

Experimental

Preparation of Reagents.—Rare earth oxides of 99.99% purity were obtained from the rare earth separation group of the Ames Laboratory of the United States Atomic Energy Commission and were converted to rare earth HEDTA chelates either by direct dissolution of the oxide in HEDTA acid or by ion exchange. The complex compounds then were recrystallized several times from water to eliminate possible impurities, and weighed specimens of each were assayed for rare earth content by ashing to R_2O_3 at 900° and weighing.

A 0.002 *M* stock solution of each rare earth chelate was prepared by dissolving the required amount of solid rare earth chelate in conductivity water. Each solution subsequently was standardized by determining its rare earth content by the usual gravimetric procedure, *i.e.*, precipitation as the oxalate followed by thermal decomposition to the oxide at 900° .

A 0.01 *M* solution of carbonate-free KOH was prepared by the method of Powell and Hiller² and was standardized against HCdCh by the method of Powell, Fritz, and James.³

Experimental Procedure.—Fifty ml. of a RCh stock solution and 10 ml. of 1 *M* KNO_3 solution were introduced into each of ten calibrated 100-ml. volumetric flasks. Varying known amounts (from 1 to 10 ml.) of 0.10 *M* KOH were added to each flask. The solutions next were diluted to 100 ml. so that they were 0.1 *M* with respect to KNO_3 and 0.001 *M* with respect to total rare earth species, and were allowed to equilibrate in a 25° water bath for 100 hr. Then, the pH of each solution was read by means of a Beckman Zeromatic pH meter, standardized against Beckman pH 7 buffer. From the pH values of the various solutions, the hydroxyl ion concentration was computed and substituted in the expression

$$K'_{RChOH} = \frac{[OH_2] - [OH^-]}{\{1.00 \times 10^{-3} - [OH_2] + [OH^-]\} [OH^-]} \quad (2)$$

where $[OH_2]$ represents the concentration of hydroxyl ion that would have resulted from the amount of base added had no association occurred.

Results

The $\log K'_{RChOH}$ values for individual rare earths given in Table I are average values computed from five to seven random points taken from a plot of pH *vs.* ml. of base added between the limits $a = 0.35$ and $a = 0.85$ (a is the ratio of moles of base added to moles of RCh originally present). The data were treated statistically so that the limits given in Table I define the interval of 90% confidence.

A real difference is apparent in the stabilities of the hydroxo complexes formed by the light and heavy rare earth HEDTA chelates. For the rare earths lanthanum through samarium the in-

TABLE I
FORMATION CONSTANTS OF THE MONOHYDROXO RARE EARTH HEDTA CHELATES

Rare earth	Atomic no.	Log K'_{RChOH}
Y	39	4.76 ± 0.05
La	57	$3.46 \pm .03$
Ce ^a	58	...
Pr	59	$3.69 \pm .07$
Nd	60	$3.59 \pm .06$
Pm	61	...
Sm	62	$3.70 \pm .06$
Eu	63	$4.03 \pm .03$
Gd	64	$3.98 \pm .07$
Tb	65	$4.52 \pm .07$
Dy	66	$4.88 \pm .04$
Ho	67	$5.12 \pm .04$
Er	68	$5.14 \pm .05$
Tm	69	$5.11 \pm .04$
Yb	70	$5.21 \pm .06$
Lu	71	$5.13 \pm .09$

^a The cerium HEDTA solutions became colored when base was added, indicating that the cerium was being oxidized to the tetravalent state.

crease in the formation constant is less than two-fold (0.24 ± 0.09 log unit) and from holmium through lutetium the increase is less than the experimental error. The difference in $\log K'_{RChOH}$ values of the light and heavy groups, however, corresponds to nearly 1.5 log units. This is extremely interesting, since the values of

$$K'_{RCh} = \frac{[RCh]}{[R^{3+}][Ch^{3-}]} \quad (3)$$

are virtually constant for the middle rare earths, samarium through holmium.^{4,5} The value of K'_{YChOH} falls between the values of K'_{TbChOH} and K'_{DyChOH} .

(4) J. E. Powell and J. L. Mackey, *Inorg. Chem.*, **1**, 418 (1962).

(5) T. Moeller, L. C. Thompson, and R. Ferrús, "Some Aspects of the Stabilities of Amine Polycarboxylic Acid Chelates of Tripositive Rare Earth Metal Ions," in "Rare Earth Research," E. V. Kleber, ed., The Macmillan Co., New York, N. Y., 1961.

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The Preparation and Properties of Some Lanthanum(III) Monotellurooxides

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Received March 24, 1962

Since isostructural monothio- and monoseleno-oxides of all the lanthanum elements have been

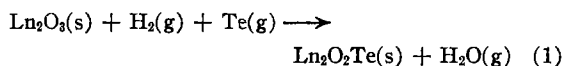
(2) J. E. Powell and M. A. Hiller, *J. Chem. Educ.*, **34**, 330 (1957).

(3) J. E. Powell, J. S. Fritz, and D. B. James, *Anal. Chem.*, **32**, 954 (1960).

reported,¹⁻⁷ it seemed probable that the corresponding monotelluro-substituted compounds could be prepared and characterized. This project was undertaken to prepare these compounds and to compare some of their physical and chemical properties with those of the corresponding sulfides and selenides.

Preparation

Weighed amounts of 99.9% pure lanthanum sesquioxides (dioxide in the case of cerium), obtained from the Michigan Chemical Company, St. Louis, Michigan, were first heated in air in a platinum crucible to constant weight and then loaded into a series of either quartz or alundum boats which were inserted into a 30-mm. quartz tube. Elemental tellurium, loaded in the boat located immediately adjacent to the hydrogen gas inlet of the quartz tube, provided tellurium vapor which was swept slowly over the sesquioxide samples by the hydrogen when the furnace in which this tube was located was heated. In addition, the hydrogen swept the reaction by-product, water, as well as excess tellurium vapor, from the tube. The temperature of the furnace, whose power input was regulated with a variable transformer, was measured with a Chromel-Alumel thermocouple and a Rubicon potentiometer and was varied from 500 to 960°, while the reaction time was varied from 4 to 12 hr. without appreciable change in the product. In all cases, excess tellurium was provided, and a residue of the element remained in the boat at the conclusion of the run. The extent to which the reaction had proceeded was followed by the gain in the weight of the sample according to the equation



Results and Discussion

Compounds of the formula $\text{Ln}_2\text{O}_2\text{Te}$, in which Ln indicates either lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, or dysprosium, were prepared. These phases range in color from chartreuse to dark olive green, with the exception of the cerium compound, which is dark red. The sesquioxides of holmium and all heavier lanthanoids reacted either only partially, as evidenced by possible extra lines in the X-ray powder photograph and a slight weight change, or not at all, even with prolonged heating at temperatures ranging from 900–1500°. Although the terbium compound is not included in

this list, cursory experiments indicate that the black oxide, Tb_4O_7 , also undergoes reaction. Evidently, as the radius of the M^{+3} ion decreases, a size is reached at which the metal ion becomes too small to permit replacement of one of the oxygen atoms in the lattice with the larger tellurium atom without a structural rearrangement.

When europium sesquioxide reacted with tellurium, the black EuTe was formed in addition to $\text{Eu}_2\text{O}_2\text{Te}$, as previously reported by Iandelli.⁸ Europium(II) telluride became the predominant species as the temperature of the reaction was elevated.

The change in weight observed when gaseous tellurium reacted with the lanthanum oxides supported the formula $\text{Ln}_2\text{O}_2\text{Te}$, the weight gain indicating a 99–100% yield of the telluride according to eq. 1. Chemical analyses of the samarium compound gave the percentages: Sm, 65.24; Te, 28.02. Calcd. for $\text{Sm}_2\text{O}_2\text{Te}$: Sm, 65.33; Te, 27.72.

That the hydrogen gas partakes in the reaction and is not simply a carrier gas was indicated by one experiment in which it was replaced with argon. No product was obtained even though the temperature of the reaction was slowly increased to 1200°.

When weighed samples of the monotelluro-oxides of praseodymium, neodymium, samarium, gadolinium, and europium were heated in a muffle furnace in air for 3-hr. periods at temperatures below 450°, they slowly gained weight; however, when the samples were heated at temperatures between 450 and 480°, they rapidly increased in weight to a constant value, the weight gain suggesting a new phase of the general formula Ln_2TeO_5 . Europium did not reach a constant weight but slowly continued to be oxidized. The colors of these phases are: Gd_2TeO_5 , white; Sm_2TeO_5 , cream; Pr_2TeO_5 , tan; Nd_2TeO_5 , blue. These phases, stable at temperatures up to 600°, produced similar X-ray powder photographs which were somewhat diffuse, particularly in the back reflection region of the film.

As the temperature was increased further, the samples were oxidized slowly until another stable form was attained, as evidenced by a constant weight in specimens heated to 750–800°. The gain in weight at this temperature indicated the formation of another phase of the general formula Ln_2TeO_6 . The colors of these phases are the same as for those described above, but the X-ray

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(3) A. Benacerraf, M. Guittard, L. Domange, and J. Flahaut, *Bull. soc. chim. France*, 1920 (1959).

(4) M. Picon and M. Patrie, *Compt. rend.*, **242**, 576 (1956).

(5) J. Flahaut and E. Attal, *ibid.*, **238**, 682 (1954).

(6) W. H. Zachariasen, *Acta Cryst.*, **2**, 60 (1949).

(7) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **73**, 3896 (1951).

(8) A. Iandelli, *Gazz. chim. ital.*, **85**, 881 (1955).

powder photographs indicate a different diffraction pattern. The color of the Eu_2TeO_8 phase is gray. At temperatures above 800° , their weight decreases, and at about 950° it corresponds to that of the sesquioxide.

Domange, Flahaut, and Chirazi⁹ have reported that the air oxidation of $\text{Ce}_2\text{O}_2\text{Te}$ produced $\text{Ce}(\text{TeO}_4)_2$, and that at 550° , this tellurate dissociated into the dioxide with vaporization of TeO_2 . However, since cerium commonly exhibits an oxidation state of four, this difference in behavior is not surprising.

When the phases Ln_2TeO_8 are heated at about 950° in a hydrogen atmosphere, they are reduced to the monotellurooxides, providing a confirmation of the analytical data. This behavior is identical with that reported for the corresponding selenium and sulfur compounds.²

X-Ray powder diffraction data, obtained with $\text{CuK}\alpha$ radiation ($\lambda_{\text{Cu}} = 1.5418 \text{ \AA}$), are listed for $\text{Nd}_2\text{O}_2\text{Te}$ in Table I. The observed density ob-

TABLE I
INTERPLANAR d SPACINGS AND RELATIVE INTENSITIES OF
 $\text{Nd}_2\text{O}_2\text{Te}$

hkl	d calcd. (\AA .)	d obsd. (\AA .)	Relative intensities ^a
102	2.925	2.928	100.00
110	2.844	2.852	47.61
004	2.131	2.132	9.04
200	2.012	2.012	18.33
114	1.705	1.705	18.33
212	1.658	1.659	32.38
204	1.462	1.461	7.85
220	1.422	1.424	3.57
106	1.339	1.339	3.57
302	1.279	1.278	7.04
310	1.272	1.272	5.23
224	1.183	1.183	2.38

^a Relative intensities were determined with a Siemens diffractometer.

tained from a pellet compacted at 20,000 p.s.i. is $5.33 \pm 0.03 \text{ g./cc.}$, compared to a calculated density of 5.40 g./cc. based on a simple tetragonal cell with one molecule per unit cell. However, because of a large number of extinctions, a suitable tetragonal space group has not been found. Unit cell dimensions and calculated densities of the isostructural compounds are listed in Table II. The d spacings obtained for $\text{Ce}_2\text{O}_2\text{Te}$ agree with those reported by Domange, Flahaut, and Chirazi,⁹ who report no attempt to index them.

The X-ray powder photographs of the isostructural phase Ln_2TeO_8 are somewhat similar to

(9) H. Domange, J. Flahaut, and A. N. Chirazi, *Bull. soc chim. France*, 150 (1959).

TABLE II
UNIT CELL DIMENSIONS AND CALCULATED DENSITIES FOR
LANTHANUM(III) MONOTELLUROOXIDES

Compound	a_0 (\AA .)	c_0 (\AA .)	Calcd. density (g./cc.)
$\text{La}_2\text{O}_2\text{Te}$	4.108 ± 5	8.687 ± 5	4.96
$\text{Ce}_2\text{O}_2\text{Te}$	4.073	8.576	5.13
$\text{Pr}_2\text{O}_2\text{Te}$	4.050	8.533	5.24
$\text{Nd}_2\text{O}_2\text{Te}$	4.023	8.519	5.40
$\text{Sm}_2\text{O}_2\text{Te}$	3.987	8.424	5.71
$\text{Eu}_2\text{O}_2\text{Te}$	3.965	8.362	5.85
$\text{Gd}_2\text{O}_2\text{Te}$	3.951	8.342	6.04
$\text{Dy}_2\text{O}_2\text{Te}$	3.916	8.260	6.36

that of the $\text{Ln}_2\text{O}_2\text{Te}$ phase in that groups of lines are present in the former where the principal lines existed in the latter, but that of the isostructural Ln_2TeO_8 series is very different. Neither of these phases, both of which possess lower than cubic symmetry, has been indexed.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission for support of this project, Mr. E. P. Benson, Jr., for preparing some of the samples, and Mrs. Susan E. Kent for measuring many of the X-ray photographs and preparing some of the samples.

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Electric Discharge Reactions of Phosphorus Trichloride and Germanium Tetrachloride

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Received April 27, 1962

If a microwave discharge is established¹ in a stream of PCl_3 vapor at 1–5 mm. pressure, the emerging vapor contains metastable species of remarkably long half-life. If this vapor is allowed to pass through a series of four traps cooled to ca. -20 , -45 , -63 , and -196° , successively, PCl_5 condenses in the ca. -20° trap, a red material is formed in the -45° trap, a yellow-tan material is formed in the -45 and -63° traps, and PCl_3 condenses in the -63 and -196° traps. The red and yellow-tan materials are non-volatile at room

(1) As described by W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1960, p. 113.