TABLE I
AZIDE–LEWIS ACID COMPLEXES

Compound	Color	Azide ν asym.	Δν from free azide[a]	Azide ν sym.	Δν from free azide[a]
$(C_6H_5)_3SiN_3 \cdot BBr_3$	Pale yellow	2208	+59	1190	−118
$(C_6H_5)_3GeN_3 \cdot BBr_3$	Pale yellow	2208	+108	1220	−50
$(C_6H_5)_3SnN_3 \cdot BBr_3$	S.o.[b]	2211	+118	...	...
$(CH_3)_3SiN_3 \cdot BBr_3$	White	2208	+67	1190	−142
$(CH_3)_3SnN_3 \cdot BBr_3$	S.o.[b]	2210	+122	...	...
$CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$	Red liq.	2210	+65	1195	−120
$(C_6H_5)_3SiN_3 \cdot SnCl_4$	S.o.[b]	2116	−33	1326	+18
$(C_6H_5)_3GeN_3 \cdot SnCl_4$	White	2131	+31	1308	+38
$(C_6H_5)_3SnN_3 \cdot SnCl_4$	White	2208	+115	1185	−80
$(CH_3)_3SiN_3 \cdot SnCl_4$	White	2110	−21	1347	+15
$CH_3N_3 \cdot SbCl_5$[8]	Green-yellow	2160	+54	1225	−146
$(CH_3)_3SiN_3 \cdot SbCl_5$	Pale yellow	2210	+69	1200	−132
$(C_6H_5)_3SiN_3 \cdot P(C_6H_5)_3$[3]	White	2018	−131	*ca.* 1260	−48

[a] See ref. 3 and 11 for infrared bands of free azides. [b] Complex studied in solution only and not isolated.

and mixed with solutions of the Lewis acid in the same solvent in a drybox under nitrogen. After mixing, a portion of the solution was removed for infrared study; the remainder was attached to a vacuum distillation apparatus and the solvent removed. The adduct was then dried *in vacuo* for several hours. Due to their great sensitivity to moisture, these adducts generally were not characterized by elemental analysis but rather by infrared spectroscopy and by hydrolysis and titration to the phenolphthalein end point.[13] The data are given in Table II. Certain of the complexes proved to be intractable and were studied only in solution.

Azidotrimethylsilane–Tin Tetrachloride.—A solution of 0.98 g. (8.5 mmoles) of $(CH_3)_3SiN_3$ in 25 ml. of CCl_4 was treated with 2.0 ml. (17.1 mmoles) of $SnCl_4$ in 5 ml. of CCl_4. After a few minutes, the solution turned opaque and a finely divided solid formed. When the solid had settled, the supernatant liquid was decanted. The white product was washed with 2 ml. of CCl_4 and dried *in vacuo*, yielding 1.22 g. (38%) of $(CH_3)_3SiN_3 \cdot SnCl_4$.

TABLE II
ANALYSES OF AZIDE–LEWIS ACID ADDUCTS

Compound	Equivalent weight	
	Calcd.[a]	Found
$(CH_3)_3SiN_3 \cdot SnCl_4$	55.2	51.1, 58.6
$(CH_3)_3SiN_3 \cdot SbCl_5$	69.0	66.0, 68.2
$(CH_3)_3SiN_3 \cdot BBr_3$	91.4	96.8
$CH_3(C_6H_5)_2SiN_3 \cdot BBr_3$	122	120
$(C_6H_5)_3GeN_3 \cdot BBr_3$	149	150

[a] Calculated on the basis of complete hydrolysis, *e.g.*, $2(CH_3)_3SiN_3 \cdot SnCl_4 + 5H_2O \rightarrow (CH_3)_6Si_2O + 2HN_3 + 2SnO_2 + 8H^+ + 8Cl^-$. Equiv. wt. = (mol. wt.)/5.

Anal. Calcd. for $C_3H_9N_3Cl_4SnSi$: C, 9.59; H, 2.41; Cl, 37.7; equiv. wt., 55.2. Found: C, 9.36; H, 2.18; Cl, 35.0; equiv. wt., 58.6.

Azidotrimethylsilane–Antimony Pentachloride.—A solution of 0.375 g. (3.2 mmoles) of $(CH_3)_3SiN_3$ in 15 ml. of CCl_4 was treated with 2 ml. (15.6 mmoles) of $SbCl_5$. The solution immediately turned pale yellow. Evaporation of solvent *in vacuo* gave very pale yellow crystals, which were washed with 0.5 ml. of cold pentane–carbon tetrachloride solution and dried *in vacuo* to give 0.85 g. (64.5%) of $(CH_3)_3SiN_3 \cdot SbCl_5$.

Anal. Calcd. for $C_3H_9N_3Cl_5SbSi$: C, 8.91; H, 2.24; Cl, 41.4; equiv. wt., 69.0. Found: C, 8.86; H, 2.11; Cl, 39.9; equiv. wt., 68.2.

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Some Observations on Uranium-Nitrogen Compounds

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Although in the past few years a number of studies have been made of the uranium nitrides, some structures and stoichiometry ranges remain in doubt. Prior to a note[1] of Didchenko and Gortsema (D and G), the work and conclusions of Rundle, *et al.*,[2] had been generally accepted. Rundle found that: (a) three nitrides exist, UN (NaCl structure), U_2N_3 (Mn_2O_3 structure), and UN_2 (CaF_2 structure); (b) solid solutions are very limited in the U–UN and UN–$U_2N_2N_3$ regions but nitrides between U_2N_3 and UN_2 exist as a single phase of intermediate structure; (c) on passing N_2 or NH_3 over U or UH_3 at elevated temperatures, a product of about $UN_{1.75}$ is obtained which at temperatures above 1000° will lose N_2 giving U_2N_3 then UN. To produce UN_2 an excess pressure of 1800 p.s.i. is needed.

Several later workers[3–8] have obtained N:U ratios <1.8, from the same general preparative technique, and (when reported) have found the same structures,

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(1) R. Didchenko and F. P. Gortsema, *Inorg. Chem.*, **2**, 1079 (1963).

(2) R. E. Rundle, N. C. Baenziger, A. S. Wilson, and R. A. McDonald, *J. Am. Chem. Soc.*, **70**, 99 (1948).

(3) A. E. Austin and A. F. Gerds, "The Uranium–Nitrogen–Carbon System," B.M.I. Report 1272 (1958).

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(6) I. H. Warren, *Can. Min. Met. Bull.*, **56**, 288 (1963).

(7) P. E. Evans and T. J. Davies, *J. Nucl. Mater.*, **10**, 43 (1963).

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compounds, and lattice sizes. Vaughan,[9] however, has described a new, denser hexagonal U_2N_3 (La_2O_3 type), which occurred in a mixture of nitrides obtained on heating massive U in N_2 between 500 and 915°. Evans[10] has suggested that this is a coherency structure, but Trzebiatowski, *et al.*,[11] have found that annealing the cubic Mn_2O_3-type U_2N_3 at temperatures $>1000°$ led to a new denser U_2N_3 phase. Recently Bugh and Bauer[12] have stated that only the three compounds found by Rundle occur and that the solubility of N_2 in solid U is <1 p.p.m. They believe the solubility range of UN to be "fairly limited," which would correlate with Cater's[13] observations on US and the general belief for UC,[14] also that UN_2 needs high pressures to form although oxygen contamination may improve the stability of the higher U_2N_3–UN_2 regions.

In their note[1] D and G's observations included (a) that UN_2 could be readily prepared by passing NH_3 over UH_3 while raising the temperature to 1000°; (b) that heating UN_2 in a tantalum crucible in argon for 4 hr. at 1200 and 1900° gave $UN_{1.33}$ and $UN_{1.22}$, respectively, while heating *in vacuo* for 3 hr. at 1950° gave $UN_{1.04}$—these three latter phases had identical NaCl lattices; (c) that studies on sintered powders of UN (up to 83% density[15]) gave electrical resistivities of $0.9–1.4 \times 10^{-4}$ ohm cm. between 300 and 1300°K. and a thermoelectric power of +50 μv./°K. at room temperature rising to +100 μv./°K. at 700°K. and falling back to +50 μv./°K. at 1300°K.

The present writers, having failed to obtain such high electrical conductivities with UN compacts prepared from N_2,[16] have attempted to reproduce the results of D and G and to examine the occurrence and stability of hexagonal U_2N_3.

Experimental Method and Results

D and G[15] prepared their UN_2 by converting a weighed amount of the metal to the hydride and passing NH_3 gas (purified through BaO and a hot UN column) over it at 800–850° for 24 hr. followed by a short heating at 1000° and cooling in NH_3 to room temperature. The composition was determined by chemical analysis for U. Oxygen contents were 0.38–0.42%.

On repeating this procedure, except for the substitution of CaH_2 and UH_3 as drier and oxygen purifier, respectively, of the initial gas, the writers have obtained $UN_{1.80}$ consistently. Duplicate analyses were completed on three different batches. The use of N_2 instead of NH_3 also gave $UN_{1.80}$. At lower temperatures smaller ratios were obtained. The lattice constant of $UN_{1.80}$ was 10.568 ± 0.002 Å. The U content was determined by oxidation to U_3O_8 before exposure to the atmosphere, although other samples remained unchanged in weight on standing for 50 hr. in air. Oxygen contents were $<0.2\%$. The only visible difference between the powders was size, batches prepared from NH_3 being much finer.

Heating either powder for 1 hr. at 1100° at a pressure of $\sim 10^{-2}$ mm. led to the formation of the hexagonal La_2O_3-type U_2N_3, the ratio being confirmed by analysis. The lattice size agreed with Vaughan's figures of $a = 3.69 \pm 0.01$ and $c = 5.83 \pm 0.01$ Å. This compound was stable in air at room temperature. Between 1150 and 1200° it broke down *in vacuo* to give UN. On heating in an argon or helium atmosphere the conversion was about 50° higher. It appeared that the UN_{2-x} on losing N_2 assumed the hexagonal U_2N_3 structure directly and despite frequent attempts the writers failed to obtain a Mn_2O_3-type X-ray pattern.

For powders heated above 1200° in argon or *in vacuo*, the only product was UN. Up to 1700° the product was stoichiometric ($UN_{1.0\pm0.02}$) but above this temperature the analyses were inconsistent, some experiments giving results as low as $UN_{0.8}$ at 1850°. This latter material may, however, be $UN_{1.0} + U$ since the chemical analysis made no distinction. The UN lattice spacings were all 4.888 ± 0.002 Å. When hot pressing, at 5000 p.s.i. in molybdenum-lined graphite dies, the powders prepared *via* NH_3 gave much denser compacts than those prepared *via* N_2, 90% of the theoretical density being easily achieved at 1650°. With these compacts, the room temperature thermoelectric powers of +52 μv./°C. and electrical resistivities of $1.1–1.4 \times 10^{-4}$ ohm cm. closely approached those reported by D and G.

Conclusions

(1) The room temperature thermoelectric data of D and G can be reproduced. (2) $UN_{2.0}$ is not readily prepared at normal pressures. (3) Hexagonal U_2N_3 exists as a stable phase. (4) The existence of a UN phase with an appreciable excess of nitrogen is very doubtful.

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Silicon Imidazolidines

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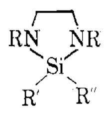
We have recently reported the preparation of spiro silaimidazolidines by the reaction of silicon tetrachloride with N,N'-disubstituted ethylenediamines.[1] We now report the synthesis of a series of monocyclic silaimidazolidines.



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