions. From the examination of the stability of $RECl$ with respect to $RECl_3$ and RE , $3RECl \rightarrow RECl_3 + 2RE$ the following relationship can be written $\Delta G = -3U_1, -2I_1, -2Lv + I_2 + I_3 + U_3 + T\Delta S$ where ΔS = entropy change, U_1 = lattice energy of $RECl$,

Table 3. Properties of Lanthanide Metals

Metal	Lv ^{*24}	M+ ground state ²¹ configuration	Promotion* ²¹ energy	excited ²¹ state configuration
La	103.0	5d ²	-	-
Ce	101.0	4f ¹ 5d ²	-	-
Pr	85.0	4f ³ 6s ¹	15.7	4f ² 5d ²
Nd	78.3	4f ⁴ 6s ¹	26.38	4f ³ 5d ²
(Pm)	79	4f ⁵ 6s ¹	27.2	4f ⁴ 5d ²
Sm	49.4	4f ⁷	54.3	4f ⁵ 5d ¹ 6s ¹
Eu	42.4	4f ⁷ 6s ¹	81.5	4f ⁶ 5d ¹ 6s ¹
Gd	95.0	4f ⁷ 5d ¹ 6s ¹	-	-
Tb	92.9	4f ⁹ 6s ¹	9.4	4f ⁸ 5d ¹ 6s ¹
Dy	69.4	4f ¹⁰ 6s ¹	30.29	4f ⁹ 5d ¹ 6s ¹
Ho	71.9	4f ¹¹ 6s ¹	28.6	4f ¹⁰ 6s ²
Er	75.8	4f ¹² 6s ¹	20.	4f ¹¹ 6s ²
Tm	95.0	4f ¹³ 6s ¹	35.61	4f ¹² 6s ²
Yb	36.4	4f ¹⁴ 6s ¹	-	-
Lu	102.2	4f ¹⁴ 6s ¹	-	-

*Units of kcal./mole.

Table 4

Ground States Configuration of the Lanthanides²¹

	M ⁰	M ⁺¹	M ⁺²	M ⁺³
La	5d ¹ 6s ²	5d ²	5d ¹	-
Ce	4f ¹ 5d ¹ 6s ²	4f ¹ 5d ²	4f ²	4f
Pr	4f ³ 6s ²	4f ³ 6s ¹	4f ³	4f ²
Nd	4f ⁴ 6s ²	4f ⁴ 6s ¹	4f ⁴	4f ³
Pm	4f ⁵ 6s ²	4f ⁵ 6s ¹	4f ⁵	4f ⁴
Sm	4f ⁶ 6s ²	4f ⁷	4f ⁶	4f ⁵
Eu	4f ⁷ 6s ²	4f ⁷ 6s ¹	4f ⁷	4f ⁶
Gd	4f ⁷ 5d ¹ 6s ²	4f ⁷ 5d ¹ 6s ¹	4f ⁷ 5d ¹	4f ⁷
Tb	4f ⁹ 6s ²	4f ⁹ 6s ¹	4f ⁹	4f ⁸
Dy	4f ¹⁰ 6s ²	4f ¹⁰ 6s ¹	4f ¹⁰	4f ⁹
Ho	4f ¹¹ 6s ²	4f ¹² 6s ¹	4f ¹¹	4f ¹⁰
Er	4f ¹² 6s ²	4f ¹² 6s ¹	4f ¹²	4f ¹¹
Tm	4f ¹³ 6s ²	4f ¹³ 6s ¹	4f ¹³	4f ¹²
Yb	4f ¹⁴ 6s ²	4f ¹⁴ 6s ¹	4f ¹⁴	4f ¹³
Lu	4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴ 6s ²	4f ¹⁴ 6s ¹	4f ¹⁴

U_3 =lattice energy of $RECl_3$, I_n = the nth ionization energy of RE, Lv =sublimation energy of RE. The values of I_1 , and I_2 vary slightly and can be assumed to be constant.²² Also, U_3 should vary slightly and can be assumed constant. The terms $-Lv$ and $+I_3$ vary in a parallel manner and can be considered together.²³ This leaves two terms (I_3-2Lv) and $-3U_1$. A third term for the promotion energy to a state with 2 valence electrons (P.E.) should be added to the relationship, $\Delta G=(I_3-2Lv)-3U_1+(P.E.)+C$.

Three of the monochlorides made have moderately low values of Lv : Gd 95.0, Tb 92.9, and Er 75.8²⁴ (units of kcal./mole). For these three the value of $(-2Lv+I_3)$ is of a sufficiently low value, along with a moderately low value of P.E., that decomposition is disfavored. For La 103.0, Ce 101.0 and Lu 102.2²⁴ the value of Lv increases to a point where the term $(-2Lv+I_3)$ is large enough that decomposition must occur, P.E. is 0 for La, Ce, and Lu. Electronically the only difference between the three is that La^+ and Ce^+ have $5d^2$ ground states and Lu^+ has a $6s^2$ ground state.

The fact that the lattice in lanthanum and cerium metal breaks down easier than lutetium as evidenced by the low melting points of lanthanum 921°C and cerium 799°C compared to lutetium 1663°C²⁵ implies that U_1 for lanthanum and cerium may be less than U_1 for lutetium, making $LuCl$ stable and $LaCl$ and $CeCl$ unstable. In order to stabilize a mono-

halide of lanthanum and cerium, the bromide system (ZrBr structure) could increase the value of U_1 to a point where LaBr and CeBr are stable. Similarly GdBr, TbBr, ErBr, and LuBr should be stable.

For neodymium and praseodymium the dipositive state must be considered as an alternate decomposition route for the monochloride. Thermodynamically a relationship can be established for the stability of the monochloride ($RECl$) with respect to the dichloride ($RECl_2$) $2RECl \rightarrow RECl_2 + RE$, $\Delta G = 2U_1 - I_1 - Lv + I_2 + U_2 + T\Delta S$, where U_2 = lattice energy of $RECl_2$, and all other terms are as stated previously. The terms I_1 and I_2 vary slightly across the lanthanides and can be assumed constant. The value for U_2 should also vary to a small extent and can be considered as constant. The trend in $+U_1$ should reflect $-Lv$ due to the large amount of metal-metal interaction in the monochloride. Therefore, $-Lv$ and $+U_1$ partially cancel each other. This removes all terms, leaving the relationship solely dependent upon the stability of $RECl_2$ with respect to $RECl_3 + RE$. Therefore, if $RECl_2$ is stable, then the stability of $RECl$ is reduced. Using this reasoning NdCl would be highly unstable and PrCl slightly less unstable. The other partially reduced metal, holmium, and all metals forming dichlorides would also have unstable monochlorides.

In summary, to form a monohalide the following are needed:

- 1) no stable +2 state
- 2) at least 2 outer electrons (or a very low promotion energy to a state with 2 electrons)
- 3) a low value for L_v

Using these criteria, the lanthanides, lanthanum and cerium, need to be investigated as the bromide. YCl and YBr both need to be investigated. The synthesis of $PrBr$ and $HoBr$ is highly doubtful. Outside of the lanthanides and Group IIIB, is the possible investigation of Uranium and Thorium. U^+ has a $3f^3 7s^2$ ground state and the Th^+ has a $5d^1 7s^2$ ground state,²¹ providing 2 or 3 valence electrons. respectively. Also, no salt-like dihalides are known. The high values of L_v for Th 142.8 and U 128 kcal./mole are the only thermodynamic factor against formation of UCl and $ThCl$. Also, if the trend shown for lanthanum, cerium, and lutetium is followed, the high melting metals, $>1000^\circ C$, form more stable monochlorides than the lower melting metals, which favors the formation of $ThCl$ and UCl .

Ternary Systems

Thermodynamically, the stability of CsRECl_3 with respect to Cs_3RECl_6 , RECl_2 and RE metal, $6\text{CsRECl}_3 \rightarrow 2\text{Cs}_3\text{RECl}_6 + 3\text{RECl}_2 + \text{RE}$, can be expressed as the following: $\Delta G = 6U_{113} + 2U_{316} + 3U_2 - L_v + 2I_3 - I_1 + T\Delta S$, where U_{113} equals the lattice energy of CsRECl_3 and U_{316} equals the lattice energy of Cs_3RECl_6 . All other terms are as previously defined. Assuming no metal-metal interactions occur, the value of U_{316} and U_{113} should vary in a smooth fashion with only small deviations across the series, La-Lu, and can be assumed constant. From previous arguments ΔS , U_2 and I_1 also can be assumed constant. This leaves the relationship $\Delta G = -L_v + 2I_3 + C$. $-L_v$ and I_3 are known to vary in a parallel manner across the lanthanide series, reaching a peak at samarium, europium, and ytterbium.²³ The stability of CsRECl_3 should parallel this increasing value of $(-L_v + I_3)$ making CsSmCl_3 , CsEuCl_3 and CsYbCl_3 the three most stable CsRECl_3 compounds.

For systems where no dipositive state exists the relationship becomes $6\text{CsRECl}_3 \rightarrow 2\text{Cs}_3\text{RECl}_6 + 2\text{RECl}_3 + 2\text{RE}$, $\Delta G = 6U_{113} + 2U_{316} + 2U_3 - 2L_v + 4I_3 - 2I_1 + T\Delta S$. Utilizing the same assumptions made previously, the relationship become $\Delta G = 2(-L_v + 2I_3) + C$ or about twice the value of a system where the dipositive state exists, demonstrating the need for a stable dipositive state in the formation of CsRECl_3 when no metal-metal interaction occurs.

Allowing metal-metal interactions to occur in CsRECl_3 as proposed for CsScCl_3 ¹⁸ produces an increase in U_{113} stabilizing the structure. The source of the metal-metal interaction in CsScCl_3 is the one outer valence shell electron found in Sc^{+2} . Examination of the dipositive lanthanides shows only $\text{La}^{+2}; 5d^1$, $\text{Gd}^{+2}; 4f^7 5d^1$, and $\text{Lu}^{+2}; 4f^{14} 6s^1$ have outer valence electrons. These three are the only dipositive lanthanides with a single outer valence electrons that could increase U_{113} to the point of stabilizing the CsRECl_3 compound.

The stability of CsRECl_3 is therefore dependent upon the following:

- 1) strong metal-metal interactions; or
- 2) a highly stable + 2 state (large value of $-Lv + I_3$)

From Statement 1, CsRECl_3 compounds may exist for lanthanum gadolinium, and lutetium. CsLaCl_3 , CsGdCl_3 , and CsLuCl_3 should all be highly colored with the low resistivity characteristic of compounds with metal-metal interactions. From the reasoning in Statement 2, CsSmCl_3 , CsEuCl_3 , and CsYbCl_3 are expected to exist, in opposition to Condition 1. The other dichloride forming metals are of lesser stability as evidenced by lower $(-Lv + I_3)$ values and should follow the example of neodymium in not forming CsRECl_3 compounds. The statement by Morss²⁶ that studies are being conducted on CsRECl_3 compounds has been the only

indication that any CsRECl_3 compounds have been produced. It can only be assumed that the CsRECl_3 compounds of samarium, europium, and ytterbium were the subject of that investigation until the results of the study are published.

Future work upon the CsRECl_3 systems should include attempts to synthesize the six CsRECl_3 compounds discussed above, along with CsYCl_3 .

Y^{+2} has one valence electron and should be intermediate to lanthanum and scandium in the properties of its CsRECl_3 compounds.

The formation of CsRECl_3 compounds should be more favored for the strong dipositive metals than for the metals that rely upon metal-metal interactions in forming CsRECl_3 , making the existence of CsLaCl_3 , CsGdCl_3 and CsLuCl_3 and possibly CsYCl_3 doubtful.

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APPENDIX 1

 $\text{Cs}_3\text{CeCl}_6^*$

dÅ	I
----	---

6.51	2
5.71	2
5.15	2
4.80	2
4.42	4
4.30	2
4.22	3
4.09	4
4.04	5
4.00	4
3.88	5
3.68	1
3.47	1
3.36	1
3.30	2
3.07	3
3.02	4
2.97	3
2.94	3
2.91	3
2.86	5
2.75	4
2.66	4
2.62	1
2.53	2
2.42	3
2.36	3
2.34	3
2.30	2
2.29	2
2.26	3
2.24	1
2.23	3
2.21	3
2.19	2
2.17	1
2.13	.5

2.03	3
2.01	2
1.96	1
1.95	2

 $\text{Cs}_3\text{PrCl}_6^*$

dÅ	I
----	---

6.63	2
5.74	2
5.19	2
4.47	4
4.32	3
4.23	2
4.13	4
4.09	5
4.04	4
3.92	5
3.72	1
3.49	1
3.38	1
3.32	3
3.09	3
3.03	3
2.99	3
3.96	2
2.93	3
2.88	5
2.76	4
2.67	4
2.62	1
2.54	3
2.42	2
2.37	3
2.34	3
2.31	2
2.30	2
2.27	3
2.25	1
2.24	3
2.22	3
2.20	2
2.14	1
2.12	1

2.04	3
2.01	2
1.96	1
1.95	3

 $\text{Cs}_3\text{NdCl}_6^*$

dÅ	I
----	---

6.67	2
5.78	2
5.19	2
4.46	4
4.32	3
4.23	2
4.13	4
4.08	5
4.03	4
3.91	5
3.81	2
3.48	1
3.38	1
3.29	3
3.08	3
3.03	4
2.98	3
2.94	1
2.92	3
2.88	5
2.74	4
2.68	4
2.62	1
2.54	2
2.42	1
2.37	3
2.33	3
2.30	2
2.29	2
2.27	3
2.24	1
2.23	2
2.22	3
2.20	2
2.18	1
2.12	1
2.10	1
2.06	1
2.03	3
2.01	2
1.96	1
1.95	3

*Intensity based on 0-5 scale.

APPENDIX 2 CsNdCl_3 COMPOSITION

<u>Observed</u>		<u>Assignment</u>	
dÅ	I*		dÅ
6.35	4	Cs_3NdCl_6	6.67
5.74	4	Cs_3NdCl_6	5.78
5.17	3	Cs_3NdCl_6	5.19
4.47	5	Cs_3NdCl_6	4.46
4.33	4	Cs_3NdCl_6	4.32
4.23	3	Cs_3NdCl_6	4.23
4.12	5	Cs_3NdCl_6	4.13
4.07	6	Cs_3NdCl_6	4.08
4.03	5	Cs_3NdCl_6	4.03
3.90	6	Cs_3NdCl_6	3.91
3.81	4	Cs_3NdCl_6	3.81
3.59	5	NdCl_2	3.57
3.48	2	Cs_3NdCl_6	3.48
3.46	2	NdOCl	3.46
3.39	1	Cs_3NdCl_6	3.38
3.34	0.5	NdOCl	3.33
3.30	4	Cs_3NdCl_6	3.29
3.07	4	Cs_3NdCl_6	3.08
3.02	5	Cs_3NdCl_6	3.03
2.97	4	Cs_3NdCl_6	2.98
2.95	0.5	Cs_3NdCl_6	2.94
2.92	4	Cs_3NdCl_6	2.92
2.88	6	Cs_3NdCl_6	2.88
2.84	3	NdOCl	2.84
2.78	5	NdCl_2	2.77
2.76	5	Nd	2.76
2.67	5	Cs_3NdCl_6	2.68
2.62	2	Cs_3NdCl_6	2.62

*Intensity based on 0-6 scale.

<u>Observed</u>		<u>Assignment</u>	
dÅ	I*		dÅ
2.59	2	NdOCl	2.59
2.52	4	NdCl ₂	2.51
2.39	4	NdCl ₂	2.38
2.36	4	Cs ₃ NdCl ₆	2.37
2.33	4	Cs ₃ NdCl ₆	2.33
2.30	3	Cs ₃ NdCl ₆	2.30
2.29	3	Cs ₃ NdCl ₆	2.29
2.28	2	NdCl ₂	2.27
2.27	4	Cs ₃ NdCl ₆	2.27
2.24	2	Cs ₃ NdCl ₆	2.24
2.23	3	Cs ₃ NdCl ₆	2.23
2.21	4	Cs ₃ NdCl ₆	2.22
2.20	3	Cs ₃ NdCl ₆	2.20
2.18	2	Cs ₃ NdCl ₆	2.18
2.15	4	NdCl ₂	2.15
2.12	2	Cs ₃ NdCl ₆	2.12
2.10	4	Cs ₃ NdCl ₆	2.10
2.06	2	Cs ₃ NdCl ₆	2.06
2.03	4	Cs ₃ NdCl ₆	2.03
2.01	3	Cs ₃ NdCl ₆	2.01
1.96	2	Cs ₃ NdCl ₆	1.96
1.95	4	Cs ₃ NdCl ₆	1.95

*Intensity based on 0-6 scale.

APPENDIX 3 CsPrCl_3 COMPOSITION

<u>Observed</u>		<u>Assignment</u>	
dÅ	I*		dÅ
6.57	2	Cs_3PrCl_6	6.63
4.46	4	Cs_3PrCl_6	4.47
4.25	4	Cs_3PrCl_6	4.23
4.12	5	Cs_3PrCl_6	4.13
4.07	4	Cs_3PrCl_6	4.09
4.03	4	Cs_3PrCl_6	4.04
3.91	5	Cs_3PrCl_6	3.92
3.31	3	Cs_3PrCl_6	3.32
3.08	3	Cs_3PrCl_6	3.09
3.03	4	Cs_3PrCl_6	3.03
2.98	4	Cs_3PrCl_6	2.99
2.97	3	Pr	2.97
2.95	3	Cs_3PrCl_6	2.96
2.88	5	Cs_3PrCl_6	2.88
2.76	4	Cs_3PrCl_6	2.76
2.68	4	Cs_3PrCl_6	2.67
2.65	2	Cs_3PrCl_6	2.62
2.60	0.5	PrOCl	2.60
2.53	3	Cs_3PrCl_6	2.54
2.42	1	Cs_3PrCl_6	2.42
2.34	4	Cs_3PrCl_6	2.34
2.29	3	Cs_3PrCl_6	2.30
2.27	2	Cs_3PrCl_6	2.27
2.23	3	Cs_3PrCl_6	2.24
2.20	2	Cs_3PrCl_6	2.20
2.04	3	Cs_3PrCl_6	2.04
1.95	3	Cs_3PrCl_6	1.96

*Intensity based on 0-5 scale

APPENDIX 4 CsCeCl_3 COMPOSITION

<u>Observed</u>		<u>Assignment</u>	
dÅ	I*		dÅ
4.80	2		
4.42	2	Cs_3CeCl_6	4.42
4.03	5	Cs_3CeCl_6	4.04
3.87	5	Cs_3CeCl_6	3.88
3.68	1	Cs_3CeCl_6	3.68
3.01	1	Cs_3CeCl_6	3.02
2.95	2	Cs_3CeCl_6	2.94
2.86	4	Cs_3CeCl_6	2.86
2.76	3	Cs_3CeCl_6	2.75
2.67	3	Cs_3CeCl_6	2.66
2.61	1	Cs_3CeCl_6	2.62
2.52	1	Cs_3CeCl_6	2.53
2.42	5	Cs_3CeCl_6	2.42
2.37	2	Cs_3CeCl_6	2.36
2.33	4	Cs_3CeCl_6	2.34
2.23	4	Cs_3CeCl_6	2.23
2.12	3	CeCl_3	2.12
2.02	3	Cs_3CeCl_6	2.03
1.95	2	Cs_3CeCl_6	1.95

*Intensity based on 0-5 scale