

# Chemical Synthesis and Structural Investigation of a New Ternary Nitride, CrWN<sub>2</sub>

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**A new ternary nitride, CrWN<sub>2</sub>, has been synthesized by the ammonolysis of a chemically derived metallorganic precursor. The structure is trigonal in the space group R3 (146) with Z=3, as determined from powder X-ray diffraction and Rietveld refinement of the resulting diffraction pattern. The refinement converged with  $R_{wp}=0.1313$ ,  $R_p=0.0962$ ,  $R_1=0.0219$ , and  $\chi^2=1.82$ . Using hexagonal notation, the unit cell of CrWN<sub>2</sub> has lattice parameters of  $a=2.8561(7)$  Å and  $c=15.606(7)$  Å. The compound is isostructural with LiMoN<sub>2</sub>, the ideal structure consisting of alternating close-packed layers of chromium in octahedral coordination with nitrogen and tungsten in trigonal prismatic coordination with nitrogen.** © 1997 Academic Press

## INTRODUCTION

In the past several years, a growing number of new ternary and higher order nitride compounds have been identified (1). The list of compounds discovered includes alkali- and alkaline-earth-transition metal nitrides, such as Ca<sub>3</sub>MN<sub>3</sub> ( $M = \text{Cr, V, Co}$ ) (2, 3, 4), Ca<sub>3</sub>MN ( $M = \text{P, As, Sb, Bi, Ge, Sn, Pb}$ ) (5), MNiN ( $M = \text{Ca, Sr, W}$ ) (6, 7), MTaN<sub>2</sub> ( $M = \text{Na, K, Rb, Cs}$ ) (8), Ba<sub>3</sub>MN<sub>4</sub> ( $M = \text{Mo, W}$ ) (9), and LiMN<sub>2</sub> ( $M = \text{Mo, W}$ ) (10, 11), and ternary transition metal nitrides, such as M<sub>3</sub>Mo<sub>3</sub>N ( $M = \text{Fe, Co, Ni}$ ) (12, 13) and MWN<sub>2</sub> ( $M = \text{Mn, Fe, Co, Ni}$ ) (14, 15, 16). In the last example, the ternary tungsten nitrides all crystallize in a layered hexagonal structure, similar to that of LiMoN<sub>2</sub> (10), in which the two metal species sit in alternating layers, each separated by a layer of nitrogen atoms. However, as pointed out by Herle *et al.* (16), there appears to be two variants in the MWN<sub>2</sub> structure which may be dependent on the electronic nature of the first row transition metal element involved. They reported that FeWN<sub>2</sub> and MnWN<sub>2</sub> are isostructural with each other with a “*c*” parameter approximately 1.2 Å larger than that for either CoWN<sub>2</sub> or NiWM<sub>2</sub>, which are also isostructural with each other. More

recently, however, Bem *et al.* (15) have resolved the FeWN<sub>2</sub> structure using a slightly different indexing scheme. They report a *c* parameter of 10.9320(4) Å for FeWN<sub>2</sub>, which differs by over 4 Å from the *c* value for the CoWN<sub>2</sub> structure and is likely due to differences in the cation stacking pattern.

Most of the above compounds have been prepared using traditional solid state synthesis approaches. In an attempt to identify new chemical based molecular routes for synthesizing these ternary transition metal nitrides, we have developed an alternative metallorganic synthesis technique (17) and have used it to prepare a fifth member of this family, CrWN<sub>2</sub>. This nitride displays “*d*” spacings and lattice parameters similar to those published for CoWN<sub>2</sub> and NiWN<sub>2</sub>. Thus we suspect that all three compounds exhibit the same crystal structure. In this paper, we describe our synthesis strategy and report on the details of the crystallographic structure of CrWN<sub>2</sub>, contrasting them with the recent structural findings on FeWN<sub>2</sub>.

## EXPERIMENTAL PROCEDURE

The synthesis procedure is comprised essentially of three sequential reaction steps: 1, the formation of a polymeric liquid precursor by the chelation of transition metal chloride species previously dissolved in acetonitrile; 2, the hydrolysis of this precursor to form a metallorganic hydroxide; and 3, the pyrolysis and ammonolysis of the hydroxide precursor to yield the ternary nitride (18).

### (A) Materials and Equipment

The inorganic metal chlorides, CrCl<sub>3</sub>·6H<sub>2</sub>O (99.995%, Aldrich) and WCl<sub>6</sub> (99.9 + %, Aldrich), were used as received. The solvent, HPLC grade acetonitrile (Fisher Scientific), and the chelating agent, triethylamine (99 + %, Sigma), were used without further purification. The water used for hydrolysis was doubly distilled and deionized to a resistivity of 18.3 Mohm-cm or greater. Electronic grade ammonia (Matheson Gas) was used for all the pyrolysis and ammonolysis treatments conducted on the mixed-metal

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precursors. All chemical manipulations were conducted in an argon-filled glovebox ( $O_2$  and  $H_2O \leq 5$  ppm; Vacuum Atmospheres) or under a protective stream of ultra high purity (UHP) nitrogen unless otherwise noted. All glassware used was acid washed with NoChromix and oven-dried prior to use.

### (B) Precursor Synthesis

The Cr–W metallorganic precursor and  $CrWN_2$  compound were prepared using a procedure similar to that which was reported by us for the preparation of other ternary transition metal nitride powders (17). Figure 1 shows a schematic of the procedure followed in this work. In the glovebox, 4–10 g samples of the two metal chlorides containing the individual metals in a 1:1 stoichiometric

molar ratio were measured into a 500 ml, three-necked round bottom flask. The flask was then loaded with a Teflon-coated magnetic stir bar and approximately 100 ml of acetonitrile. After appropriately sealing the flask, it was transferred to a fume hood and connected to the UHP nitrogen line. Once the chlorides were thoroughly dissolved, triethylamine was added to the solution through a septum using a syringe and needle. The amount of triethylamine needed for chelation was determined assuming complete replacement of chlorine from both metal chloride species by triethylamine. Since the chelation reaction of triethylamine is in general exothermic, and some hydrogen chloride gas does evolve, the triethylamine was added at a slow rate of approximately 2 ml/min. In this case, for the Cr–W–N system, the chelation reaction occurs nearly instantaneously as evidenced by color changes in the acetonitrile solution.

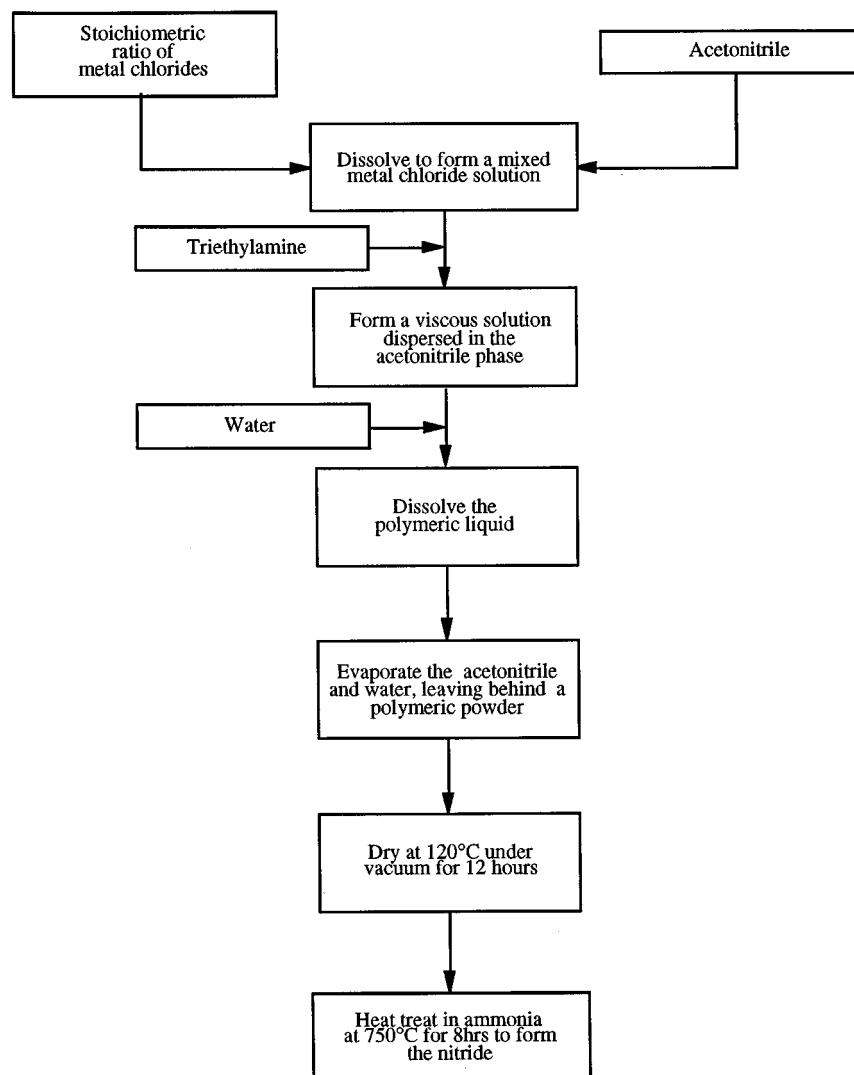


FIG. 1. Flowsheet showing the procedure used to synthesize the ternary nitride in this study.

After the addition of triethylamine was complete, the flask was shaken to ensure complete reaction and to promote mixing of the different species.

Once the polymeric liquid precursor was prepared, the flask was opened and approximately 100 ml of water was added to the parent liquor with vigorous stirring. The entire liquor was then heated to evaporate off the acetonitrile and to force the hydrolysis reaction. Once the reaction was complete, the excess water was evaporated, leaving behind dark green, highly agglomerated powder. The powder was further dried at 120°C under a vacuum for approximately 12 h, after which it was lightly crushed using an agate mortar and pestle.

### (C) Pyrolysis and Ammonolysis

A sample of each powder precursor was weighed into a high purity aluminum nitride crucible and placed into a 2½ inch diameter quartz flow-through tube furnace. The back end of the tube furnace was connected to a mineral oil bubbler and the front end was connected to the gas line. Prior to initiating the heat treatment, the tube was purged for twenty minutes with pre-pure nitrogen, then purged for another ten minutes with ammonia gas. The powder samples were fired in 120 ml/min flowing ammonia under the following sequence of heat treatment conditions: 1, ramp from room temperature to 120°C at 15°C/min and hold at 120°C for 1 h; 2, ramp from 120°C to 750°C at 3°C/min and hold at 750°C for 8 h; and 3, allow the samples to furnace cool.

### (D) Chemical Analysis and Crystal Structure Determination

Each powder product formed by ammonolysis was examined by energy dispersive X-ray analysis using an EDAX, DX-4 analyzer to semiquantitatively verify the ratio of the metal species in the compounds. Once verified, quantitative chemical analyses of the powders were conducted by Galbraith Laboratories (Knoxville, Tennessee). They employed a wet chemical analysis technique to determine the concentration of the metal species, combustion analyses to evaluate the nitrogen, carbon, and oxygen contents, and ion chromatography to determine the chlorine level.

In preparing the samples for X-ray analysis, the powders were mixed with acetone to form a slurry and ground for approximately 15 min using an agate mortar and pestle. The samples were then side loaded into standard brass sample holders for X-ray diffraction analysis. The diffraction measurements were conducted on a Rigaku  $\theta$ - $\theta$  diffractometer with graphite monochromated CuK $\alpha$  radiation using the following settings: step scan; 5–130° range, 0.02° step size, and 10 s collection time. Prior to the X-ray measurements, the diffractometer was aligned using an NBS silicon standard

for accurate peak positions. An initial set of lattice parameters was obtained by least-squares refinement of the angular positions of the eighteen reflections obtained in the  $2\theta$  range of  $30^\circ \leq 2\theta \leq 85^\circ$ . Rietveld refinements were then carried out using the RIETAN-94 (19, 20) program over the entire 5–130° range of the X-ray diffraction data. A pseudo-Voigt function (21) was employed to model the peak shapes. The parameters which were refined included: the positional coordinates of nitrogen and chromium, the lattice parameters, and the thermal displacement factors for each atom.

## RESULTS AND DISCUSSION

Semiquantitative analysis of several powder samples using EDAX consistently gave Cr/W ratios of near unity, in good agreement with the expected value of 1.0. Similarly, results from the chemical analyses, shown in Table 1, verify the stoichiometry of the ammonolyzed Cr–W compound to be CrWN<sub>2</sub>. The nitrogen deficiency observed in this compound is similar to that reported for other ternary transition metal nitrides, such as FeWN<sub>2</sub> and MnMoN<sub>2</sub> (15). It should be noted that all the impurities (O, C, Cl) that would normally be expected to be found in high levels in a product derived from this type of chemical synthesis approach are all relatively low in concentration (below 1000 ppm). Unlike the ternary alkali metal-transition metal nitrides, CrWN<sub>2</sub> appears to be quite stable to moisture and oxygen, as verified by the identical diffraction pattern and constant lattice parameters obtained even after atmospheric exposure of the compound for several months.

The observed  $d$  spacings and intensities from the powder XRD pattern for CrWN<sub>2</sub> are displayed in Table 2. The pattern was indexed to a hexagonal unit cell with  $a = 2.8561(7)$  Å and  $c = 15.606(7)$  Å and is similar to that reported for LiMoN<sub>2</sub> (10), with systematic absences in the (10  $l$ ) and the (00  $l$ ) lines. This corresponds to a choice of two space groups for the structure:  $R\bar{3}m$  (No. 166) and  $R3$  (No. 146). The only difference between these two space groups is the nitrogen coordination about the tungsten atoms;  $R\bar{3}m$  places the tungsten in octahedral holes, while  $R3$  places it in

**TABLE 1**  
**Chemical Analysis of the Ammonolyzed Cr–W Compound**

Concentration (atom % or ppm)	Sample 1	Sample 2	Sample 3
% Cr	25.37	25.66	25.41
% W	25.13	25.18	25.21
% N	49.49	49.15	49.36
ppm C	968	852	981
ppm O	526	687	743
ppm Cl	733	691	547

**TABLE 2**  
X-ray Powder Diffraction Data of CrWN<sub>2</sub>

(hkl)	d spacing (Å)	relative intensity
003	5.202	80
006	2.601	29
101	2.443	100
012	2.358	52
104	2.089	32
015	1.939	39
009	1.734	6
107	1.656	19
018	1.532	9
110	1.428	26
113	1.377	15
1010	1.320	5
0012	1.301	5
116	1.252	19
201	1.233	14
0111	1.231	8
022	1.222	5
205	1.150	8
119	1.102	6
027	1.082	7

trigonal prismatic sites (10). A series of preliminary refinements comparing each space group with the experimental data indicated that the best fit was achieved with the R3 space group. Thus, further structural analysis and refinement was limited to this space group only. Once the crystal structure was refined, bond lengths for the various nearest neighbor combinations were calculated to determine the validity of the structure. The refinement converged with  $R_{wp} = 13.13\%$ ,  $R_p = 9.62\%$ ,  $R_1 = 2.19\%$ , and  $\chi^2 = 1.82$ . The results of the refinement and the atomic positions are listed in Table 3. Selected bond distances and angles are given in Table 4. Figure 2 shows a comparison of the experimental plot with that obtained by refinement, along with the calculated residuals. Figure 3 shows a model of the unit cell and the arrangement of the stacked polyhedra consistent with the Rietveld refinement and XRD data.

The proposed structure determined for CrWN<sub>2</sub> is isostructural with LiMoN<sub>2</sub>, consisting of alternating hexagonal close-packed sheets of chromium, nitrogen, tungsten, nitrogen, etc., with the chromium atoms sandwiched within the octahedral interstices of the two adjacent nitrogen layers and the tungsten atoms sitting in trigonal prismatic coordination between the two neighboring nitrogen layers. Referring to the unit cell in Fig. 3(a), the arrangement of the layers along the *c*-axis can be represented as *AbCaCaBcBcAbA*, where the upper case letters, *A*, *B*, and *C*, represent the hcp metal layers and the close-packed nitrogen layers are equated with the lower case letters, *a*, *b*, and *c*. Alternatively, the structure can be viewed as a set of polyhedra, with layers of edge-sharing CrN<sub>6</sub> octahedra alternating with layers of

**TABLE 3**  
Results of the X-ray Rietveld Refinement for CrWN<sub>2</sub> in Space Group R3

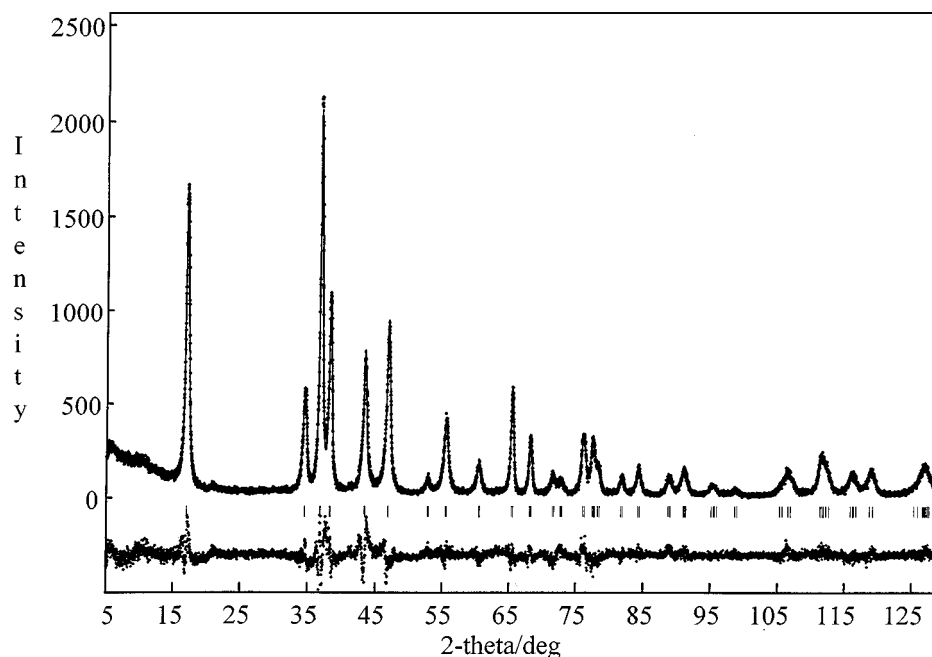
Formula weight	263.86				
<i>a</i> , <i>c</i> (Å)	2.8561(7), 15.606(7)				
<i>V</i> (Å <sup>3</sup> )	110.2(5)				
<i>Z</i>	3				
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	11.920				
<i>T</i> (°C)	23 ± 1				
Powder color	Black				
2 $\theta$ max (deg)	130.0				
X-ray radiation ( $\lambda$ )	CuK $\alpha_1$ ( $\lambda = 1.5406$ Å)				
Monochromator	Graphite				
<i>R</i> <sub>wp</sub>	0.1313				
<i>R</i> <sub>p</sub>	0.0962				
<i>R</i> <sub>1</sub>	0.0219				
$\chi^2$	1.82				
Atomic parameters for CrWN <sub>2</sub>					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	100 <i>U</i> <sub>iso</sub> (Å <sup>2</sup> )	Occupancy
Cr	0	0	0.8251(7)	0.6(0)	1
W	0	0	0	0.1(5)	1
N(1)	0	0	0.2629(6)	1.8(4)	1
N(2)	0	0	0.4068(5)	1.6(6)	1

edge-sharing WN<sub>6</sub> trigonal prisms, stacked in the following order along the *c*-axis: *AA'BB'CC'*, where *A*, *B*, and *C* are the CrN<sub>6</sub> layers and *A'*, *B'*, and *C'* are the WN<sub>6</sub> layers.

Bem *et al.* reported a similar structural arrangement for FeWN<sub>2</sub>, ideally consisting of alternating layers of edge-shared FeN<sub>6</sub> octahedra and edge-shared WN<sub>6</sub> trigonal prisms. However, there is a difference of 4.675 Å in the *c* parameter, or roughly two metal and two nitrogen layers, between this structure and that proposed for CrWN<sub>2</sub>, which results from a different stacking sequence for FeWN<sub>2</sub>: *AbAbAcAcA*. Note that in FeWN<sub>2</sub> the metal layers are stacked along the *c*-axis directly upon one another ad infinitum and the nitrogen layers are stacked in an *A, B, A, B*, arrangement, thus defining a hexagonal unit cell. In CrWN<sub>2</sub>, the metal layers are stacked upon each other only in pairs and these pairs are shifted over each other in

**TABLE 4**  
Selected Bond Distances and Angles in CrWN<sub>2</sub>

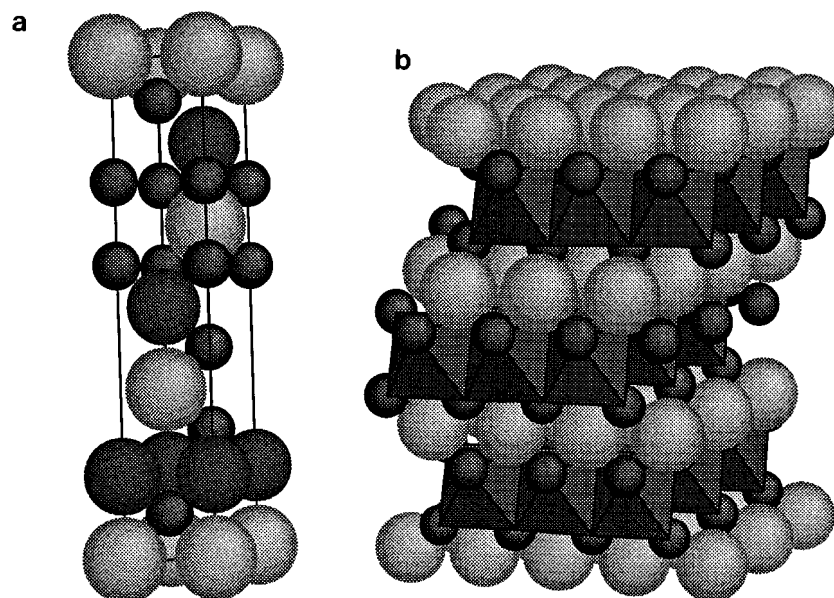
Bond distances (Å)		Bond angles (°)	
Cr–Cr	2.856(2)	N(1)–Cr–N(1)	76.09
Cr–N(1)	2.318(9)	N(1)–Cr–N(2)	80.65
Cr–N(2)	2.116(3)	N(2)–Cr–N(2)	84.95
W–W	2.856(2)	N(1)–W–N(1)	87.86
W–N(1)	1.981(3)	N(1)–W–N(2)	68.59
W–N(2)	2.008(9)	N(2)–W–N(2)	89.43
N(1)–N(2)	2.245(6)		



**FIG. 2.** The observed (dotted) and calculated (solid) X-ray diffraction profile for CrWN<sub>2</sub>. Tic marks below the diffractogram represent the allowed Bragg reflections. The residual line is located at the bottom of the figure.

a manner similar to that seen in fcc stacking: *A, B, C, A, B, C...*, where *A, B,* and *C* now represent paired chromium–tungsten close-packed layers. Likewise, if the nitrogen layers are viewed separately, they too are stacked as

coplanar pairs, with the pairs arranged in an *A, B, C* array. Because of the *A, B, C* stacking sequence, the layers do not define a hexagonal crystal structure, but a trigonal structure instead.



**FIG. 3.** Proposed structure for CrWN<sub>2</sub>: (a) unit cell and (b) extended polyhedra model. In (a), the dark gray, large spheres represent the chromium atoms, the light gray, large spheres represent the tungsten atoms, and the small, dark gray spheres represent the nitrogen atoms. In (b), the octahedral chromium positions are shown as filled polyhedra. The tungsten and nitrogen positions are indicated again by the large and small spheres, respectively.

The metal–metal and metal–nitrogen bond distances found in CrWN<sub>2</sub> are similar to those found in other ternary transition metal nitrides in this family. The Cr–N bond distances in CrWN<sub>2</sub> of 2.318(9) Å and 2.116(3) Å compare well with that for the Fe–N bond FeWN<sub>2</sub>, 2.145(5) Å (15). Likewise, the W–N bonds in CrWN<sub>2</sub> of 1.981(3) Å and 2.008(9) Å are similar to that found in β: MnWN<sub>2</sub> of 2.258(2) Å (22) and in FeWN<sub>2</sub>, 2.156(5) Å (15). As noted by Bem *et al.* for FeWN<sub>2</sub>, the metal–nitrogen bond lengths in these ternary transition metal nitrides are significantly longer in comparison to bond lengths existing in the alkali- and alkaline-earth–transition metal nitrides. For example, the Cr–N bond distances in Ca<sub>3</sub>CrN<sub>3</sub> (2), U<sub>2</sub>CrN<sub>3</sub> (23), Th<sub>2</sub>CrN<sub>3</sub> (23), and Ce<sub>2</sub>CrN<sub>3</sub> (24) range from 1.730(12) to 1.932(7) Å and the W–N bond distances in Na<sub>3</sub>WN<sub>3</sub> (25) and Ba<sub>3</sub>WN<sub>4</sub> (9) range from 1.78(1) to 1.93(1) Å, nearly 10–20% shorter than the Cr–N and W–N bonds in CrWN<sub>2</sub>. The longer metal–nitrogen bond lengths imply that the bonding in CrWN<sub>2</sub> is at least partially covalent. Similarly, the separation between opposing sheets of nitrogen atoms is 2.245(6) Å which is shorter than the in-plane N–N separation of 2.856(2) Å. This observation also suggests that the metal–nitrogen bond is substantially covalent in nature and implies that there may be direct bonding between opposing nitrogen layers. Electronic structure calculations reported by Singh (26) on LiMoN<sub>2</sub> support this conclusion. It was found that this prototype structure for CrWN<sub>2</sub> consists of strongly covalent MoN<sub>2</sub> sheets with unusually pronounced direct N–N bonding across the trigonal prismatic coordinated molybdenum atoms. Further, it was determined that the lithium layers interact ionically with the MoN<sub>2</sub> sheets to form the three-dimensional crystal and band structures. Similar electronic structure calculations could determine the nature of bonding of the Cr layers to the WN<sub>2</sub> sheets in CrWN<sub>2</sub>.

### CONCLUSIONS

We have synthesized a new ternary transition metal nitride, CrWN<sub>2</sub>, by the ammonolysis of a metallorganic hydroxide precursor at 750°C. This nitride is found to be isostructural with LiMoN<sub>2</sub>, crystallizing in a trigonal structure which consists of alternating layers of chromium in octahedral coordination with nitrogen and tungsten in trigonal prismatic coordination with nitrogen. On the basis of the reported indexing of CoWN<sub>2</sub> and NiWN<sub>2</sub>, both of these compounds are expected to be isostructural with CrWN<sub>2</sub>. The other two known members of this family of nitrides, MnWM<sub>2</sub> and FeWN<sub>2</sub>, have been found to exhibit a similar layered, though hexagonal based, structure. The difference between the CrWN<sub>2</sub> and FeWN<sub>2</sub> crystal structures stems from a basal shift in the metal layers of CrWN<sub>2</sub> as they are stacked along the *c*-axis direction. No such shift occurs in the FeWN<sub>2</sub> structure, as the metal layers are stacked dir-

ectly one upon another. This shift gives rise to a longer *c* parameter to accommodate the longer repeat distance in the stacking sequence of CrWN<sub>2</sub>. It is expected that as more of these ternary transition metal nitrides are synthesized, a wide variety of stacked layer arrangements similar to the crystal structures described above will be found.

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### REFERENCES

1. F. J. DiSalvo and S. J. Clarke, *Curr. Opin. Solid State Mat. Sci.* **1**, 241 (1996).
2. D. A. Vennos, M. E. Badding, and F. J. DiSalvo, *Inorg. Chem.* **29**, 4059 (1990).
3. D. A. Vennos and F. J. DiSalvo, *J. Solid State Chem.* **98**, 318 (1992).
4. T. Yamamoto, S. Kikkawa, and F. Kanamaru, *J. Solid State Chem.* **119**, 161 (1995).
5. M. Y. Chern, D. A. Vennos, and F. J. DiSalvo, *J. Solid State Chem.* **96**, 415 (1992).
6. M. Y. Chern and F. J. DiSalvo, *J. Solid State Chem.* **88**, 459 (1990).
7. A. Gudat, S. Haag, R. Kniep, and A. Rabenau, *J. Less-Common Met.* **159**, L29 (1990).
8. H. Jacobs and E. von Pinkowski, *J. Less-Common Met.* **146**, 147 (1989).
9. A. Gudat, P. Hohn, R. Kniep, and A. Rabenau, *Z. Naturforsch. B* (1992).
10. S. H. Elder, L. H. Doerrer, F. J. DiSalvo, J. B. Parise, D. Guyomard, and J. M. Tarascon, *Chem. Mater.* **4**, 928 (1992).
11. P. S. Herle, M. S. Hegde, N. Y. Vasanthacharya, J. Gopalakrishnan, and G. N. Subbanna, *J. Solid State Chem.* **112**, 208 (1994).
12. J. D. Houmes, D. S. Bem, and H.-C. zur Loye, in "MRS Symposium Proceedings: Covalent Ceramics II: Non-Oxides" (A. R. Barron, G. S. Fischman, M. A. Fury, and A. F. Hepp, Eds.), Vol. 327, p. 153. Materials Research Society, Boston, 1993.
13. D. S. Bem, C. P. Gibson, H.-C. zur Loye, *Chem. Mater.* **5**, 397 (1993).
14. D. S. Bem, J. D. Houmes, and H.-C. zur Loye, in "Materials Science Forum: Soft Chemistry Routes to New Materials: Chimie Douce" (J. Rouxel, M. Tournoux, and R. Brec, Eds.), Vols. 152–153, p. 183. Trans Tech Publications, Switzerland, 1993.
15. D. S. Bem, C. M. Lampe-Onnerud, H. P. Olsen, and H.-C. zur Loye, *Inorg. Chem.* **35**, 581 (1996).
16. P. S. Herle, N. Y. Vasanthacharya, M. S. Hegde, and J. Gopalakrishnan, *J. Alloys and Comp.* **217**, 22 (1995).
17. K. S. Weil and P. N. Kumta, *Mat. Sci. Eng. B* **38**, 109 (1996).
18. M. A. Sriram, K. S. Weil, and P. N. Kumta, *J. Appl. Organomet. Chem.*, in press.
19. F. Izumi, in "The Rietveld Method" (R. A. Young, Ed.), Chap. 13. Oxford University Press, Oxford, 1993.
20. Y.-I. Kim and F. Izumi, *J. Ceram. Soc. Jpn.* **102**, 401 (1994).
21. P. Thompson, D. E. Cox, and J. B. Hastings, *J. Appl. Cryst.* **20**, 79 (1987).
22. D. S. Bem and H.-C. zur Loye, previously unpublished results briefly reported in reference 15.
23. R. Benz and W. H. Zachariasen, *J. Nucl. Mat.* **37**, 109 (1970).
24. S. Broll and W. Jeitschko, *Z. Naturforsch.* **50b**, 905 (1995).
25. D. Ostermann, U. Zachwieja, and H. Jacobs, *J. Alloys Comp.* **190**, 137 (1992).
26. D. J. Singh, *Phys. Rev B* **46**, 9332 (1992).