Reactions of Lithium Nitride with Cerium, Thorium, and Hafnium: Formation of Li_2CeN_2, Ce_2N_2O, Li_2ThN_2, and Li_2HfN_2

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The solid-state reactions of lithium nitride with Ce, Th, Hf and CeN, ThN, and HfN have been followed by differential thermal analysis, thermogravimetric analysis, and *X*-ray powder diffraction methods. Reaction with the metals was found to proceed by formation of the mononitride with the ternary nitride Li_2MN_2 as the final product. The compound Ce_2N_2O was obtained by the reaction of Li_2CeN_2 and Li_2O or CeN and CeO_2. The reaction of lithium nitride with hafnium gave the ternary nitride Li_2HfN_2 which is found to be isostructural with the known nitride Li_2ZrN_2.

THIS study of the reactions of lithium nitride with cerium, hafnium, and thorium and their nitrides was conducted as part of a general study of the reactions of liquid lithium containing dissolved nitrogen with the above elements and their oxides. Previous studies [1] of liquid lithium–metal oxide reactions have shown that the nitrogen dissolved in the liquid metal is very reactive towards solid metals. The solid-state reactions of lithium nitride are therefore of use in the characterisation of compounds which may be formed at high nitrogen activities in the liquid metal.

A previous study [2] has shown that lithium nitride reacts with cerium mononitride at 600 °C in a nitrogen atmosphere to form the ternary nitride Li_2CeN_2. The powder pattern of the ternary nitride was indexed in a hexagonal cell with $a = 3{\cdot}55$ and $c = 5{\cdot}496$ Å. By comparison with the isostructural compound Ce_2O_2S the space group was found to be $P\bar{3}m$. A ternary nitride Li_2ThN_2 has been prepared [3] by the reaction of lithium nitride and thorium in an atmosphere of ammonia at temperatures between 700 and 1000 °C. This compound also crystallises in a hexagonal unit cell with $a = 6{\cdot}39$ and $c = 5{\cdot}54$ Å and space group $P\bar{3}$.

We have conducted a series of experiments from which we may determine the temperatures at which the ternary nitrides are formed and what intermediate compounds are produced during the course of reaction. It will be shown that reaction proceeds by the initial nitriding of the metal to give the mononitride which then reacts to form the ternary nitride. The previously unreported ternary nitride Li_2HfN_2 was also prepared by similar methods and its thermal stability investigated.

EXPERIMENTAL

Reagents.—Commercially available metal powders were used with a nominal purity of 99·9% except for hafnium which contained *ca.* 3% zirconium. Lithium nitride was prepared by the direct reaction of lithium with purified nitrogen at 370 °C, this temperature being that at which the rate of reaction of nitrogen with liquid lithium is a maximum.[4] The reaction was carried out on a vacuum frame, aliquots of nitrogen being added until no further absorption was observed. The heavy-metal nitrides were prepared by heating the powdered metal in a stream of ammonia in the temperature range 300—700 °C for 3 to 4 h.

Solid-state Reactions.—These reactions were carried out in a stainless-steel crucible contained in a stainless-steel tube attached to Quickfit glass sockets by means of Kovar seals. Mixtures of the reactants were prepared in an argon-filled drybox and loaded into the stainless-steel tubes. A glass tap was fitted onto the tube so that the tube could be removed from the drybox and attached to a vacuum frame without exposing the reactants to the atmosphere. All reaction products were transferred to the drybox prior to their examination. The apparatus used for differential thermal analysis (d.t.a.) and thermogravimetric (t.g.a.) analyses have been described.[5,6] Thermal analyses were first carried out over the temperature range 20—700 °C. Where the d.t.a. curve showed several thermal effects the experiment was repeated and heating stopped after each heat change and the sample removed for *X*-ray diffraction. In this way the phases formed at each thermal effect were characterised. Similar methods were also employed for the thermogravimetric analyses. Samples weighing between 0·3 and 0·9 g and 0·02 and 0·05 g were used in the t.g.a. and d.t.a. methods respectively.

Analysis.—The products were hydrolysed by water to give the heavy-metal oxide, ammonia, and lithium hydroxide. The nitrogen content was obtained by the Kjeldahl method, lithium content by titration and flame photo-

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[1] C. C. Addison, M. G. Barker, and J. Bentham, *J.C.S. Dalton*, 1972, 1035.

[2] D. Halot and J. Flahaut, *Compt. rend.*, 1971, **272**, C, 465.

[3] A.-P. Palisaar and R. Juza, *Z. anorg. Chem.*, 1971, **384**, 1.

[4] E. Masdupuy and F. Gallais, *Inorg. Synth.*, 1954, **4**, 1.

[5] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1513.

[6] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 9.

metry, the heavy-metal content by gravimetric determination of the oxide after heating to constant weight at 600 °C, and oxygen content by difference.

X-Ray Diffraction Data.—Powder diffraction patterns were recorded using a Phillips PW1050/25 vertical goniometer mounted on a PW1010 stabilised *X*-ray generator. Cu-K_α radiation was used throughout. Lattice parameters were calculated from traces recorded at $\frac{1}{8}^\circ$ 2θ/min but in one instance the step-scan technique was used to record the pattern of Li_2ThN_2 with the diffractometer stepping in increments of 0·01° 2θ/min.

RESULTS AND DISCUSSION

Li_2CeN_2. Reactions of lithium nitride with cerium or cerium nitride were carried out under various atmospheres such that the ratio N : Ce was 2 : 1. The results of these experiments are presented in Table 1.

TABLE 1

Reactions of lithium nitride with cerium and cerium nitride

Expt. no.	Reactants	Conditions	Products
1	$5Li_3N + 3Ce$	NH_3, 550 °C, 4 h	Li_2CeN_2 + trace CeN
2	$5Li_3N + 2Ce$	NH_3, 590 °C, 5 h	Li_2CeN_2
3	$Li_3N + CeN$	NH_3, 570 °C, 1 day	Li_2CeN_2 + CeN
4	$5Li_3N + 3Ce$	N_2 (30 cmHg) 605° C, 1 day	Li_2CeN_2 + trace CeN
5	$2Li_3N + 3Ce$	N_2 (1 atm), 640 °C, 1 day	Li_2CeN_2
6	$Li_3N + CeN$	N_2 (25 cmHg) 600 °C, 1 day	Li_2CeN_2 + trace CeN
7	$2Li_3N + Ce$	Vacuum, 605 °C, 1 day	CeN + Li_2CeN_2
8	$Li_3N + CeN$	Vacuum, 610 °C, 1 day	Li_2CeN_2 + CeN
9	$3Li_3N + Ce$	N_2 (25 cmHg) 680 °C, 2 days	Li_2CeN_2

TABLE 2

X-Ray diffraction pattern of Li_2CeN_2

d/Å	I/I_0	h	k	l	d/Å (from ref. 2)
5·46	59	0	0	1	5·43
3·078	39	1	0	0	3·066
2·736	7	0	0	2	2·720
2·684	100	1	0	1	2·669
2·046	35	1	0	2	2·038
1·823	2	0	0	3	1·817
1·777	10	1	1	0	1·773
1·691	12	1	1	1	1·686
1·569	10	1	0	3	1·565
1·539	2	2	0	0	1·535
1·491	5	1	1	2	1·486
1·482	9	2	0	1	—
1·341	5	2	0	2	1·363
1·273	3	1	1	3	1·270
1·251	4	1	0	4	1·247
1·176	3	2	0	3	1·174

The red-orange ternary nitride, Li_2CeN_2, was found in the products of all the reactions. The formula was originally obtained by chemical analysis for a single-phase product (experiment nos. 2 and 5) (Found: Li, 7·8; Ce, 76·65; N, 15·0. Calc. for Li_2CeN_2: Li, 7·69; Ce, 76·92; N, 15·39%). This was later confirmed by comparison of the *X*-ray powder pattern published by Halot and Flahaut.[2] The compound Li_2CeN_2 was found to have a hexagonal structure, $a = 3·556$, $c = 5·473$ Å. The full *X*-ray diffraction pattern is given in Table 2.

In nearly all reactions a higher ratio of Li_3N to Ce was needed for the formation of Li_2CeN_2 than that required by the equation

$$2Li_3N + 3Ce + 2N_2 \longrightarrow 3Li_2CeN_2$$

In the case of reactions performed in flowing ammonia, this is due to the low temperature sublimation of lithium amide which is formed as an intermediate in the reaction. The slow decomposition of lithium nitride *in vacuo* at temperatures above 550 °C accounts for the same effect observed for reactions carried out at a reduced pressure in nitrogen or *in vacuo*.

Cerium mononitride, CeN, was observed in the products of all reactions in which complete reaction to the ternary nitride did not occur.

The reaction of lithium nitride with cerium in a stream of ammonia was followed by d.t.a. (Table 3). The strong exothermic change observed at 215 °C was attributed to two reactions occurring simultaneously.

TABLE 3

Differential thermal analyses

Reaction	Atmosphere	(t/°C)	Transition
$Li_3N + Ce$	NH_3	215	str. exo.
		430	br. endo.
		520	w. br. exo.
$2Li_3N + 3Ce$	N_2	330	w. exo.
		560	br. exo.
		635	w. exo.
$3Li_3N + Th$	vacuum	320	w. exo.
		505	br. exo.
		600	w. exo.
$5Li_3N + 3Th$	N_2	295	w. exo.
		535	sh. exo.
		620	w. exo.
$Li_3N + Hf$	N_2	308	w. exo.
		515	str. exo.
		658	w. exo.

str. = strong, w. = weak, br. = broad, sh. = sharp, exo. = exothermic, endo. = endothermic.

$$Li_3N + 2NH_3 \longrightarrow 2LiNH_2$$

$$2Ce + 2NH_3 \longrightarrow 2CeN + 3H_2$$

At 430 °C a broad endothermic transition indicates the melting of lithium amide. This was almost immediately followed by a small, broad, exothermic change at 520 °C, indicating the reaction to form the ternary nitride Li_2CeN_2.

$$\underset{\text{(excess)}}{LiNH_2} + CeN \longrightarrow Li_2CeN_2 + NH_3$$

The reaction of a compressed 2 : 3 stoicheiometric mixture of lithium nitride and cerium in purified flowing nitrogen was followed by d.t.a. and t.g.a. The small exothermic change observed at 330 °C appears to be due to either slightly non-stoicheiometric lithium nitride absorbing nitrogen or to the formation of a cerium–nitrogen solid solution. An effect at *ca.* 330 °C was observed in all d.t.a. experiments involving lithium nitride and the metals in a nitrogen atmosphere. At 560 °C a broad exothermic change occurs due to the formation of cerium mononitride. The t.g.a., which was carried out with an identical heating rate to that used for the d.t.a. experiment, shows a small weight increase, commencing at 520 °C, indicating the formation of some cerium mononitride. This was followed by a change in the rate of increase in weight which approximately corresponds with the small exothermic peak on the d.t.a. at 635 °C, resulting from the formation of the ternary nitride Li_2CeN_2. The rate of absorption indicated by the increase in weight, becomes much greater as the temperature approaches 700 °C.

T.g.a. shows the absorption of 1·96 mol equiv. of nitrogen which is close to the expected 2 mol equiv. required by the equation

$$2Li_3N + 3Ce + 2N_2 \longrightarrow 3Li_2CeN_2$$

When the temperature of the t.g.a. was kept constant at 530—540 °C a weight increase equivalent to 1·53 mol equiv. of nitrogen was observed which is in agreement with the results of the *X*-ray diffraction analysis showing the formation of CeN together with small quantities of Li_2CeN_2 and Li_3N.

The density of a sample of Li_2CeN_2 was measured as 4·41 g ml^{-1} which gives a value of 1 for the number of molecules per unit cell. The density is in good agreement with that of 4·35 g ml^{-1} obtained by Halot and Flahaut.[2]

Ce_2N_2O.—When the ternary nitride Li_2CeN_2 was decomposed at 1000 °C in the presence of lithium oxide the product was cerium mononitride plus another phase. On heating a 3 : 1 mixture of cerium mononitride and cerium dioxide at 1040 °C *in vacuo* or at 1100 °C in 20 cmHg of nitrogen a sage green product was obtained, which had an indentical *X*-ray pattern to the unknown phase found above. By comparison with *X*-ray data for Th_2N_2O,[7] the phase was identified as Ce_2N_2O.

TABLE 4

X-Ray diffraction pattern of Ce_2N_2O

d/Å	I/I_0	h	k	l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
3·357	18	1	0	0	0·05274	0·05263
3·025	16	0	0	2	0·06492	0·06480
2·937	100	1	0	1	0·06888	0·06883
2·249	18	1	0	2	0·11745	0·11743
1·940	21	1	1	0	0·15788	0·15789
1·731	18	1	0	3	0·19832	0·19843
1·680	2	2	0	0	0·21048	0·21052
1·633	18	1	1	2	0·22271	0·22269
1·619	12	2	0	1	0·22661	0·22672
1·514	1	0	0	4	0·25926	0·25920
1·469	3	2	0	2	0·27527	0·27532
1·380	0·5	1	0	4	0·31184	0·31183
1·291	7	2	0	3	0·35634	0·35632
1·269	0·25	2	1	0	0·36850	0·36841
1·243	9	2	1	1	0·38453	0·38461
1·194	6	1	1	4	0·41703	0·41709

Ce_2N_2O has a hexagonal cell $a = 3{\cdot}880$, $c = 6{\cdot}057$ Å and the *X*-ray pattern is presented in Table 4. Analyses performed on this phase confirmed the formulation (Found: Ce, 85·9; N, 8·4. Calc. for Ce_2N_2O: Ce, 86·42; N, 8·64%).

Li_2ThN_2. The conditions used, and the products formed in the reactions of lithium nitride with thorium or thorium nitride are given in Table 5. A ternary nitride phase was found in the products of all the reactions. A formula of Li_2ThN_2 was obtained by chemical analysis on the product of a solid-state reaction which has been shown to be monophasic by *X*-ray diffraction (experiment no. 2) (Found: Li, 5·5; Th, 83·9; N, 10·4. Calc. for $LiThN_2$: Li, 5·1; Th, 84·7; N, 10·3%).

TABLE 5

Solid-state reactions * of lithium nitride with thorium and thorium nitride

Expt. no.	Reactants	Conditions	Products
1	$5Li_3N + 3Th$	Nitrogen (55 cmHg) 540 °C	$Li_2ThN_2 + Th + ThN$
2	$5{\cdot}2Li_3N + 3Th$	Nitrogen (42 cmHg) 600 °C	Li_2ThN_2
3	$5Li_3N + 3Th$	Nitrogen (1 atm) 490 °C	$Th + ThN + Li_2ThN_2 + Li_3N$
4	$2Li_3N + 3Th$	Nitrogen (1 atm), 640 °C	Li_2ThN_2
5	$3Li_3N + 1Th$	Vacuum, 590 °C	Li_2ThN_2 + trace ThN
6	$2Li_3N + 1ThN$	Ammonia, 570 °C	Li_2ThN_2

* All reactions were carried out for a period of 1 day.

At first sight the *X*-ray powder pattern of Li_2ThN_2 may be indexed on the basis of a cubic unit cell with $a = 7{\cdot}827$ Å. Palisaar and Juza[3] have, however, shown that the compound has a hexagonal unit cell with the dimensions $a = 6{\cdot}39$ and $c = 5{\cdot}54$ Å. To corroborate this fact a step-scan of the diffraction pattern was carried out over the higher angle lines at $d = 1{\cdot}843$ and $1{\cdot}749$ Å. Resolution of these lines became apparent and the reflections due to the 300 and 003 planes and the 113 and 220 planes was clearly observed. The cell constants obtained from the step-scan experiments were $a = 6{\cdot}388$ and $c = 5{\cdot}536$ Å, in very good agreement with those found by Palisaar and Juza.

The compound Li_2ThN_2 is formed far more readily by a solid-state reaction of lithium nitride and thorium *in vacuo* (experiment no. 5) than was the cerium ternary phase Li_2CeN_2 by the analogous reaction.

The reactions of various stoicheiometric mixtures of lithium nitride and thorium *in vacuo* were followed by d.t.a. (Table 3). The exothermic effect at 320 °C was again observed. *X*-Ray diffraction patterns of the reaction mixture heated to just above 320 °C showed two changes from the original pattern: (a) a change in the relative intensities of the lines due to Li_3N; (b) a slight broadening of the lines due to Th.

The exothermic effect at 320 °C may therefore be attributed to either the redistribution of nitrogen in lithium nitride or the dissolution of nitrogen by thorium metal, or to a combination of the two.

The formation of thorium mononitride at 505 °C

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[7] R. Benz and W. H. Zachariasen, *Acta Cryst.*, 1966, **21**, 838.

gave rise to a broad exothermic peak on the d.t.a. trace. A smaller exothermic peak at 600 °C indicates the formation of the ternary nitride, Li_2ThN_2, with the evolution of lithium vapour:

$$2Li_3N + Th \xrightarrow{320\ ^\circ C} 2Li_3N + Th(N)$$

$$2Li_3N + Th(N) \xrightarrow{505\ ^\circ C} Li_3N + ThN + 3Li$$

$$Li_3N + ThN \xrightarrow{600\ ^\circ C} Li_2ThN_2 + Li$$

D.t.a. of the reactions of lithium nitride and thorium in a partial pressure of nitrogen, showed a great similarity to those obtained from the vacuum reactions. Formation of the mononitride, ThN, occurred at a higher temperature than when carried out *in vacuo* giving rise to a slightly sharper exothermic peak at 535 °C. A small exothermic peak at 620 °C was due to the formation of the ternary nitride Li_2ThN_2. A plot of the pressure of nitrogen over the reaction mixture during the d.t.a. showed that the nitrogen pressure drops sharply between 520 and 560 °C followed by a steady decrease up to 610 °C, where a final sharp drop in the nitrogen pressure accompanies the formation of Li_2ThN_2.

$$2Li_3N + 3Th \xrightarrow[295\ ^\circ C]{N_2} 2Li_3N + 3Th(N)$$

$$2Li_3N + 3Th(N) \xrightarrow[535\ ^\circ C]{N_2} 2Li_3N + 3ThN$$

$$2Li_3N + 3ThN \xrightarrow[620\ ^\circ C]{N_2} 3Li_2ThN_2$$

The result of a t.g.a. of a pellet of composition $2Li_3N$ to 3Th in nitrogen, which had been previously passed over heated titanium and copper at 800 °C to remove oxygen, gave some exact information on the actual quantity of nitrogen absorbed during the reaction. An increase in weight due to the absorption of nitrogen commences at 500 °C and proceeds at a steady rate up to 600 °C. Between 600 and 640 °C an increase in the absorption rate occurs due to the formation of Li_2ThN_2. The reaction reached completion in 20 min when the temperature was held at 640 °C. The total weight increase corresponded to the absorption of 1·99 mol equiv. nitrogen for every 3 g-atom of thorium:

$$2Li_3N + 3Th + 2N_2 \longrightarrow 3Li_2ThN_2$$

The density of Li_2ThN_2 was measured as 6·76 g ml^{-1} which gives a value of 3 molecules per unit cell. This figure agrees with the *X*-ray density published by Palisaar and Juza for a stoicheiometry $Li_{2\cdot17}ThN_{1\cdot96}$.

Li_2HfN_2.—A number of solid-state experiments were carried out involving the reaction of lithium nitride with hafnium (Table 6). The ternary nitride Li_2HfN_2 was characterised by chemical analysis of the product from experiment 5 (Found: Li, 6·7; Hf, 79·8; N, 13·4. Calc. for Li_2HfN_2; Li, 6·4; Hf, 80·8; N, 12·8%).

The hafnium ternary nitride was far more difficult to prepare than the corresponding Li_2MN_2-type phases of cerium and thorium. Reaction of the metal itself with lithium nitride was found to be unsatisfactory: heating stoicheiometric mixtures up to temperatures of 800 °C in nitrogen or vacuum (experiments 1 and 2) gave no reaction; however the ternary phase was found as a minor product of a 2 : 1 Li_3N/Hf reaction in hydrogen (experiment No. 3). Following the result of this experiment a small quantity of hafnium was heated in hydrogen at 500—600 °C for 2 to 3 h. The reactions of this hydrided hafnium, designated Hf(H), are illustrated by experiments 5 and 6 in Table 6. The hydriding of the hafnium activated the hafnium towards reaction with lithium nitride, and at temperatures above 600 °C the Li_2HfN_2 phase was readily formed. Reactions in the temperature range 680 to 720 °C in a partial pressure of nitrogen were found to be the best conditions for preparing the ternary nitride.

TABLE 6

Solid-state reactions * in the Li/Hf/N system

Expt. no.	Reactants	Conditions (°C)	Products
1	$5Li_3N + 2Hf$	Vacuum, 720 °C	$Li_3N + Hf$
2	$2Li_3N + 1Hf$	Nitrogen (16 cmHg), 780 °C	$Li_3N + Hf$
3	$2Li_3N + 1Hf$	Ammonia, 560 °C, 2 h	Hf + Hf(N)
4	$2Li_3N + 1Hf$	Hydrogen, 660 °C, 3 h	Small amount Li_2HfN_2
5	$5Li_3N + 2Hf(H)$	Nitrogen (21 cmHg), 615 °C, 2 days	Li_2HfN_2
6	$2Li_3N + 1Hf(H)$	Nitrogen (28 cmHg) 650 °C	Li_2HfN_2 + trace Hf(N)

* All experiments were carried out for a period of 1 day unless otherwise stated.

Heating the ternary nitride Li_2HfN_2 *in vacuo* at temperatures in the region of 650 °C caused a slow decomposition to the mononitride, HfN, although the ternary phase was usually observable in the *X*-ray diffraction pattern after a period of 10 h. As a result of this observation it would be expected that Li_2HfN_2 would not be observed as a major product of reactions of hafnium dioxide and hafnium in liquid lithium when the excess of lithium was removed by vacuum distillation.

A d.t.a. was performed on a 1 : 1 lithium nitride to hafnium (hydrided) mixture in a steady flow of purified nitrogen (Table 3). The characteristic small exothermic peak at 308 °C may be assigned to either nitrogen rearrangement in the lithium nitride or nitrogen solution in the metal. The strong exothermic peak at 515 °C was probably associated with the formation of the mononitride, HfN. The smaller exothermic peak due to the formation of the ternary nitride Li_2HfN_2 occurred at 658 °C, which was in agreement with the higher temperature required to prepare Li_2HfN_2 compared with either Li_2CeN_2 or Li_2ThN_2.

The *X*-ray powder diffraction pattern of Li_2HfN_2 (Table 7) was found to be almost identical with that

TABLE 7

X-Ray diffraction pattern of Li_2HfN_2

d/Å	I/I_0	h	k	l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
5·456	84	0	0	1	0·01999	0·01996
2·817	40	1	0	0	0·07489	0·07488
2·727	6	0	0	2	0·07989	0·07984
2·503	100	1	0	1	0·09488	0·09484
1·959	40	1	0	2	0·15477	0·15472
1·818	1	0	0	3	0·17959	0·17964
1·626	10	1	1	0	0·22464	0·22464
1·558	10	1	1	1	0·24461	0·24460
1·527	8	1	0	3	0·25451	0·25452
1·408	3	2	0	0	0·29947	0·29952
1·397	4	1	1	2	0·30443	0·30448
1·364	8	2 0	0 0	1 4	0·31945	0·31948 0·31936
1·251	3	2	0	2	0·37938	0·37936
1·227	2	1	0	4	0·39425	0·39424
1·212	2	1	1	3	0·40432	0·40428

reported [3] for the ternary nitride Li_2ZrN_2 and to be very similar to that of Li_2CeN_2. The cell constants of the three compounds are given in Table 8.

TABLE 8

Crystallographic data for the ternary nitrides of Ce, Zr, and Hf

Compound	a	c	c/a	z	Space group	Ref.
Li_2ZrN_2	3·282	5·460	1·664	1	$P\bar{3}2/m1$	3
Li_2HfN_2	3·253	5·457	1·678	1		This work
Li_2CeN_2	3·557	5·496	1·545	2	$P\bar{3}m$	2
Li_2CeN_2	3·556	5·473	1·539	1		This work

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