[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

# The Preparation, Crystal Structure and Some Properties of SmN, EuN and YbN[1]

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SmN, EuN and YbN were prepared by the direct combination of the metals with nitrogen. All three were found to have a NaCl-type structure with the followng lattice parameters: 5.0481 ± 0.0008, 5.007 ± 0.004 and 4.7852 ± 0.0008 A., respectively. A differential thermal analysis–thermogravimetric analysis of SmN in an atmosphere of moist nitrogen is reported. The decomposition curves showed a plateau indicating a thermally stable compound corresponding to a molecular weight of SmO(OH).

## Introduction

The nitrides of samarium, europium and ytterbium have not been reported although the nitrides of some of the lighter rare earths are known. Besides the intrinsic interest in the preparation and investigation of the properties of new compounds, the nitrides of these elements are important because they are isomorphous with the monoxides and hence knowledge of their structure will aid in the identification of the lower oxides.

## Experimental Part

**Materials.**—The samarium, ytterbium and lanthanum metals, greater than 99.9% pure, were obtained from Ames Laboratories, Ames, Iowa. The europium metal was prepared according to the method of Spedding and Daane[3] by the reduction of $Eu_2O_3$ (99.8% pure, obtained from Research Chemicals, Inc., Burbank, California) with lanthanum metal.

**Procedure.**—The metal filings were put in a small molybdenum boat which was placed in a Vycor tube along with a large quantity of titanium turnings. The tube was evacuated to better than $10^{-5}$ mm. pressure and maintained there for 4–6 hours. Tank nitrogen was then passed over the titanium, which had been warmed, and through the system. The system was sealed off and the titanium turnings were heated to a dull red. The sealed system was heated for 12–16 hours at 800° with europium and samarium filings and at 1020° with ytterbium filings.

When the treatment was completed the samples were removed to an argon-filled dry-box where they were opened. Capillaries were filled with the samples; they were then removed and sealed immediately.

Because the reaction of ytterbium with nitrogen proceeded so slowly, another preparation of YbN was investigated. Ytterbium turnings were placed in a Vycor reaction vessel, which was then set in the Vycor tube and evacuated. Hydrogen obtained from the thermal decomposition of $UH_3$ was admitted and the system heated at 500° for 12 hours. Powder diagrams of this material indicated it was $YbH_2$.[4] Nitrogen, purified by passage over activated copper and titanium turnings, was admitted and the Vycor tube was heated for 12 hours at a constant temperature differing among several runs from 600 to 1000°. Because of the apparent stability of both these compounds, it was unnecessary to work in a dry-box.

X-Ray powder diagrams were taken with a 114.7 mm. Debye–Scherrer powder camera. Cu K$\alpha$ ($\alpha_1$ = 1.54051 × $10^{-8}$ cm.) radiation was used for the samarium and ytterbium samples and Fe K$\alpha$ ($\alpha_1$ = 1.93597 × $10^{-8}$ cm.) radiation was used for the europium samples. The intensity was calculated according to the formula $I = LPAjF^2T$ (where $LP = (1 + \cos^2 2\theta)/\sin^2\theta\cos\theta$; $A$ is the absorption factor calculated according to the method of Bradley[5]; $T$ is the temperature factor calculated from an estimated characteristic temperature $\theta$, equal to 350; $j$ is the multiplicity factor which is the same for both lines; $F$ is the structure factor[6] with the atom form factor for samarium corrected for dispersion with iron radiation according to the method of Dauben and Templeton.[7]

The ytterbium sample diagrams obtained from the direct combination of Yb + $N_2$ could not be indexed precisely because of small particle size. Therefore, to obtain crystal growth these samples were placed in a tantalum crucible which was set inside a tantalum distillation tube. This tube was removed from the dry-box and heated by radiation from inductively heated shields to 1400° in a high vacuum or in an atmosphere of argon. Powder diagrams were taken of both the distillate and the residue.

The samarium samples were analyzed quantitatively with a micro-Kjeldahl apparatus for nitrogen content and were found to be greater than 90% SmN. However, the X-ray diagrams showed no additional phase and it is believed that the Kjeldahl method used gave consistently low results. The intensities of the reflections from planes (331) and (420) were determined with a powder spectrometer using iron radiation. The ytterbium and europium preparations were analyzed qualitatively for nitrogen.

Samples of SmN were placed on a thermal balance and weight uptake was recorded as moist nitrogen was passed over the samples at a constant temperature of 50°. At the end of 20 hours the sample was no longer gaining weight. The temperature was then elevated at about 10°/min. and a differential thermal analysis curve was obtained along with curves for the temperature and weight of the sample. Such data were not obtained for ytterbium and europium nitrides.

## Results and Discussion

The black compounds, SmN, EuN and YbN were found to be of the NaCl-type structure with lattice parameters of 5.0481 ± 0.0008, 5.007 ± 0.004 and 4.7852 ± 0.0008 Å., respectively. These lattice parameters were obtained as an average of a series of determinations, with the error listed twice the root-mean-square error.

Figure 1 shows a plot of the lattice parameters of seven rare earth nitrides which have been determined against the crystal radii of their tripositive ions. The value of LaN is from the data of Young and Ziegler,[8] while the values of CeN, PrN and NdN are from the work of Iandelli and Botti[9] (converted from kX. units). This plot shows a linear correlation between the lattice parameters of most of the nitrides so far determined and their crystal radii (from the data of Templeton and Dauben[10]).

The intensities of the reflections from planes (331) and (420) were carefully measured; these planes reveal the type of structure in the face centered cubic system and are most sensitive to chang-

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[2] Allied Chemical and Dye Fellow, 1954–1955.

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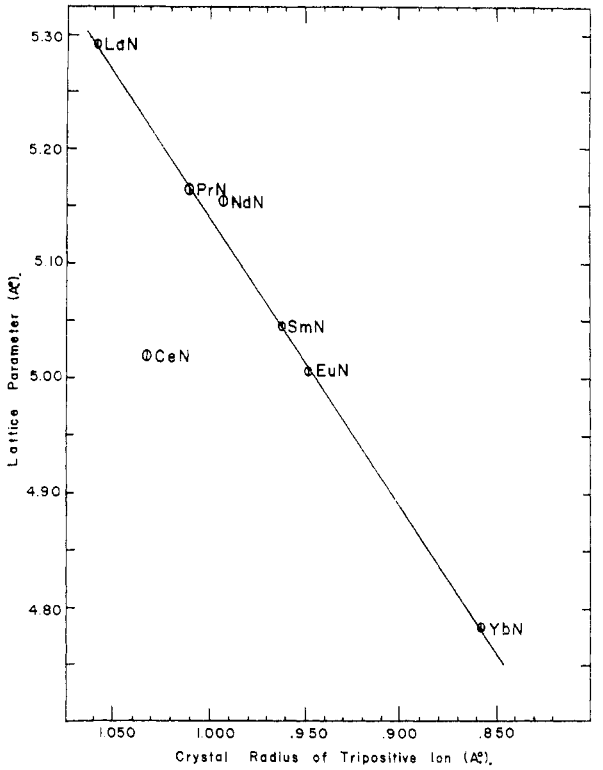

Fig. 1.—Comparison of the lattice properties of rare earth nitrides.

ing anion composition. The observed ratio of intensities for SmN determined with the powder spectrometer was $I_{420}/I_{311} = 1.57 \pm 0.08$ as compared to a calculated ratio of 1.49. The ratios of the intensities of these lines in the YbN and EuN diagrams were determined by visual observation to be approximately the same as in the samarium nitride diagrams.

Samples of SmN gained weight rapidly while being weighed. Such a gain would be expected if the nitride were being hydrolyzed to the hydroxide as reported for LaN, PrN and CeN,[11] and PuN.[12] However, the weight uptake did not agree with the theoretical amount as calculated from the equation

$$SmN + 3H_2O \longrightarrow Sm(OH)_3 + NH_3$$

provided it was assumed that the $NH_3$ was not retained in the solid. Likewise, the ratio of the maximum weight of the sample after hydrolysis to the final weight of the sesquioxide was not a constant and the difference was greater than could be attributed to any metal present in the system. Powder diagrams of this material, hydrated at room temperature for about one week, suggested that it was amorphous.

To check further this behavior, four samples of SmN were placed in the differential thermal analysis–thermogravimetric analysis (DTATGA) apparatus,[13] hydrated and thermally decomposed in a moist nitrogen atmosphere. During the hydrolysis, tests of the exit gas indicated the presence of ammonia. The final hydrated material prior to decomposition showed only a slight trace of nitrogen. Figure 2 is a plot of the fourth run after heating was begun. At about 80° the hydrolysis product began to lose zeolytic water which was present in varying amounts in the four samples. At about 130° the loss of non-crystalline water was complete leaving $Sm(OH)_3$ which is thermally stable with only slight loss in weight in an interval of about 120°. At 250° the $Sm(OH)_3$ decomposes rapidly, at first, to a temperature of about 375°. This break in the weight curve corresponds roughly to a compound of molecular weight 183.4 (SmO(OH)). Decomposition continues slowly up to 425° then more rapidly to 475° and slowly goes to $Sm_2O_3$ at about 850° where decomposition is complete.

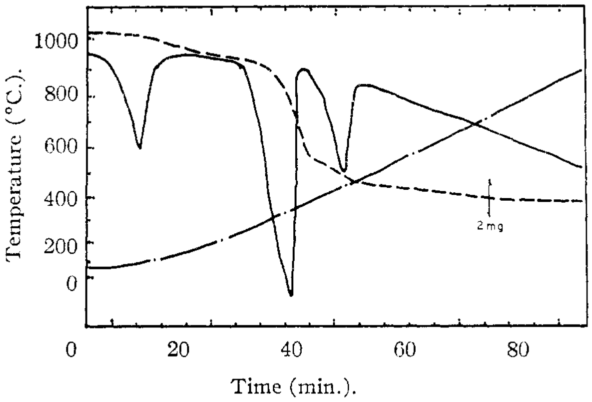

Fig. 2.—DTATGA curve of hydrolyzed SmN ($Sm(OH)_3$).

The D.T.A. curve indicates a strong endothermic reaction in the initial drying. This is followed by a second much larger endothermic reaction as $Sm(OH)_3$ decomposes to something approximating SmO(OH). The final peak accompanies the final loss of water to approach $Sm_2O_3$.

X-Ray powder diagrams were made of the material of molecular weight corresponding to $Sm(OH)_3$. $H_2O$ (hexagonal, $a_0 = 6.36 \pm 0.03$ Å., $C_0 = 3.66 \pm 0.03$ Å.), $Sm(OH)_3$ (hexagonal, $a_0 = 6.36 \pm 0.03$ Å., $C_0 = 3.66 \pm 0.03$ Å.), SmO(OH) (only two diffuse lines), and $Sm_2O_3$ (body centered cubic). The parameters for the hexagonal $Sm(OH)_3$ are about what would be expected from an extrapolation of the data of Zachariasen,[14] and are not in agreement with the data of Fricke and Sertz[15] for $Sm(OH)_3$.

The first two runs in the DTATGA apparatus showed a large exothermic reaction ending at about 260.° It is believed that this was due to a small metal impurity (not detected in X-ray powder diagrams), which oxidizes at a slightly elevated temperature in the presence of water vapor.

Duval[16] had heated the wet precipitated samarium hydroxide and had observed no break in the curve when $Sm(OH)_3$ decomposed. In order to check this difference in behavior between the precipitated hydroxide and that produced by the hy-

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drolysis of samarium nitride three additional DTATGA runs were made. In the first, $Sm(OH)_3$ was precipitated, washed, and vacuum dried at room temperature; the weight and DTA curves were largely without character. In a second run the $Sm(OH)_3$ was precipitated, washed and dried at 110° for six hours. An X-ray powder diagram of the dried material showed a complex lattice of large cell dimension quite different from the hexagonal structure of the $Sm(OH)_3$ produced by hydrolysis of SmN. A DTATGA run on this material was in general aspect similar to the vacuum dried material and both had a large amount of water, $Sm(OH)_3 \cdot 2.3H_2O$ and $Sm(OH)_3 \cdot 2.8H_2O$, respectively. A third preparation similar to the second but from which almost all the water ($Sm(OH)_3 \cdot 0.12\ H_2O$) had been removed showed the same hexagonal structure reported above and gave DTATGA curves very similar to the ones observed from the hydrolyzed SmN. That is, a sharp break in the weight curve at 375° with DTA peaks corresponding to the initial endothermic decomposition of $Sm(OH)_3$ and of a composition around SmO(OH).

The $Sm(OH)_3 \cdot 2.8H_2O$ and other highly hydrated materials apparently have water incorporated within the crystal lattices. This water is completely lost only at temperatures far above the decomposition temperature of $Sm(OH)_3$, hence, the latter decomposes rapidly without indicating the low molecular weight hydrated material.

All the samples of EuN contained a trace contaminant exhibiting a complex powder diagram which was believed to be an oxide. Because of this impurity and the scarcity of europium, no additional work was done on EuN.

Samples of YbN prepared by direct combination of the metal with nitrogen always contained some unreacted metal. Even at 1000°, 200° above the melting point of ytterbium, the reaction did not go to completion. When these samples containing metal and YbN were distilled in a high vacuum ($10^{-5}$ mm.), both ytterbium metal and YbN were found in the distillate. A complete distillation occurred if sufficient time was allowed at 1400°. This may imply a high vapor pressure for YbN. SmN heated to 1600° did not exhibit any tendency to distil. This suggests a considerable thermal stability and low vapor pressure. Samples of YbN prepared by the reaction of $YbH_2$ and $N_2$ at 1000° were monophasic. At lower temperatures conversion was not quantitative.

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# The Heat of Precipitation and Formation of Silver Molybdate

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The heat of precipitation of silver molybdate has been determined from two series of calorimetric experiments. From these data and the results of earlier investigators, we calculate the heat of formation of $Ag_2MoO_4$ to be $-200.4$ kcal./mole and the free energy and entropy of solution of $Ag_2MoO_4$ to be $+15.6$ kcal./mole and $-9.4$ cal./deg. mole, respectively.

As part of a systematic investigation of the thermochemistry of molybdenum, it was desired to have reliable values for the heats of formation and precipitation or solution of one or more slightly soluble molybdates. Therefore, the heat of precipitation of $Ag_2MoO_4$ has been carefully determined, and from this quantity several thermodynamic calculations have been made.

## Experimental

The high-precision solution calorimeter used in this investigation has been previously described in some detail.[1] The silver nitrate was Mallinckrodt Analytical Reagent crystals. Fisher Certified Reagent sodium molybdate ($Na_2MoO_4$) was dried for 24 hours at 110° and found by analysis to be 46.7% Mo as compared with the calculated value of 46.6%. The analysis was done by the permanganate method.[2]

The calorimeter used in this investigation has been checked periodically by determining the heat of solution of potassium chloride.[1] Agreement with reported values is excellent.[3,4] All heats of reaction have been carried out at 25.0 ± 0.5°.

## Results

The heat of reaction of crystalline $Na_2MoO_4$ with dilute solutions of $AgNO_3$ was measured to determine the heat of precipitation of $Ag_2MoO_4$. The calorimetric reaction may be written as eq. 1

$$Na_2MoO_4(c) + AgNO_3\ (\text{excess dil. soln.}) = Ag_2MoO_4(c) + AgNO_3\ (\text{dil. soln.}) + NaNO_3\ (\text{dil. soln.})\quad \Delta H_1 \qquad (1)$$

The results of these experiments are given in Table I. The heats were actually determined to the nearest 0.02 kcal./mole, but because of the spread of values they are reported only to the nearest 0.1 kcal./mole. All determinations were made using 950 cc. of solution.

To calculate the standard heat of formation of $Ag_2MoO_4$ from the experimental values of $\Delta H_1$, it is necessary to know the heats of formation of $Na_2MoO_4(c)$,[1] $NaNO_3(aq)$[3] and $AgNO_3(aq)$.[3] We

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