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Structure of Ta₃N₅ at 16 K by Time-of-Flight Neutron Diffraction

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Abstract. Polycrystalline tritantalum pentanitride (Ta₃N₅) has been prepared from the reaction of TaCl₅ with ammonia, and its structure has been refined from time-of-flight neutron diffraction data. $M_r = 612.88$, orthorhombic, *Cmcm*, $a = 3.8862$ (1), $b = 10.2118$ (2), $c = 10.2624$ (3) Å, $V = 407.26$ (3) Å³, $Z = 4$, $D_x = 9.99$ g cm⁻³, neutron time-of-flight, Rietveld refinement, wR_p , R_p , reduced $\chi^2 = 0.061$, 0.043, 4.21 for data collected at 16 K. Ta₃N₅ crystallizes with the pseudobrookite (Fe₂TiO₅) structure. Irregular TaN₆ octahedra share edges and corners.

Introduction. Several authors have mapped out the phase diagram of the Ta–N system (Brauer & Zapp, 1954; Schönberg, 1954*b*). γ -Ta₂N crystallizes with close-packed metal atoms; the N atoms fill the octahedral sites. ϵ -TaN has the B35 structure type which consists of very densely packed metal atoms; N atoms fill deformed octahedral holes (Brauer & Zapp, 1953; Christensen & Lebeck, 1978). Ta₄N₅ and Ta₅N₆ can be prepared as thin films and have been analyzed by electron diffraction (Terao, 1971). At elevated temperatures, δ' -Ta_nN_x forms with the rock-salt structure (Gatterer, Dufek, Ettmayer & Kieffer, 1975). Thin films of δ -Ta_nN_{0.8–0.9} are reported with the hexagonal WC structure (Brauer & Mohr-Rosenbaum, 1971). Some of these interstitial nitrides

are probably contaminated with traces of oxygen and carbon.

The nitrides of most interest to us are the fully nitrated stoichiometric ones. TaON forms with the baddelyite (ZrO₂) structure in which Ta atoms are irregularly seven coordinated; oxygen and nitrogen are regularly three and four coordinated (Armytage & Fender, 1974; Brauer, Weidlein & Strähle, 1966; Weishaupt & Strähle, 1977). The compounds MTaN₂ ($M = K, Rb, Cs$) form with Ta in four coordination in the filled β -cristobalite structure, while NaTa₂N₂ forms with Ta in six coordination in the α -NaFeO₂ structure (Jacobs & Pinkowski, 1989).

The binary compound, the vermilion Ta₃N₅, has been known for many years (Moureu & Hamblet, 1937). It is reported to have the pseudobrookite (Fe₂TiO₅) structure. Although the unit cell was originally given as metrically tetragonal (Brauer & Weidlein, 1965), its structure has been refined as orthorhombic (Strähle, 1973) and monoclinic (Terao, 1977). If it were truly isomorphic with high-temperature Ti₃O₅ (Åsbrink & Magnéli, 1959), Ta₃N₅ would be monoclinic. The reported structure also contains an unusually short Ta...Ta distance for a compound in which Ta–Ta bonding is not expected so that, in view of the uncertainty about the space group, we felt that it warranted further investi-

gation. We report here neutron-diffraction studies which confirm and refine Strähle's orthorhombic structure.

Experimental. TaCl₅ was heated under flowing ammonia gas; the gas had been purified as the liquid over sodium. The temperature was slowly increased to 1023 K where a rapid conversion to Ta₃N₅ occurred. The air-stable, maroon-colored material was ground under acetone. X-ray diffraction indicated the presence of single-phased Ta₃N₅. The details of the synthesis will be published elsewhere (Rauch & DiSalvo, 1991).

Pulsed neutron-diffraction data were collected at 16 K on the Neutron Powder Diffractometer (NPD) of the Manuel Lujan, Jr Neutron Scattering Centre at Los Alamos National Laboratory. The powder data were refined with the use of the General Structure Analysis system (GSAS), a Rietveld profile analysis code which minimizes $\sum w(I_o - I_c)^2$ (Larson & Von Dreele, 1990). Data from the four highest-resolution detector banks ($\pm 148^\circ$, $\pm 90^\circ$) were used which provided 6295 reflections in the range $0.42 < d < 4.0$ Å (27 920 profile points). The scattering lengths used were 6.91 and 9.30×10^{-15} m for Ta and N, respectively. The 99 variables refined included scale factors, 12 background coefficients for each bank used in a cosine Fourier series technique, four profile coefficients for each bank (β_0 , β_1 , σ_1 , σ_2) (Von Dreele, Jorgensen & Windsor, 1982), two absorption coefficients (one for each \pm bank pair) (Hewat, 1979; Rouse, Cooper & Chakera, 1970), diffractometer zero constants, lattice parameters and 26 modeling parameters. The refinement converged; the structural results are given in Tables 1 and 2.* An examination of *R* values against parity class revealed no unusual trends. The strongest peak on a final difference Fourier synthesis was 0.8% the height of an N atom (the strongest scatterer). A representative diffraction profile is displayed in Fig. 1.

Discussion. Our structure determination confirms and refines that proposed by Strähle (1973). Terao suggested a similar structural model but proposed the space group *C2/m* (Terao, 1977) based on analogy with Ti₃O₅ at high temperature (Åsbrink & Magnéli, 1959). We transformed our orthorhombic model to the monoclinic setting and found that an unstable refinement in *C2/m* was not statistically better than the refinement in *Cmcm*: the difference profile curve was identical, and the structural param-

Table 1. Structure of Ta₃N₅ at 16 K*

	Site	x	y	z	100U _{eq} (Å ²)	φ (V)
Ta(1)	4(c)	0	0.1971 (1) [0.19757 (5)]	$\frac{1}{2}$	0.56 0.37	-54.7
Ta(2)	8(f)	0	0.13455 (7) [0.13429 (4)]	0.55906 (7) 0.56010 (5)	0.60 0.37	-54.0
N(3)	4(c)	0	0.76322 (7) [0.763 (1)]	$\frac{1}{2}$	0.85 0.5	37.3
N(4)	8(f)	0	0.04701 (6) [0.0470 (8)]	0.11949 (5) 0.119 (1)	1.00 0.5	35.5
N(5)	8(f)	0	0.30862 (6) [0.3097 (9)]	0.07378 (5) 0.073 (1)	0.83 0.4	38.5

* Space group *Cmcm*, this study: $a = 3.88617$ (9), $b = 10.2118$ (2), $c = 10.2624$ (3) Å; room-temperature study in brackets (Strähle, 1973): $a = 3.893$, $b = c = 10.264$ Å. U_{eq} is defined as $\frac{1}{3}$ the trace of the anisotropic temperature factor coefficients.

Table 2. Anisotropic temperature factors (Å²) for Ta₃N₅ at 16 K*

	100U ₁₁	100U ₂₂	100U ₃₃	100U ₂₃
Ta(1)	0.48 (3)	0.83 (3)	0.37 (3)	0
Ta(2)	0.37 (2)	0.75 (2)	0.69 (3)	0.01 (2)
N(3)	0.80 (3)	0.86 (3)	0.88 (3)	0
N(4)	1.36 (2)	0.81 (2)	0.83 (2)	-0.08 (2)
N(5)	0.70 (2)	0.83 (2)	0.95 (2)	0.12 (2)

* $U_{12} = U_{13} = 0$.

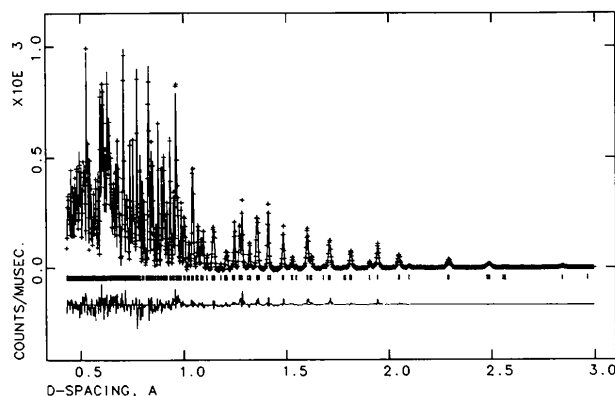


Fig. 1. Neutron-diffraction profile fit for Ta₃N₅ at 16 K ($2\theta = +148^\circ$ detector bank). The data points are shown as '+' marks, and the solid line is the calculated profile. The difference curve at the bottom is on the same scale. The background has been subtracted.

eters did not move more than 1–2 standard deviations away from those of the starting model. We therefore conclude that if Ta₃N₅ is actually monoclinic it is too close to orthorhombic to discern.

The structure of Ta₃N₅ is composed of octahedra of N atoms centered by Ta atoms. Since the N atoms are both three and four coordinated, the octahedra are irregular. The bond lengths are given in Table 3. Both Ta atoms have six Ta...Ta contacts shorter than 3.8 Å (the next-nearest neighbor distance). Figs. 2 and 3 display the structure projected on (100).

* Lists of the observed diffraction profiles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54220 (127 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Shortest Ta—Ta distances derived from oxide and oxynitride materials are typically 3.3 Å, although compounds in which metal–metal bonding might be expected contain shorter distances (*e.g.* Ta₄SiTe₄ 2.98 Å). Shortest Ta—Ta distances for some structures are tabulated in Table 4. The structure for Ta₃N₅ proposed by Strähle, which we confirm, contains a short Ta(2)—Ta(2) distance of 3.00 Å, although the other Ta—Ta distances are over 3.25 Å.

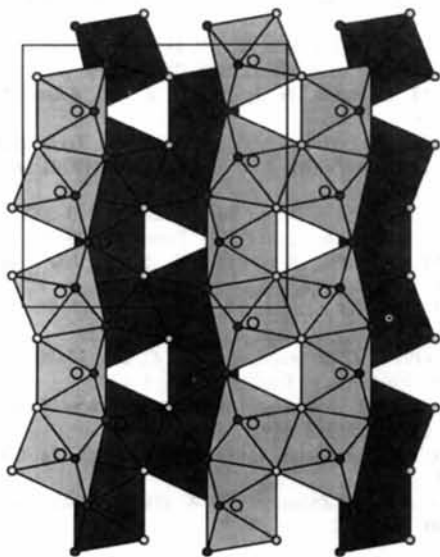


Fig. 2. Projection of the Ta₃N₅ structure onto (100). The *b* axis is horizontal and the *c* axis is vertical. The dark-shaded octahedra are displaced by *a*/2 from the lighter ones. Dark circles represent the four-coordinated N atoms, while the lighter circles represent the three-coordinated N atoms. Larger circles represent Ta atoms within the octahedra.

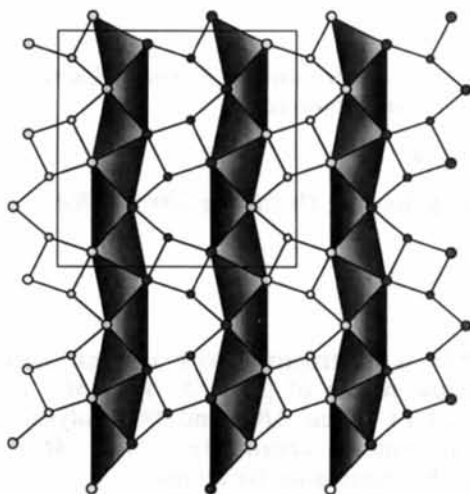


Fig. 3. Projection of the Ta₃N₅ structure on to (100) emphasizing anion coordination. Larger circles again represent Ta atoms. The edge-sharing tetrahedra are centered by N atoms. The shading of the circles indicates displacement by *a*/2.

Table 3. Bond distances (Å) and angles (°) for Ta₃N₅

Ta(1)—2Ta(2)	3.2353 (8)	Ta(2)—N(4)	2.0388 (9)
Ta(1)—4Ta(2)	3.2513 (7)	Ta(2)—2N(5)	2.0335 (3)
Ta(1)—2N(3)	2.0571 (5)	Ta(2)—N(5)	2.240 (1)
Ta(1)—2N(4)	2.035 (1)	N(3)—2Ta(1)	2.0571 (5)
Ta(1)—2N(5)	2.1372 (8)	N(3)—2Ta(2)	2.2203 (8)
Ta(2)—Ta(1)	3.2353 (8)	N(4)—Ta(1)	2.035 (1)
Ta(2)—2Ta(1)	3.2513 (7)	N(4)—Ta(2)	1.9550 (8)
Ta(2)—Ta(2)	3.004 (1)	N(4)—Ta(2)	2.0388 (9)
Ta(2)—2Ta(2)	3.287 (1)	N(5)—Ta(1)	2.1372 (8)
Ta(2)—N(3)	2.2203 (8)	N(5)—2Ta(2)	2.0335 (3)
Ta(2)—N(4)	1.9550 (8)	N(5)—Ta(2)	2.240 (1)
N(3)—Ta(1)—N(3)	141.67 (7)	N(4)—Ta(2)—N(5)	104.31 (3)
N(3)—Ta(1)—N(4)	104.31 (2)	N(4)—Ta(2)—N(5)	161.01 (4)
N(3)—Ta(1)—N(5)	79.93 (3)	N(5)—Ta(2)—N(5)	79.56 (3)
N(4)—Ta(1)—N(4)	82.30 (5)	N(5)—Ta(2)—N(5)	145.70 (5)
N(4)—Ta(1)—N(5)	81.05 (2)	Ta(1)—N(3)—Ta(1)	141.67 (7)
N(4)—Ta(1)—N(5)	163.35 (5)	Ta(1)—N(3)—Ta(2)	98.88 (1)
N(5)—Ta(1)—N(5)	115.60 (6)	Ta(2)—N(3)—Ta(2)	123.91 (5)
N(3)—Ta(2)—N(4)	99.55 (4)	Ta(1)—N(4)—Ta(2)	105.14 (4)
N(3)—Ta(2)—N(4)	177.96 (5)	Ta(1)—N(4)—Ta(2)	157.34 (4)
N(3)—Ta(2)—N(5)	78.48 (2)	Ta(2)—N(4)—Ta(2)	97.51 (4)
N(3)—Ta(2)—N(5)	99.44 (3)	Ta(1)—N(5)—Ta(2)	95.28 (4)
N(4)—Ta(2)—N(4)	82.49 (4)	Ta(1)—N(5)—Ta(2)	102.41 (2)
N(4)—Ta(2)—N(5)	78.52 (3)	Ta(2)—N(5)—Ta(2)	100.44 (3)
N(4)—Ta(2)—N(5)	101.06 (3)	Ta(2)—N(5)—Ta(2)	145.70 (5)

Table 4. Shortest Ta...Ta distances in assorted materials

Compound	Number	Distance (Å)	Reference
Ta	8	2.86	Mueller (1977)
<i>ε</i> -TaN	2	2.91	Christensen & Lebeck (1978)
Ta ₂ SiTe ₄	8	2.97	Badding & DiSalvo (1990)
Ta ₂ CoN ₅	6	2.98	Schönberg (1954a)
Ta ₃ N ₅	6	2.99	Fontbonne & Gilles (1969)
Ta ₃ MnN ₄	6	3.02	Schönberg (1954a)
<i>β</i> -Ta ₂ N	6	3.03	Conroy & Christensen (1977)
Ta ₂ N ₃	6	3.04	Fontbonne & Gilles (1969)
<i>δ</i> -Ta ₂ N	12	3.07	Gätterer, Dufek, Etmayer & Kieffer (1975)
NaTa ₂ N ₂	6	3.13	Jacobs & Pinkowski (1989)
TaON	2	3.23	Armytage & Fender (1974)
RbTaO ₃	3	3.24	Serafin & Hoppe (1980)
TaI ₃	2	3.31	Müller (1979)
TaTe ₂	4	3.32	Brown (1966)
<i>α</i> -TaS ₂	6	3.35	Jelinek (1962)
TaBO ₃	4	3.40	Zaslavskij & Zvincuk (1953)
Ta ₃ N ₅	1	3.00	This study

Bond-valence parameters appropriate for metal–metal bonding have recently been derived (O'Keeffe & Brese, 1991). These predict the length of a Ta—Ta single bond to be $R = 2.78$ Å and using the expression (Brown & Altermatt, 1985) for the valence v of a bond of length d : $v = \exp[(R - d)/0.37 \text{ Å}]$, the short bond in Ta₃N₅ corresponds to a valence of 0.55. Note, however, that in a material such as MgO (where the Mg...Mg distance is shorter than in elemental Mg), each of the twelve closest 'bonds' is calculated to have a valence of 0.3, although it is generally accepted that there is no metal–metal bonding in this case.

Electrostatic potentials (ϕ) reported in Table 1 are calculated assuming integral non-overlapping spherical charges (Tosi, 1964). Since the potentials at both Ta sites are similar, both metal atoms are equivalently surrounded by opposite charges. Therefore, based on bond valence as well as Madelung potential calculations, we believe the close Ta...Ta distance is more a constraint of the pseudobrookite structure than a result of metal–metal bonding.

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Structure of BaCuP₂O₇

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Abstract. Barium copper pyrophosphate, $M_r = 374.8$, triclinic, $P\bar{1}$, $a = 7.353(2)$, $b = 7.578(2)$, $c = 5.231(1) \text{ \AA}$, $\alpha = 90.83(2)$, $\beta = 95.58(2)$, $\gamma = 103.00(2)^\circ$, $V = 282.5(1) \text{ \AA}^3$, $Z = 2$, $D_x = 4.41 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 112.5 \text{ cm}^{-1}$, $F(000) = 342$, $T = 298 \text{ K}$, $R = 3.4\%$ for 1207 observed reflections. The structure of

BaCuP₂O₇ is isostructural with that of BaCoP₂O₇. Both show planes of $[(MP_2O_7^{2-})_2]_\infty$, $M = \text{Cu, Co}$, composed of mixed MO_5 and PO_4 polyhedra and square-pyramidal coordination for M , linked together by interplanar Ba atoms.

Introduction. Two types of structures are found for solid-state diphosphates, $A_2P_2O_7$ ($A = \text{bivalent cation}$): thortveitite and dichromate (Cruickshank,

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