

## Synthesis and Characterization of a New Ternary Nitride, $\text{Ca}_3\text{VN}_3$

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We have synthesized a new ternary nitride,  $\text{Ca}_3\text{VN}_3$ , from the binary nitrides at high temperature. The refined structure was solved in the  $P2_1/m$  space group with lattice constants  $a = 6.717(2)$ ,  $b = 5.064(2)$ ,  $c = 6.720(3)$  Å,  $\beta = 78.88(3)^\circ$ ,  $Z = 2$ ,  $R = 3.2\%$ , and  $R_w = 3.7\%$ . The structure is related to the recently reported  $\text{A}_3\text{MN}_3$  compounds (D. A. Vennos, M. E. Badding, and F. J. DiSalvo, *Inorg. Chem.* **29**, 4059, 1990) with sheets of  $[\text{VN}_3]^{6-}$  trigonal planar units and calcium ions.  $\text{Ca}_3\text{VN}_3$  is insulating with  $\text{V}^{3+}$  in the low-spin state,  $S = 0$ . © 1992 Academic Press, Inc.

### Introduction

Recently we have reported the synthesis and properties of alkaline earth-transition metal nitrides (*I–3*). A new structure type was observed in  $\text{Ca}_3\text{CrN}_3$  (*1*), which consists of sheets of trigonal planar  $[\text{CrN}_3]^{6-}$  units separated by Ca ions. This was the first solid state example of a transition metal in a trigonal planar environment of nitrogen atoms. The low Cr site symmetry ( $C_{2v}$ ) and high covalency of the Cr–N bonding leads to a low-spin  $\text{Cr}^{3+}$  ( $S = \frac{1}{2}$ ) state.  $\text{Ca}_3\text{CrN}_3$  is the only  $\text{Cr}^{3+}$  compound known to be low spin. Since our report of  $\text{Ca}_3\text{CrN}_3$ , more alkaline earth-transition metal nitride structures have been reported to contain this  $[\text{MN}_3]^{6-}$  unit; for example,  $\text{Ba}_3(\text{Sr}_3)\text{FeN}_3$  (*4*) and  $\text{Ca}_6\text{Fe}(\text{Ga})\text{N}_5$  (*5*). Although none of these structures are isotypic, they share a common structural feature: planes of  $[\text{MN}_3]^{6-}$  anions separated by alkaline earth cations. However, magnetic properties of these compounds were not reported.

We report the synthesis, structure, and properties of a new compound,  $\text{Ca}_3\text{VN}_3$ , containing  $[\text{VN}_3]^{6-}$  anions which are separated by  $\text{Ca}^{2+}$  ions.

### Experimental

*Starting materials.* Vanadium nitride was prepared by heating vanadium metal (2N5, –325 mesh) in flowing nitrogen (prepurified by passing through finely divided copper at  $150^\circ\text{C}$  and then activated alumina) at  $1050^\circ\text{C}$  for 15 hr. Granules of Ca (2N) were reacted at  $1000^\circ\text{C}$  for 2 days in flowing nitrogen (prepurified as above) to yield pure  $\text{Ca}_3\text{N}_2$ . The binary products were identified by X-ray powder diffraction methods. Since both  $\text{Ca}_3\text{N}_2$  and  $\text{Ca}_3\text{VN}_3$  are air-sensitive, all manipulations were carried out in an argon-filled glove box.

*Synthesis of  $\text{Ca}_3\text{VN}_3$ .*  $\text{Ca}_3\text{VN}_3$  was prepared as small single crystals by heating Ca granules in a vanadium foil boat to  $950^\circ\text{C}$  in 12 hr under Ar, soaking at  $950^\circ\text{C}$  for 18.5 hr under a backpressure of  $\text{N}_2$  which allowed slow diffusion of  $\text{N}_2$  into the Ar-filled reac-

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tion zone, followed by cooling at  $22.5^\circ/\text{hr}$  to  $500^\circ\text{C}$ , and finally cooling to room temperature in 5 hr. In order to obtain single crystals of the product, it was imperative that the heat up be under Ar and that the reaction take place slowly by indiffusion of  $\text{N}_2$ . Crystals were not obtained unless we strictly adhered to this heating schedule. The reaction yielded a distribution of brown needle crystals up to 0.5 mm in length which were used in the structure determination. Microprobe analysis of the crystals indicated the presence of Ca and V at a Ca : V ratio of approximately 3.5 : 1.

The compound was then prepared as a polycrystalline phase by heating a pressed pellet of an intimate mixture of  $\text{Ca}_3\text{N}_2$  (0.391 g, 2.64 mmol) and VN (0.172 g, 2.64 mmol) in a sealed molybdenum tube at  $1350^\circ\text{C}$  for 30 hr. X-ray powder diffraction indicated a nearly pure  $\text{Ca}_3\text{VN}_3$  with a small amount of unidentified impurity phase. The intensity of the strongest impurity diffraction peak in our best material was 13% as intense as the strongest peak of the majority phase. Other preparative conditions always produced larger quantities of the impurity phase. This product was used for both magnetic susceptibility and electrical resistivity measurements.

*Structure determination.* Unit cell symmetry and approximate lattice constants were obtained from axial photographs of a brown crystal mounted along the needle axis. A  $0.25 \times 0.045 \times 0.018\text{-mm}^3$  crystal sealed in a 0.3-mm glass capillary under argon was used in the structure determination. Data were collected on Syntex  $P2_1$  4 circle diffractometer using  $\text{MoK}\alpha$  radiation ( $0.71069 \text{ \AA}$ ) and a graphite monochromator. The unit cell dimensions were refined using 25 independent reflections in the  $2\theta$  range  $15^\circ$ – $25^\circ$ . An appreciable decay of approximately 25% was observed during data collection according to three check reflections measured every 50 reflections. This decay was monotonic in time and was likely due

to the slow decomposition of  $\text{Ca}_3\text{VN}_3$  in the X-ray beam. The data were scaled appropriately to correct for crystal decomposition using XDISK (6). The choice of space groups was reduced to  $P2_1$  and  $P2_1/m$  by systematic absences, and the structure was solved in the  $P2_1/m$  space group. Refinement in the noncentrosymmetric space group resulted in no significant change in the structure or  $R$  factors. An empirical absorption correction was applied (the psi scan) and after averaging symmetry related reflections, 468 unique reflections with  $F > 3\sigma(F)$  were used to solve the structure.

The structure determination and refinement were performed using Nicolet SHELXTL Plus (6) software running on a Microvax computer. The function minimized in the least squares refinement was  $\sum w(|F_o| - |F_c|)^2$  with  $w = \sigma^{-2}$ . Anisotropic refinement of all atoms (43 parameters) converged to  $R = 3.2\%$  and  $R_w = 3.7\%$ . Table I summarizes data collection parameters. Atomic positions are listed in Table II.

After the structure was solved, the powder patterns taken on a Scintag XDS2000 diffractometer could be indexed. The observed pattern minus the impurity peaks matched that calculated by Lazy Pulverix (7) on the basis of the single crystal data.

*Electrical properties.* The resistance of a pellet of  $\text{Ca}_3\text{VN}_3$  was measured in a small press inside the glove box. The two pistons were electrically insulated from each other, allowing a two-point measurement of the resistance. The resistance determined on a pellet 4.5 mm in diameter and approximately 3 mm thick was larger than  $30 \text{ M}\Omega$  (the upper limit of our measurement apparatus) yielding a lower limit to the resistivity on the order of  $10^7 \text{ }\Omega\text{cm}$ .

*Magnetic susceptibility.* The magnetic susceptibility of the sample was measured by the Faraday technique as previously described (8). The susceptibility of a polycrystalline sample sealed in a thin-walled high-purity quartz tube was determined to be field

TABLE I  
SUMMARY OF CRYSTAL AND DIFFRACTION  
DATA FOR  $\text{Ca}_3\text{VN}_3$

Space group	$P2_1/m$
Z	2
$a, b, c$ , (Å)	6.717(2), 5.064(2), 6.720(3)
$\beta$ (deg)	78.88(3)
$V$ (Å <sup>3</sup> )	224.3(2)
Density, calc (g/cm <sup>3</sup> )	3.157
T (K) data collection	298
Crystal dimensions (mm)	0.25 × 0.045 × 0.018
Absorption coeff (mm <sup>-1</sup> )	5.334
2 $\theta$ max (deg), scan type	55, $\omega - 2\theta$
Octants collected	$hkl; -h-kl; -hkl; h-kl$
X-ray radiation	$\text{MoK}\alpha$
Monochromator	Graphite
Measured reflections	1109
Observed reflections <sup>a</sup>	468
Independent reflections	572
$F(000)$	208
Number of parameters	43
Largest diff peak ( $e^-/\text{Å}^3$ )	0.73
$R^b, R_w^c$ (%)	3.2, 3.7

<sup>a</sup>  $F_o > 3\sigma(F_o)$ .

<sup>b</sup>  $R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ .

<sup>c</sup>  $R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum(w|F_o|^2)]^{1/2}$ ,  $w = \sigma(F_o)^{-2}$ .

independent at room temperature, indicating that no ferromagnetic impurities were present. Figure 1 shows the results of a temperature-dependent study between 4 and 300 K at a magnetic field strength of 13.6 kG.

TABLE II  
POSITIONAL PARAMETERS FOR  $\text{Ca}_3\text{VN}_3$

Atom	Site	x	y	z
V	2e	0.8028(2)	0.25	0.3028(2)
Ca(A)	2e	0.3915(2)	0.25	0.8915(2)
Ca(B)	2e	0.9021(2)	0.25	0.8297(2)
Ca(C)	2e	0.3298(2)	0.25	0.4022(2)
N(A)	2e	0.6268(9)	0.25	0.1271(9)
N(B)	2e	0.3180(10)	0.75	0.4315(9)
N(C)	2e	0.9317(10)	0.75	0.8159(9)

## Results and Discussion

The structure of  $\text{Ca}_3\text{VN}_3$  (Fig. 2) consists of trigonal planar  $[\text{VN}_3]^{6-}$  anions separated by calcium ions. A view down the unique axis clearly shows the stacking arrangement of the eclipsed units. Neighboring  $[\text{VN}_3]^{6-}$  anions are displaced by  $\frac{1}{2}$  in  $z$  and the orientation of the triangle is reversed (Fig. 3). Although the three V–N bond distances are within 0.016 Å of each other, the bond angles reduce the symmetry of the anion to  $C_{2v}$ , similar to  $\text{Ca}_3\text{CrN}_3$ . A list of relevant bond distances and angles can be found in Table III.

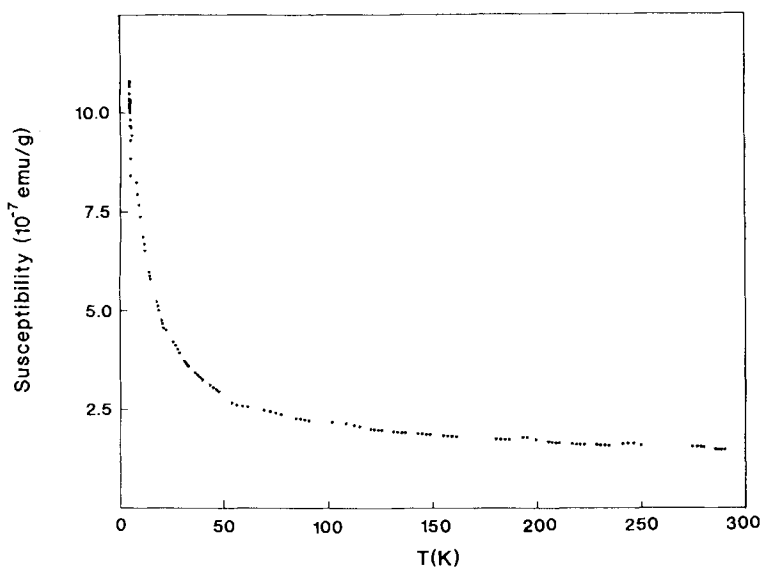


FIG. 1. Temperature dependence of the magnetic susceptibility of  $\text{Ca}_3\text{VN}_3$ .

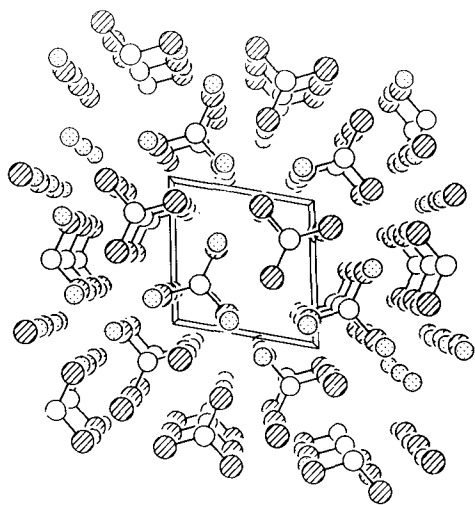


FIG. 2. A view of  $\text{Ca}_3\text{VN}_3$  down the unique axis. The Ca atoms are dotted circles, the V atoms are open circles, and N atoms are completely hatched circles.

The average V–N distance (1.83 Å) is close to the Cr–N distance in  $\text{Ca}_3\text{CrN}_3$ , indicating multiple metal–nitrogen bonding. Each Ca atom is coordinated by three nitrogen atoms and two calcium atoms in the same plane, and by two nitrogen atoms above and below that plane at  $2.54 \pm 0.01$  Å. The three coordinated nitrogen atoms subtend an angle of  $170^\circ$ , creating a quite asymmetric environment about the central

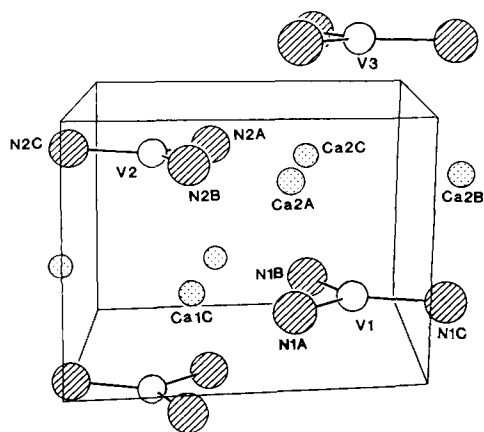


FIG. 3. A view perpendicular to the unique axis shows the stacking arrangement and the labels used to identify atoms in Table III. Some atoms in the unit cell are not included for clarity.

Ca. The in-plane Ca–N distances for each of the three inequivalent Ca's are: Ca(A) 2.443, 2.625, and 2.634 Å; Ca(B) 2.447, 2.503, and 2.818 Å; Ca(C) 2.445, 2.494, and 2.804 Å. The shorter Ca–N distances are comparable to those observed in  $\text{Ca}_3\text{N}_2$  (2.46 Å),  $\text{Ca}_3\text{BiN}$  (2.45 Å) (3), and  $\text{CaNiN}$  (2.50 Å) (2). The closest Ca–Ca distance between planar units (3.39 Å) is slightly longer than that in  $\text{Ca}_3\text{N}_2$  (3.16 Å) (9).

The V–V distances are much too long for

TABLE III  
IMPORTANT DISTANCES (Å) AND ANGLES (Degrees) IN  $\text{Ca}_3\text{VN}_3$

Bond distances		Bond angles	
V(1)–V(2)	5.086(2)	N(1C)–V(1)–N(1A)	114.8(3)
V(1)–V(3)	5.064(2)	N(1C)–V(1)–N(1B)	130.7(3)
V(1)–Ca(2C)	3.232(2)	N(1B)–V(1)–N(1B)	114.8(3)
V(1)–Ca(2A)	3.237(2)		
V(1)–Ca(2B)	3.233(2)		
V(1)–N(1B)	1.820(6)		
V(1)–N(1A)	1.827(7)		
V(1)–N(1C)	1.811(6)		
Ca(2A)–N(2B)	2.616(6)		
Ca(2A)–N(1A)	2.539(1)		
Ca(2A)–N(1A)	2.443(6)		
Ca(1C)–N(1A)	2.445(6)		

any metal–metal interactions (shortest distance 5.06 Å from V1 to V3 in Fig. 3). As expected from the long V–V distances,  $\text{Ca}_3\text{VN}_3$  is insulating. The susceptibility can be fit with a simple Curie–Weiss expression,

$$\chi_g = \chi_o + C_g/T + \theta,$$

and we obtain  $\chi_o = 1.24 \times 10^{-7}$  emu/g,  $C_g = 9.04 \times 10^{-6}$  emu/g, and  $\theta = 5$  K (with a mean square deviation of 2.1%). The small value of  $C_g$  indicates that the temperature dependence arises from a paramagnetic impurity. If the V had a moment appropriate to  $\text{V}^{3+}$  ( $S = 1$ ), the value of  $C_g$  would be  $4.70 \times 10^{-3}$  emu/g. We conclude that V in  $\text{Ca}_3\text{VN}_3$  and in the impurity phase present in the sample must be nonmagnetic. Since an unknown impurity is present, a definitive value of  $\chi_o$  for  $\text{Ca}_3\text{VN}_3$  cannot be determined from this measurement. The  $S = 0$  assignment for  $\text{V}^{3+}$  in  $\text{Ca}_3\text{VN}_3$  is consistent with the low site symmetry and the low-spin configuration in  $\text{Ca}_3\text{CrN}_3$ .

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