

Direct Solvothermal Synthesis of Early Transition Metal Nitrides

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Solvothermal reactions of TaCl_5 with LiNH_2 in benzene result in nanocrystalline Ta_3N_5 at 500 or 550 °C. The ~ 25 nm Ta_3N_5 particles have a band gap of 2.08–2.10 eV. The same reactions in mesitylene resulted in a higher crystallization temperature and large amounts of carbon incorporation due to solvent decomposition. Reactions of $\text{Ta}(\text{NMe}_2)_5$ with LiNH_2 under the same conditions resulted in TaN. Rocksalt-type MN phases are obtained for Zr, Hf, or Nb when their chlorides (ZrCl_4 , HfCl_4 , or NbCl_5) or dialkylamides ($\text{M}(\text{NETMe})_4$, $\text{M} = \text{Zr, Hf}$) are reacted with LiNH_2 under similar conditions. With the amides, there is some evidence for nitrogen-rich compositions ($\text{HfN}_{>1}$), and carbon is incorporated into the products through pyrolysis of the dialkylamide groups.

Introduction

Early transition metal nitrides such as NbN, ZrN, HfN, and TaN exhibit high chemical stability and useful physical properties including hardness, high wear resistance, electrical conductivity, and superconductivity.¹ Nitrogen-rich phases like Zr_3N_4 ,^{2,3} Hf_3N_4 ,^{2,4} and Ta_3N_5 ⁵ have interesting properties very different from those of the mononitrides. Ta_3N_5 has a band gap of 2.08 eV and is a useful red pigment and an active photocatalyst.^{6,7} Zirconium and hafnium nitrides change from conducting to insulating materials as the composition changes from MN to M_3N_4 and have applications in cryogenic thermistors and in Josephson junctions.⁸

There is increasing interest in synthesizing metal nitrides as nanocrystalline powders to design and engineer new products that would utilize size- and shape-dependent physi-

cal properties. High-temperature combination of the elements typically yields mononitrides (MN) or metal-rich phases as agglomerated refractories.⁹ Conversion of the oxides by carbothermal reduction or ammonolysis has similar results, with the notable exception of forming Ta_3N_5 from Ta_2O_5 .⁷ Decomposition of the molecular precursors¹⁰ and sol–gel-type approaches¹¹ have also been used to some extent in making nitrides with small particle sizes.

In the solid state, metathetical reactions between metal halides and nitrogen sources including Li_3N , LiNH_2 , NaN_3 , and Ca_3N_2 have proved effective at producing nitrides.^{12–14} These are extremely exothermic reactions, but nanoparticulate products can be obtained by diluting the reaction mixture with unreactive inorganic filler materials.¹⁴ For the early transition metals, the MN phases are usually the outcome. In one modification to these processes, Ta_3N_5 was produced from the reaction of TaCl_5 with LiNMe_2 , but in this case, the initial product was amorphous, and annealing under ammonia at 700 °C was needed to obtain Ta_3N_5 .¹³

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Solvothermal conditions are desirable for metathesis reactions because the heat produced can be absorbed by the solvent, resulting in more controlled growth of small-scale crystallites. For example, the reaction of BCl_3 with Li_3N at 250 °C in benzene results in cubic BN, whereas the same conditions with BBr_3 result in hexagonal BN.¹⁵ Similarly, nanocrystalline GaN (30 nm), InN (<30 nm), CrN (25 nm), and ZrN (180 nm) can be obtained from reactions of the respective chlorides with Li_3N in benzene at 400 °C or lower.¹⁶ The solvothermal reaction of GaCl_3 or Ga cupferron with $(\text{Me}_3\text{Si})_2\text{NH}$ yields small (3–15 nm) GaN crystallites, and here it was found to be possible to limit aggregation and reduce particle size by adding *N*-cetyl-*N,N,N*-trimethylammonium bromide as a capping agent.¹⁷ The reaction of GaCl_3 with NaN_3 in toluene or THF at up to 260 °C led to nanocrystalline (<3 nm) GaN.¹⁸ NaN_3 did not decompose under the reaction conditions, which was taken as evidence that N_3^- ions were transferred to Ga. InN (10 nm) and Cu_3N have been produced similarly.¹⁹ At higher temperatures, 10–20-nm-sized ZrN and NbN can be obtained from reactions of the chlorides with NaN_3 .²⁰ Here, a reduction–nitridation mechanism was suggested in which NaN_3 thermally decomposes, Na reduces the metal chloride, and the resulting metal particles react with nitrogen.

Here, we report on solvothermal reactions of early transition metal chlorides and dialkylamides with LiNH_2 in mesitylene and benzene, to produce ZrN, HfN, NbN, Ta_3N_5 , and TaN.

Experimental Section

All manipulations were carried out under dry nitrogen. Mesitylene and benzene were distilled from Na and CH_3OH from NaOCH_3 . TaCl_5 (99.999%), HfCl_4 (99.5%), ZrCl_4 (99.99%), NbCl_5 , $\text{Hf}[\text{N}(\text{CH}_3\text{C}_2\text{H}_5)]_4$ (99.95%), and $\text{Zr}[\text{N}(\text{CH}_3\text{C}_2\text{H}_5)]_4$ (99.8%) were bought from Aldrich and used as supplied. $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ was donated by Epichem and used as supplied. LiNH_2 was synthesized by reacting 1.6 M $n\text{-BuLi}$ in hexane (Aldrich) with excess sodium dried ammonia at –78 °C, filtering, and drying the product under a vacuum.

All syntheses were carried out in a 75 cm³ autoclave (Parr 4740CH). Typically, TaCl_5 (0.6 g) was placed in the silica liner and covered with 15 cm³ of mesitylene or benzene. A total of 0.192 g (5 molar equivalents) of LiNH_2 was added, and the mixture was stirred. The autoclave was then heated to 500 or 550 °C for 24 h, as described in the text. After cooling to room temperature, the

mixture was transferred to a Schlenk tube inside the glove box. The solid was collected by filtration, washed with dry methanol three times, and dried under a vacuum. Reagent quantities were varied according to reaction stoichiometry. For comparison, a Ta_3N_5 standard was produced by a standard solid-state method.⁷

Powder X-ray diffraction (PXD) patterns were collected under nitrogen with a Siemens D5000 diffractometer using Cu K α 1 radiation. The phases present were identified by comparison with the JCPDS database²¹ and patterns refined using the GSAS package.²² Crystallite sizes were extracted from the Lorentzian component of the profile coefficients as described in the GSAS manual. Transmission electron microscopy (TEM) was carried out with an accelerating voltage of 300 kV in a JEOL JEM3010 microscope with an Oxford Inca EDX detector. Samples were prepared by ultrasound dispersal in toluene, followed by deposition on carbon-coated Cu grids. Scanning electron microscopy was performed on a JEOL JSM5910 microscope with an accelerating voltage of 10 kV. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA851e under high-purity nitrogen (Air Products BiP grade) or 60% O_2 /40% N_2 . C, H, N, metal, and halogen analyses were carried out by Medac Ltd. (Egham, Surrey, U.K.). Diffuse reflectance UV–visible spectra were collected using a Perkin Elmer Lambda 35 spectrometer with an integrating sphere in the range of 400–800 nm.

Results and Discussion

Previously, we showed²³ that refluxed or solvothermal reactions of TaCl_5 with LiNH_2 yielded amorphous products that could be annealed to Ta_3N_5 but could not crystallize this material directly. Contamination by LiTaO_3 was found with commercial LiNH_2 , and large amounts of carbon in a non-semiconducting Ta_3N_5 -type material were obtained with high-purity LiNH_2 . It is a common finding for refractory materials from solvothermal reactions that crystallization requires an annealing step; a similar approach has recently been used by Gillan and Barry in the synthesis of transition metal phosphides.²⁴ The acquisition of new equipment meant that we could now work at higher temperatures, so it was hoped that annealing could be avoided. Hence, the main aim of this work was to synthesize Ta_3N_5 directly under solvothermal conditions. The second aim was to investigate which nitrides form under the same conditions with Zr, Hf, and Nb on the basis that the conditions of the solvothermal reactions are relatively gentle compared with solid-state routes and new nitrogen-rich phases might be obtained. Third, the use of dialkylamide metal sources, instead of the chlorides, was investigated, as these are known to produce nitrides when reacted with ammonia^{2,25} and could remove the possibility of chloride contamination of the products.

1. Reactions between TaCl_5 and LiNH_2 . TaCl_5 was dissolved in benzene or mesitylene, mixed with LiNH_2 , and heated in a sealed autoclave at 500 or 550 °C. The strongly

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Table 1. Products from Solvothermal Reactions of TaCl₅ with LiNH₂^a

conditions	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	crystallite size/nm	%C, %N
mesitylene 550 °C	3.894(1)	10.182(2)	10.286(2)	24	11, 6
benzene 500 °C	3.896(2)	10.231(4)	10.286(4)	24	1.4, 9
benzene 550 °C	3.895(3)	10.217(6)	10.287(6)	25	1.6, 9.5
Ta ₂ O ₅ /NH ₃ 800 °C ⁷	3.8907(2)	10.2279(3)	10.2758(4)	25	0, 10.6

^a PXD data were refined using the Ta₃N₅ structure type.^{7,23} Ta₃N₅ contains 11% N.

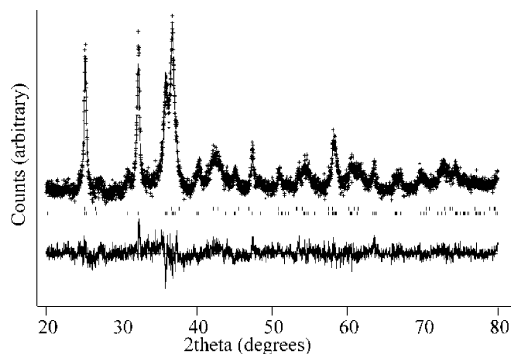


Figure 1. Fit to the PXD data for the product of the reaction of TaCl₅ with LiNH₂ in benzene at 550 °C. Crosses mark the data points; the upper continuous line, the calculated profile; and the lower continuous line, the difference. Lower tick marks are the positions of allowed reflections in the Ta₃N₅ structure; upper tick marks, the Ta₄N₅ structure.

colored TaCl₅ solutions were colorless after heating, showing that the TaCl₅ had reacted fully. The products were washed several times with methanol to remove the LiCl byproduct but also any unreacted TaCl₅ or LiNH₂ as methoxides. At 500 °C with mesitylene, the product was amorphous,²³ whereas at 550 °C, a crystalline, Ta₃N₅-type material was obtained. With benzene, the product was crystalline at both 500 and 550 °C, though at 450 °C, an amorphous material was obtained. Table 1 lists crystallographic and other data on the crystalline products from these reactions, and Figure 1 shows an example of one of the refined PXD data sets.

The product from the reaction in mesitylene at 550 °C was black in color. Combined with the high carbon content of the product, this indicates considerable charring of the solvent. However, this does demonstrate that Ta₃N₅ can be crystallized directly in a solvothermal process at a lower temperature than used in its synthesis in the solid state.⁷ The composition is highly nitrogen-deficient, and small amounts of H (0.6%) and Cl (0.8%) were also present. The crystallographic *b* axis is particularly sensitive to composition variations in Ta₃N₅ and is usually linked with defects or oxide ions in the lattice;^{7,23} here, the shortening of the *b* axis compared with the standard sample is also consistent with deviation from the Ta₃N₅ composition. The TGA profile in oxygen shows a mass loss (~14 %) between 400 and 800 °C, Figure 2, corresponding mainly to oxidation of elemental C. The reaction of Ta₃N₅ with oxygen to yield Ta₂O₅ should result in a mass gain of 8.15%. The IR spectrum showed strong ν NH (~3400 cm⁻¹) and δ NH₂ (~1400 cm⁻¹) features as well as a broad ν MN band (~600 cm⁻¹), suggesting that some amide groups remained, and it may be that the

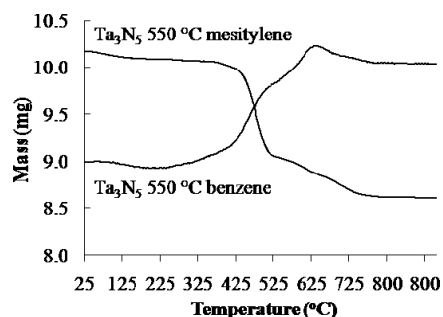


Figure 2. TGA traces under 60% O₂ of Ta₃N₅ produced in benzene or mesitylene at 550 °C. The mass loss in the mesitylene trace is due to burning of the carbon contaminant phase. The sample was heated to 800 °C at a constant rate, then maintained at this temperature for 20 min.

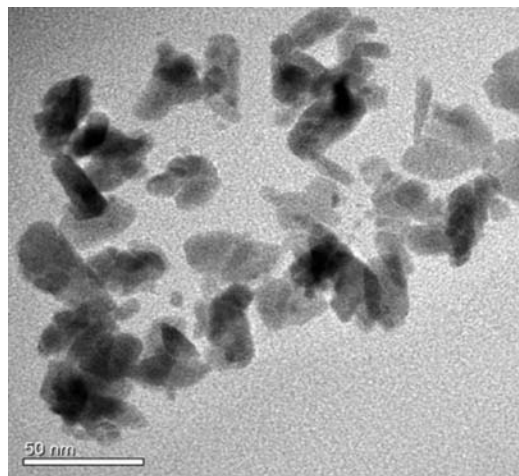


Figure 3. TEM image of the product of reaction between TaCl₅ and LiNH₂ in mesitylene at 550 °C.

decomposition of these is responsible for the extra weight loss. If so, the nitrogen content of the main phase would be even lower. It is likely that a significant portion of the C is in the elemental form, but the presence of some carbon in the Ta₃N₅ lattice cannot be ruled out and seems likely from the extremely anion-deficient composition that would otherwise result. The PXD shows small amounts of a Ta₄N₅ impurity as well as a small amount of amorphous scattering at low angles, presumably due to the carbon. TEM (Figure 3) shows elongated particles of 20–25 nm, consistent with the crystallite size of 20 nm derived from PXD.

When the same reaction was carried out with benzene as the solvent, the products were of terracotta color with no visual signs of solvent charring. PXD patterns again showed a small amount of Ta₄N₅ as a second phase, presumably through reduction of a portion of the tantalum. The lattice parameters, Table 1, are close to those of the Ta₃N₅ standard with much smaller deviations in the *b* axis. Further, the carbon content of these materials is low, and the nitrogen content is high. Diffuse reflectance UV–visible spectra, Figure 4, show a step just above 2 eV, showing that these low-carbon nitride materials are semiconducting. The band gap is 2.08 eV for the sample produced at 550 °C and 2.10 eV at 500 °C, compared with literature values of 2.06–2.08 eV.^{6,7} These samples were found to contain very little Cl (0.2% or less), and the H content was also lower than that of the sample produced in mesitylene (<0.5%). TGA (Figure

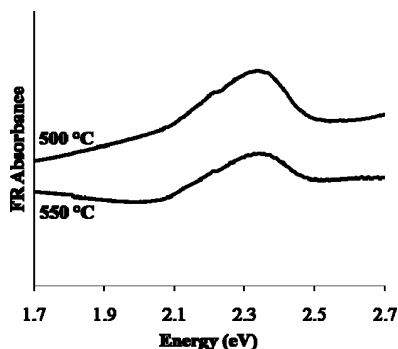
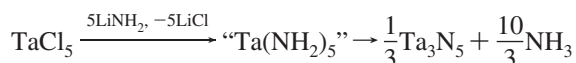


Figure 4. Diffuse reflectance UV/visible spectra of Ta_3N_5 made in benzene at 500 and 550 °C showing the step in absorption at the band edge.

2) showed a mass gain as expected for $\text{Ta}_3\text{N}_5 \rightarrow \text{Ta}_2\text{O}_5$. The IR spectrum contained a broad band around 600 cm^{-1} (νMN) and only very weak νNH and δNH_2 features. TEM shows fairly isotropic particles of around 20 nm diameter, again matching closely the PXD-derived crystallite size, with electron diffraction showing the textured rings corresponding to the lattice spacings of Ta_3N_5 (Figure 5). Previously, we suggested that in annealed samples the Li salts present in the impure products provided a flux for the growth of crystalline rods.²³ In these reactions, crystallization occurs in a solvent, and this clearly inhibits rod growth; hence, the nanocrystalline products are essentially isotropic.

The formation of Ta_3N_5 must take place *via* stepwise substitution of chloride groups and condensation with the elimination of NH_3 :



A strong odor due to ammonia is obvious when the autoclave is opened. The differences between the products of reactions in mesitylene or benzene are striking. In benzene, crystallization occurs at a lower temperatures, and there is very little solvent decomposition. Hence, the carbon content of the products is low, and semiconducting compositions are obtained. TaCl_5 is a little more soluble in benzene than in mesitylene, but the TaCl_5 is fully consumed in reactions carried out in either solvent. It is likely that the higher carbon content in the mesitylene-derived samples is in some way responsible for the higher annealing temperatures, possibly through carbide incorporation into the Ta_3N_5 -type product. Due to the lower degree of decomposition, benzene is by far the preferred solvent for these reactions despite its toxicity.

Taking account of the silica liner, the available space in the autoclave is approximately 60 cm^3 . The critical point conditions of benzene/mesitylene are $T_c = 289/364\text{ °C}$ and $P_c = 49/31\text{ bar}$. Under the reaction conditions, the solvents are supercritical fluids with densities of 0.22 g cm^{-3} . Calculated pressures for 15 cm^3 of solvent at 550 °C are ~ 195 (benzene) and ~ 125 (mesitylene) bar. The higher pressure with benzene could also contribute to the lower crystallization temperature.

In view of the low solvent density, an additional question is whether the reactions are genuinely solvothermal or a

solid-state process under a dense vapor. The product morphology suggests some solubilization of one of the reagents at the point when the reactions are occurring as the products are finely powdered, not annealed agglomerates. The solid-state reaction between TaCl_5 and LiNH_2 is self-propagating and highly exothermic.¹³ More importantly, the solid-state reaction, carried out at 300 °C followed by annealing under ammonia at 700 °C, yielded cubic TaN, not Ta_3N_5 as found here.¹³ Ta_3N_5 is stable in ammonia to at least 900 °C.⁷

The benzene density under the reaction conditions described above is a significant fraction of the critical density (0.30 g cm^{-3}), and hence it is not unreasonable to assume some solvent behavior. However, in order to test the effect of higher solvent density, some reactions of TaCl_5 with LiNH_2 were carried out with 30 cm^3 of benzene (density $\sim 0.44\text{ g cm}^{-3}$) at 550 °C. Using the same quantities of reagents as described above, a secondary phase was observed in addition to Ta_3N_5 . This was indexed with a face-centered cubic cell ($a = 4.91\text{ Å}$) and closely resembles Li_2NH , though the lattice parameter deviates significantly and it probably incorporates some Ta or Cl. The addition of a small excess of TaCl_5 to the reaction mixture ($\sim 20\%$) resulted in samples without this secondary phase. Structure refinements on the Ta_3N_5 -type samples gave lattice parameters of $a = 3.8976(12)$, $b = 10.235(4)$, and $c = 10.279(3)\text{ Å}$ and a crystallite size of 14 nm. The lattice parameters are comparable with those shown in Table 1, but the higher pressure does lead to a reduction in the crystallite size. The loss of Ta from the reactions with a larger amount of solvent suggests better solvation and the removal of some Ta from the part of the autoclave where the LiNH_2 is placed. Amorphous samples produced by refluxing TaCl_5 and LiNH_2 in mesitylene or by heating the same reaction in an autoclave at 500 °C crystallized in the solid state between 500 and 600 °C.²³ It is arguable that the role of the solvent herein could be in controlling the early reaction stages rather than mediating the reaction at the temperature at which crystallization is carried out. However, the solid-state crystallization of amorphous tantalum nitride only occurred at 500 °C when oxygen-containing salts were present as impurities.²³ In these new reactions, crystallization occurs directly without oxygen impurities, and hence some solvent mediation of the reactions is likely.

2. Reactions of NbCl_5 , ZrCl_4 , and HfCl_4 with LiNH_2 .

NbCl_5 was reacted with LiNH_2 in mesitylene or benzene at 550 °C following the same procedures as for Ta, yielding black products. With mesitylene, there was considerable charring of the solvent. PXD patterns of both samples, Figure 6, matched cubic NbN. The product from mesitylene also had peaks corresponding to graphitic C. Refinement of the PXD patterns yielded lattice parameters of $a = 4.335(2)\text{ Å}$ (benzene) and $a = 4.339(3)\text{ Å}$ (mesitylene) compared with literature values of $4.391\text{--}4.394\text{ Å}$ for NbN and 4.382 ($\text{NbN}_{0.844}$), 4.388 ($\text{NbN}_{0.88}$), and 4.377 ($\text{NbN}_{0.90}$) Å for N-deficient compositions.²¹ The average crystallite size was refined as 9 nm (benzene) or 6 nm (mesitylene). Stoichiometric NbN would contain 13% N, and analysis shows 12%

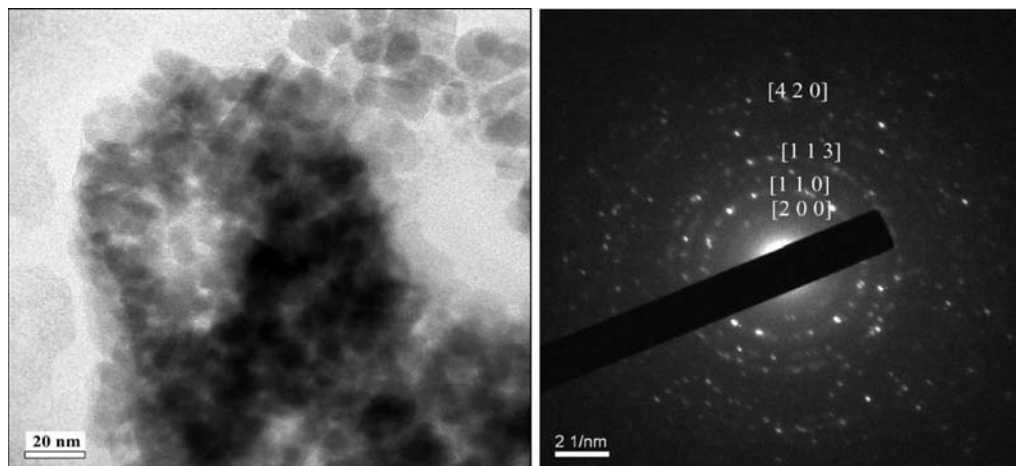


Figure 5. TEM image and ED pattern of Ta_3N_5 produced in benzene at 550 °C.

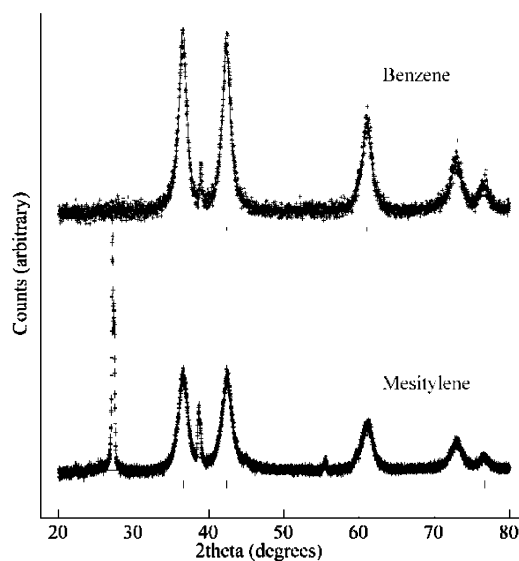


Figure 6. PXD patterns of NbN made in benzene and mesitylene. Crosses mark the data points; the continuous lines, the calculated profile; and tick marks, the positions of allowed reflections in the NbN structure. The sharp peak at 26° in the mesitylene sample is from the carbon impurity. All peaks from the sample holder are at 38, 44, and 56°.

(benzene) and 9% (mesitylene). However, the mesitylene-derived product contains 31% C (cf. 2% from benzene), so the ratio of Nb/N is close to 1:1 in both cases. Both samples contained low levels (<1%) of H and Cl. TGA under oxygen (Figure 7) showed a mass gain in the benzene-derived product of ~12%, followed by a small mass loss. In the mesitylene-derived sample, the oxidation of NbN (~11% mass gain around 300 °C) was fairly well resolved from the burning of elemental C (34% mass loss around 430 °C). As with the analogous Ta reactions, IR showed strong νNH and δNH_2 features in the product from mesitylene, but these were very weak with benzene. TEM revealed a homogenous distribution of isotropic particles of around 6–8 nm consistent with the particle size derived from the PXD patterns (Figure S1, Supporting Information), with ED again showing textured rings at the d spacings associated with the NbN structure. At 500 °C with benzene as the solvent, the composition was essentially the same as at 550 °C (2% C, 11% N), but the crystallite size was around 3 nm, and

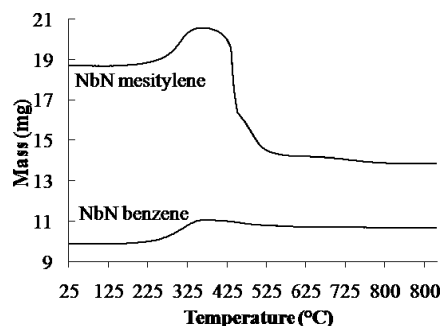
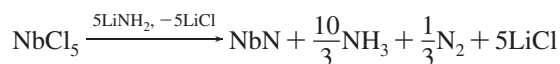


Figure 7. TGA traces under 60% O_2 of NbN produced in benzene or mesitylene at 550 °C. The mass gains are due to $\text{NbN} \rightarrow \text{Nb}_2\text{O}_5$, whereas the mass loss in the mesitylene trace is due to burning of the carbon contaminant phase. The sample was heated to 800 °C at a constant rate, then maintained at this temperature for 20 min.

significant amorphous scattering was observed in the PXD patterns ($a = 3.426(5)$ Å) in addition to the Bragg reflections.

No higher nitrides of Nb are known, and under these conditions, only NbN was obtained. NbN is a superconductor ($T_c \sim 15$ K) and shows superior wear resistance compared with TiN, so in nanoparticulate form, it may be of interest for incorporation into superhard nanocomposites.²⁶ NbN formation requires the reduction of niobium, presumably balanced by N_2 evolution:



It was possible in this case to conclusively show that carbon is incorporated in its elemental form when mesitylene is the solvent since, unlike with the Ta samples, it crystallized. Its oxidation was also resolved from the NbN oxidation in the TGA trace. These results further support the conclusion that solvothermal reactions in mesitylene are not as clean as those performed in benzene.

Reactions of ZrCl_4 or HfCl_4 (0.5 g) with LiNH_2 (4 molar equivalents) were carried out in benzene at 550 °C, as described above. In both cases, the dark green products were

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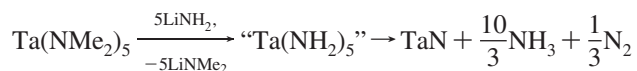
Table 2. Rocksalt-Type MN Products from Solvothermal Reactions of Metal Dialkylamides with LiNH₂

conditions	<i>a</i> / Å	literature ²¹ <i>a</i> /Å	crystallite size/nm	%C, %N	%N in ideal MN
Hf(NEtMe) ₄ , 500 °C	4.484(4)	4.512–4.550	3	4, 10	7.3
Hf(NEtMe) ₄ , 550 °C	4.512(2)	4.512–4.550	4	3, 8	7.3
Zr(NEtMe) ₄ , 550 °C	4.551(2)	4.573–4.600	9	4, 13	13.3
Ta(NMe ₂) ₅ , 500 °C	4.305(2)	4.331–4.339	8	15, 7	7.2

the MN phase according to PXD (ZrN, *a* = 4.530(5) Å, cf. 4.573–4.600;²¹ the Hf pattern was too broad to refine). Both samples contained about 1% C, and the N analysis was broadly in line with that expected for the MN phase, 11.2% in ZrN (13.3% calculated) and 6.9% in HfN (7.3% calculated). These samples always contained MNCl and amorphous material as well as the metal nitride. It is possible with variations in the ratio between the reagents that this might provide a useful route to these interesting materials, but it does not appear to be an effective route to the pure MN materials in nanocrystalline form for M = Zr or Hf.

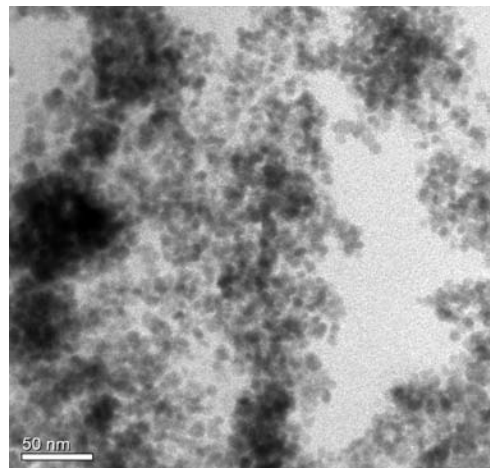
3. Reactions between Metal Dialkylamides and LiNH₂. Early transition metal dialkylamides react with ammonia to produce polymeric materials that decompose cleanly to yield nitrides at relatively low temperatures.^{25,27} LiNH₂ is an obvious replacement for ammonia in such reactions. This is also a halide-free route and for Zr and Hf could provide a means of avoiding the MNCl impurity phases described above.

Reactions were carried out in benzene with 4 (M = Zr, Hf) or 5 (M = Ta) molar equivalents of LiNH₂:



The lithium dialkylamide byproduct was removed by reaction with methanol, and filtration of the methanol solutions left black powders. This process should also remove any excess metal amide or LiNH₂ starting material and the respective methoxides. In all cases, the rocksalt-type MN phases were obtained with broad reflections in the PXD patterns, Figure S2, Supporting Information. Refined lattice parameters and carbon and nitrogen analyses are listed in Table 2.

With Hf(NEtMe)₄, the reactions were tried at 450, 500, and 550 °C. At 450 °C, the product was amorphous. At 500 and 550 °C, crystalline products were obtained. The higher-temperature sample of these two is closer in stoichiometry to the expectation for HfN, and the lattice parameter is within the expected range, though care should be taken with lattice parameters refined from such small crystallite sizes. The 500 °C sample appears to be slightly N-rich. It is well known that high nitrogen contents can be obtained in rocksalt-structured thin films obtained by chemical vapor deposition (CVD) from hafnium amides and ammonia—these are then

**Figure 8.** TEM image of TaN produced from Ta(NMe₂)₅ and LiNH₂.

insulating and have been discussed as gate dielectrics.²⁸ Hf₃N₄ has been obtained from Hf(NMe₂)₄ and ammonia with a rhombohedrally distorted rocksalt structure.² Here, the nitrogen-rich phase does not appear to have this distortion, and the data were refined with a cubic rocksalt structure.

For Ta and Zr, reactions were performed at 500 or 550 °C, and the nitrogen content of the products was close to that expected for the stoichiometric MN phases, suggesting that the carbon present is in elemental form. However, the signs of solvent decomposition observed with mesitylene (loss of solvent volume and solvent discoloration) were not seen here. Hence, the carbon is most likely to come from pyrolysis of the dialkylamide groups that are still attached to the metal. This is also consistent with the higher carbon content obtained with Ta(NMe₂)₅ than with the ethylmethylamides (Zr, Hf) where β-hydride elimination is possible on half of the alkyl groups. In all cases, TEM (Figure 8) showed well-separated isotropic particles with sizes comparable with those obtained from the PXD refinements (Table 2).

With Zr and Hf, the product of reaction with LiNH₂ is structurally the same whether the chloride or the dialkylamide is used. In all cases, a reduction in the formal oxidation state from +4 to +3 is observed, though there is evidence in one of the Hf reactions for a nitrogen-rich composition. With Zr and Hf, the route based upon the chlorides suffers from incomplete reaction and contamination by MNCl phases. With Ta, the products are different. When TaCl₅ is used, the oxidation state is maintained (→ Ta₃N₅), whereas with the amide, it is reduced from +5 to +3 (Ta(NMe₂)₅ → TaN). It has been reported previously that the use of dialkylamides with ammonia can cause a predisposition toward rocksalt structures by the formation of [MN]_n ladders.^{27,29} This has been used to explain the tendency to form rocksalt lattices in early transition metal nitrides formed by CVD even when nitrogen-rich compositions are deposited.

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Conclusions

Reactions of TaCl₅ and NbCl₅ with LiNH₂ in benzene under solvothermal conditions result in nanocrystalline Ta₃N₅ or NbN. Use of benzene as the solvent results in low levels of carbon contamination, and the Ta₃N₅ samples show semiconducting properties. When mesitylene was used, large amounts of carbon were incorporated due to solvent decomposition at the temperatures required to crystallize these nitrides. This was a less successful route to zirconium, and hafnium nitrides as MNCI impurities were always found. Substitution of the metal chlorides with dialkylamides led in all cases to crystallization of the MN phase.

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Supporting Information Available: Additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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