drolysis with concentrated aqueous ammonia and pyridine as already described.[6]

The dehydration studies were carried out in an apparatus which consisted of a sample tube connected to both an outlet tube and a tube with a stopcock leading to a U-trap. The trap was in turn joined to a mercury manometer. At the beginning of each of the dehydration experiments the whole system including the sample was evacuated to 0.1 mm. Subsequent manipulations involved heating the sample, collecting the water in the U-trap (cooled with liquid nitrogen), and allowing the water collected to vaporize in a portion of the system which had a known volume and which was at room temperature.

The results of a series of runs in which the sample was heated at 400° or above are given in Table I. The siloxane from the first run was not removed prior to the second run. In all but the last run the samples were heated at 460–470° for 2 to 4 hr. The sample in the final run was first heated at 330° for 2 hr. and then it was slowly heated to 400°. No observable amounts of gas were evolved below 400° but at 400° water was evolved rapidly for less than 15 min. and then the reaction ceased.

The amounts of water evolved during the formation of $HO(PcSiO)_xH$ indicate that the minimum value of x is greater than 10 ($n_2/n_1 = 0.90$), perhaps nearer 10^2 ($n_2/n_1 = 0.99$). The siloxane obtained was a blue air-stable powder. (It subsequently was shown to be soluble and stable for short periods in concentrated H_2SO_4.[7])

Elemental analysis of the siloxane did not differentiate between a short and a long chain polymer but did serve to indicate that gross decomposition had not occurred.

Anal. Calcd. for $C_{32}H_{16}N_8SiO$: C, 69.05; H, 2.90; N, 20.13. Found: C, 68.71; H, 3.07; N, 19.63. (*Anal.* Calcd. for $PcSi(OH)_2$: C, 66.88; H, 3.16; N, 19.50.)

Thermal Stability of the Polymer.—The polymer of the last run was heated further in the manometer system after evacuating the system and closing it off. The polymer withstood 520° *in vacuo* for 2.5 hr. with no detectable gas evolution and no discoloration of itself or the apparatus. Its infrared spectrum also was unchanged. At 550° for 1 hr. it produced 3.3 mm. of pressure in the apparatus along with a green sublimate on the walls of the sample tube. Another sample of the polymer when heated at 625° in the same setup gave evidence of more rapid decomposition by yielding 13.6 mm. of pressure in 15 min.

Infrared End Group Information.—It has been reported that the spectra of $PcSi(OH)_2$[5a] and $HO(PcSiO)_2H$[5b] have strong bands at 831 and 841 cm.$^{-1}$, respectively. These were assigned tentatively to the presence of the SiOH grouping. Spectra of KBr disks of the polymer showed only a very weak band at 840 cm.$^{-1}$. Spectra of a series of KBr disks with mixtures of siloxane and $PcSi(OH)_2$ containing the same total weight of phthalocyanine and KBr but with increasing amounts of $PcSi(OH)_2$ showed absorption near 831 cm.$^{-1}$ of increasing intensity (although the increase in intensity was not according to Beer's law). With high concentrations the maximum was at 831 cm.$^{-1}$, but at low concentrations it was shifted toward 840 cm.$^{-1}$. At 1.1 mole % there was a very small broad band including both 840 and 831 cm.$^{-1}$. If the 840-cm.$^{-1}$ band in the siloxane was due to OH end groups and its extinction coefficient was not much smaller than those of the 831 and 841-cm.$^{-1}$ bands in $PcSi(OH)_2$ and $HO(PcSiO)_2H$, the small intensity of this band was consistent with the small end group content indicated by the water evolution studies.

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[6] R. D. Joyner, R. G. Linck, J. Cekada, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **15**, 387 (1960); R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).

[7] J. E. Owen and M. E. Kenney, *Inorg. Chem.*, **1**, 334 (1962).

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On the Properties of Trimethyl Silyl Azide[1]

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Received May 29, 1962

West and Thayer[2] report the preparation of trimethyl silyl azide of 90% purity. We have prepared and completely characterized this compound using a modification of a synthetic technique described by Wiberg[3] for inorganic silicon azides. The modification used was similar to that employed by West and Thayer. Unlike these workers, we have been able to obtain this substance in a virtually pure state.

The compound $(CH_3)_3SiN_3$ was prepared by the treatment of trimethyl chlorosilane with sodium azide in the presence of catalytic amounts of aluminum azide using tetrahydrofuran as a solvent. The crude product can be distilled at atmospheric pressure at approximately 85°. The crude product was purified by a brief treatment with anhydrous aluminum chloride to remove traces of tetrahydrofuran,[4] followed by repetitive fractional condensation, carried out in a standard vacuum apparatus, through a series of U-tube traps maintained at −30, −50, and −196°. The product was retained at −50°.

TABLE I

	Temp., °C.				
	−30	−23	0	5	29
Obsd.	1.66	2.77	12.1	16.3	57.8
Calcd.	1.65	2.75	12.2	16.1	58.2

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[1] This research was supported in part by the Air Force Office of Scientific Research under Contract No. AF 49(638)927 and in part by a National Science Foundation Coöperative Fellowship.

[2] R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962).

[3] E. Wiberg and H. Michaud, *Z. Naturforsch.*, **9b**, 500 (1954).

[4] Extended periods of contact between trimethyl silyl azide and aluminum chloride result in a loss of trimethyl silyl azide through conversion to the chloride.

TABLE II

Freq., cm.$^{-1}$	700	755	850	1090	1145	1155	1260	1320	1430	2050	2180	2250	2600	3000	3520
Intensity	s	s	s	s	s	s	vs	vs	m	w	vs	w	w	s	m

The compound was identified by means of its analysis. *Anal.* Calcd. for $(CH_3)_3SiN_3$: Si, 24.4; C, 31.3; H, 7.9; N, 36.5. Found: Si, 24.4; C, 32.0; H, 8.1; N, 37.5. Apparent molecular weight in the vapor phase: Calcd. for $(CH_3)_3SiN_3$: 115. Found: 115.

The melting point of trimethyl silyl azide was observed to be $-95 \pm 1°$ under autogenous pressure. It exhibits the vapor pressure values reported in Table I.

The calculated values in the above table were obtained from the equation: $\log p_{\text{mm}} = (-1915/T) + 8.102$. The value of the normal boiling point extrapolated from these data is 87°.

Trimethyl silyl azide exhibits the infrared absorptions reported in Table II.

The absorption at 1320 cm.$^{-1}$ is characteristic of the symmetrical azide stretching frequency.

Like West and Thayer we were impressed by the stability of this covalent azide. The methyl derivative requires temperatures as high as 500° to induce thermal decomposition. A sample of this substance heated at 200° for 8 hr. was recovered essentially unchanged.

The photolysis of this azide produces nitrogen and a trace of hydrogen, along with a non-volatile oil which we are attempting to characterize further. Pyrolysis or similar decomposition induced by a mercury arc results in a mixture of volatile products consisting of hydrogen, nitrogen, methane, ethane, ethylene, acetylene, hydrogen cyanide, hydrazoic acid, and ammonium azide along with a non-volatile polymer. The nature of these products would raise some question as to the correctness of West and Thayer's statement that the thermal decomposition of this azide is similar to that of organic azides.

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A New Family of Rare Earth Compounds[1]

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Received February 28, 1962

During a study of the phase equilibrium relationships in rare earth sesquioxide–alumina systems,[2] a new type of rare earth compound, having an oxide ratio of 2:1 and the general formula $A_4B_2O_9$, was discovered. The only previously known rare earth aluminates have oxide ratios of 1:12, 3:5, and 1:1.

Experimental

In all instances the starting materials used in making these compounds were coprecipitated hydroxides which were dried below 400°. The initial rare earth solutions were prepared from oxides or hydroxides which were at least 99.8% pure, with most of them being 99.9% pure. X-Ray diffraction examination of the coprecipitated hydroxides indicated that nearly all of them were noncrystalline.

The compounds were formed by heating the starting materials in air for several weeks at 1400°. The products which resulted were generally too finely divided for study with the petrographic microscope and the presence of the new compound was established by powder X-ray diffractometer techniques. In a number of instances, the compound was formed from the molten state with an iridium strip-furnace; these crystals were suitable for study with the petrographic microscope.

Results

This compound, with the general formula $A_4B_2O_9$, is another double oxide of the rare earths (A) and smaller trivalent cations (B). When aluminum is the B ion, the 2:1 compound can be formed with the intermediate and small rare earths from europium through ytterbium. When gallium is the B ion, the compound can be formed with the largest of the rare earths, those of lanthanum through erbium having been synthesized. The molar composition has not been established beyond doubt because it has not been possible to make enough pure material for a chemical analysis or single crystals suitable for a structural analysis. The 2:1 composition is most likely since, under equilibrium conditions, it yields a single phase, while two phases often are detected with neighboring compositions.

X-Ray powder data for $Y_4Al_2O_9$, a typical member of this series, are given in Table I. Its optical properties are: biaxial negative, $n_\alpha \sim 1.82_6$, $n_\beta = 1.83_0$, $n_\gamma \sim 1.83_2$ (precision in $n = 0.003$), $2V > 50°$. The 2:1 rare earth aluminates

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(1) Contribution No. 61-65, College of Mineral Industries, The Pennsylvania State University.

(2) I. Warshaw and R. Roy, *Am. Ceram. Soc. Bull.*, **38**, 169 (1959).