

The phase-equilibrium study (Kanke, Takayama-Muromachi & Kato, 1990) showed that the present phase has a homogeneity region represented by $K_xV_2O_5$ ($0.49 \leq x \leq 0.54$). Therefore, it is not appropriate to formulate this compound as the stoichiometric compound KV_4O_{10} . The above-mentioned structure cannot contain K ions in excess of $K_{0.50}V_2O_5$. Detailed study is needed to determine the sites of the excess K ions in a potassium-rich compound.

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Structure of Nonasodium α -Triniobatopentadecawolframodiphosphate–Acetonitrile–Water (1/2/23), $Na_9[P_2W_{15}Nb_3O_{62}].2CH_3CN.23H_2O$

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Abstract. $Na_9[P_2W_{15}Nb_3O_{62}].2C_2H_3N.23H_2O$, $M_r = 4974$, triclinic, $P\bar{1}$, $a = 13.341$ (5), $b = 15.890$ (6), $c = 21.395$ (7) Å, $\alpha = 87.85$ (3), $\beta = 77.18$ (3), $\gamma = 71.87$ (3)°, $V = 4200$ (5) Å³, $Z = 2$, $D_x = 3.79$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 214.6$ cm⁻¹, $F(000) = 4264$, $T = 295$ K, $R = 0.062$ for 6966 independent data [$I \geq 3\sigma(I)$]. The anion has the well-known α - $(P_2W_{18}O_{62})^{6-}$ structure with three Nb atoms substituting for the W atoms in one of the two W_3O_{13} caps consisting of three edge-linked WO_6 octahedra. Despite orientational disorder (*ca* 28:72) which partly exchanges the caps, small differences in corresponding bond lengths in the two ends are apparent.

Introduction. This work stems from the continuing studies in this laboratory of trisubstituted heteropolytungstate anions as soluble metal oxide analogues, and in particular of the chemistry of derivatives formed by covalent attachment of catalytically active organometallic groups to surface O atoms of these polyoxoanions. The complete structural characterization of, *e.g.*, $(Bu_4N)_7[(C_5Me_5)Rh.P_2W_{15}Nb_3O_{62}]$ and $(Bu_4N)_7[(C_6H_6)Ru.P_2W_{15}Nb_3O_{62}]$ (Edlund, Saxton, Lyon & Finke,

1988), which are soluble in non-protic polar organic solvents, has been hindered by the failure to obtain single crystals suitable for X-ray work. We have therefore attempted to grow single crystals of mixed-cation (tetraalkylammonium + alkali metal) salts of these complexes. The compound whose structure we report was obtained unexpectedly in the course of this work. This is fortunate since the $(P_2W_{15}Nb_3O_{62})^{9-}$ anion has proved to be the best of the polyoxoanions examined to date for covalently attaching ('supporting') organometallic catalyst precursors, *e.g.* $[(1,5\text{-cod})Ir.P_2W_{15}Nb_3O_{62}]^{8-}$ (Finke, Lyon, Nomiya, Sur & Mizuno, 1990).

Experimental. A solution of $(Bu_4N)_9(P_2W_{15}Nb_3O_{62})$ (Edlund, Saxton, Lyon & Finke, 1988) in MeCN was treated with a solution of $NaBF_4$ in MeCN, and ethyl acetate was then added to precipitate $(Bu_4N)_{6-x}Na_{3+x}(P_2W_{15}Nb_3O_{62})$ ($x = 0$ or 1). A solution of the latter (1.0 g) in 1:1 CD_3CN/CH_3CN (4 ml) to which 3 drops of water had been added deposited a few well-formed colorless prisms of the title compound on standing in an NMR tube for 48 h at 293 K. The amount of material (*ca* 20 mg) precluded a full elemental analysis. Calc. for $Na_9(P_2W_{15}Nb_3O_{62}).2CH_3CN.23H_2O$: Na 4.32, W 57.5%; found: Na 4.24, W 57.5% (Mikroanalytisches Labor Pascher, Remagen, Federal Republic

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Table 1. Atomic coordinates (W, Nb $\times 10^5$; other atoms $\times 10^4$) and equivalent isotropic (W , Nb) or isotropic thermal parameters (\AA^2) for $\text{Na}_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]\cdot 2\text{CH}_3\text{CN}\cdot 23\text{H}_2\text{O}$

$$B_{\text{eq}} = (8\pi^2/3)\sum_i U_i a_i^* a_i$$

	x	y	z	B_{eq}
W(1)	63511 (16)	60820 (13)	17508 (9)	1.45 (8)
W(2)	59018 (17)	60882 (14)	33811 (9)	1.56 (8)
W(3)	84685 (17)	54932 (14)	24896 (9)	1.61 (8)
W(4)	47121 (13)	45779 (11)	17925 (7)	1.16 (6)
W(5)	42456 (13)	46031 (11)	33962 (7)	1.22 (6)
W(6)	65101 (14)	39637 (11)	42044 (7)	1.25 (6)
W(7)	90477 (13)	33643 (11)	33172 (7)	1.25 (6)
W(8)	95574 (13)	33607 (11)	15602 (7)	1.24 (6)
W(9)	74901 (13)	39407 (11)	8262 (7)	1.17 (6)
W(10)	47415 (13)	22095 (11)	17605 (7)	1.20 (6)
W(11)	42854 (13)	22174 (11)	33648 (7)	1.23 (6)
W(12)	65517 (14)	15927 (11)	41608 (7)	1.24 (6)
W(13)	90925 (13)	9897 (11)	32718 (7)	1.22 (6)
W(14)	95938 (13)	9850 (11)	15288 (7)	1.24 (6)
W(15)	74951 (13)	15686 (11)	8035 (7)	1.13 (6)
Nb(1)	64115 (22)	-1548 (19)	16825 (12)	1.4 (1)
Nb(2)	59840 (22)	-1493 (19)	33047 (12)	1.4 (1)
Nb(3)	85479 (22)	-7505 (18)	24081 (12)	1.4 (1)
P(1)	6934 (8)	4081 (7)	2517 (5)	1.2 (2)
P(2)	6971 (8)	1500 (7)	2479 (5)	1.0 (2)
Na(1)	7002 (13)	7780 (11)	547 (7)	2.5 (3)
Na(2)	2954 (17)	-1522 (14)	2359 (9)	4.5 (4)
Na(3)	2570 (15)	-715 (13)	927 (8)	3.5 (4)
Na(4)	47 (16)	3296 (13)	-226 (9)	4.0 (4)
Na(5)	182 (17)	6891 (15)	1677 (10)	4.8 (5)
Na(6)	5840 (17)	7985 (14)	4548 (10)	4.6 (5)
Na(7)	6393 (25)	1435 (21)	6078 (14)	8.8 (8)
O(1)	6024 (21)	6946 (18)	1264 (12)	1.9 (5)
O(2)	5274 (20)	6995 (17)	3898 (11)	1.4 (5)
O(3)	9449 (22)	5989 (19)	2475 (12)	2.4 (6)
O(4)	3819 (20)	4997 (17)	1308 (11)	1.5 (5)
O(5)	3045 (23)	5078 (19)	3916 (13)	2.6 (6)
O(6)	6032 (21)	4173 (18)	5034 (12)	1.8 (5)
O(7)	221 (20)	3238 (16)	3550 (11)	3.5 (5)
O(8)	921 (22)	3185 (18)	1237 (12)	2.3 (6)
O(9)	7520 (20)	4177 (17)	29 (11)	1.7 (5)
O(10)	3807 (20)	2371 (17)	1274 (11)	1.6 (5)
O(11)	3091 (21)	2346 (18)	3904 (12)	2.0 (5)
O(12)	6093 (21)	1499 (17)	4955 (11)	1.7 (5)
O(13)	261 (21)	563 (18)	3517 (12)	2.0 (5)
O(14)	917 (21)	536 (18)	1188 (12)	1.9 (5)
O(15)	7565 (20)	1435 (17)	-22 (11)	1.6 (5)
O(16)	6086 (23)	-801 (19)	1141 (13)	2.6 (6)
O(17)	5347 (24)	-777 (20)	3851 (13)	2.9 (6)
O(18)	9609 (23)	-1745 (20)	2351 (13)	2.8 (6)
O(19)	6902 (18)	5062 (15)	2518 (10)	0.6 (4)
O(20)	5778 (21)	4072 (17)	2535 (11)	1.7 (5)
O(21)	7697 (18)	3644 (15)	1892 (10)	0.6 (4)
O(22)	7355 (19)	3599 (16)	3097 (10)	0.9 (4)
O(23)	6976 (20)	520 (17)	2478 (11)	1.3 (5)
O(24)	5785 (18)	2067 (15)	2543 (10)	0.8 (4)
O(25)	7712 (19)	1618 (16)	1864 (11)	1.1 (5)
O(26)	7373 (19)	1635 (16)	3059 (10)	0.9 (5)
O(27)	7693 (22)	6144 (18)	1875 (12)	2.1 (6)
O(28)	7370 (20)	6153 (17)	3176 (11)	1.5 (5)
O(29)	5672 (20)	6663 (17)	2593 (11)	1.4 (5)
O(30)	5668 (24)	-475 (20)	2509 (13)	2.8 (6)
O(31)	7471 (21)	-946 (17)	3105 (11)	1.7 (5)
O(32)	7823 (21)	-907 (18)	1743 (12)	1.9 (5)
O(33)	5179 (21)	5612 (18)	1829 (12)	1.9 (5)
O(34)	4767 (19)	5597 (16)	3332 (11)	1.2 (5)
O(35)	6392 (22)	5127 (18)	3921 (12)	2.1 (6)
O(36)	8813 (21)	4582 (17)	3086 (11)	1.6 (5)
O(37)	9124 (21)	4617 (17)	1835 (11)	1.7 (5)
O(38)	7214 (22)	5156 (19)	1139 (12)	2.3 (6)
O(39)	5238 (21)	989 (17)	1775 (11)	1.7 (5)
O(40)	4823 (20)	1003 (17)	3299 (11)	1.3 (5)
O(41)	6438 (21)	549 (17)	3889 (11)	1.8 (5)
O(42)	8870 (19)	-48 (16)	3030 (10)	1.0 (5)
O(43)	9229 (18)	-41 (15)	1792 (10)	0.6 (4)
O(44)	7193 (19)	548 (16)	1072 (10)	1.0 (5)
O(45)	3762 (22)	4956 (18)	2610 (12)	2.2 (6)
O(46)	5202 (19)	4117 (16)	3948 (11)	1.1 (5)
O(47)	9559 (20)	3062 (16)	2425 (11)	1.3 (5)
O(48)	7989 (19)	3758 (16)	4110 (10)	1.0 (5)
O(49)	8952 (19)	3723 (16)	820 (10)	1.0 (5)
O(50)	6025 (19)	4095 (16)	1163 (11)	1.2 (5)
O(51)	3789 (19)	2282 (16)	2593 (10)	0.9 (5)
O(52)	5266 (19)	2148 (16)	3903 (11)	1.1 (5)

Table 1 (cont.)

	x	y	z	B_{eq}
O(53)	8042 (22)	1135 (19)	4078 (12)	2.3 (6)
O(54)	9623 (19)	1181 (16)	2391 (11)	1.3 (5)
O(55)	8963 (19)	1079 (16)	780 (10)	1.0 (5)
O(56)	6042 (20)	2145 (17)	1147 (11)	1.6 (5)
O(57)	4533 (20)	3450 (17)	1890 (11)	1.4 (5)
O(58)	4153 (20)	3462 (17)	3298 (11)	1.5 (5)
O(59)	6767 (20)	2727 (17)	4190 (11)	1.6 (5)
O(60)	8974 (19)	2196 (16)	3428 (11)	1.2 (5)
O(61)	9559 (21)	2187 (17)	1409 (11)	1.7 (5)
O(62)	7721 (21)	2704 (18)	765 (11)	1.8 (5)
O(63)	8453 (25)	7405 (21)	1229 (14)	3.3 (7)
O(64)	9170 (28)	2575 (23)	-683 (15)	4.4 (8)
O(65)	8101 (29)	6238 (24)	186 (16)	4.7 (8)
O(66)	8471 (27)	8114 (23)	-121 (15)	4.2 (8)
O(67)	4427 (24)	-1590 (20)	2815 (13)	3.0 (6)
O(68)	1717 (27)	-1511 (23)	1721 (15)	4.3 (8)
O(69)	5824 (26)	8504 (22)	-122 (15)	3.9 (7)
O(70)	7581 (28)	7549 (23)	3828 (15)	4.4 (8)
O(71)	3635 (28)	-137 (23)	128 (15)	4.4 (8)
O(72)	6251 (32)	6575 (27)	5044 (18)	6 (1)
O(73)	3134 (28)	-3022 (23)	2665 (16)	4.6 (8)
O(74)	4160 (30)	-1453 (25)	1286 (17)	5.4 (9)
O(75)	6166 (34)	9198 (29)	5086 (19)	7 (1)
O(76)	1835 (39)	6349 (33)	1984 (22)	9 (1)
O(77)	7193 (32)	2723 (27)	5949 (18)	6 (1)
O(78)	9656 (31)	4427 (25)	-942 (17)	5 (1)
O(79)	1688 (43)	-1184 (36)	3299 (24)	10 (1)
O(80)	2874 (56)	149 (47)	3906 (32)	15 (2)
O(81)	9524 (28)	9080 (24)	420 (16)	3 (1)
O(82)	2253 (36)	4289 (30)	973 (20)	4 (1)
O(83)	8422 (41)	9146 (34)	4415 (23)	2 (2)
N(1)	2670 (56)	10018 (49)	2085 (32)	10 (2)
N(2)	6645 (53)	2937 (43)	-916 (29)	9 (2)
C(1)	2433 (75)	10703 (66)	2265 (41)	10 (3)
C(2)	1792 (76)	11819 (66)	2256 (42)	12 (3)
C(3)	5868 (53)	3289 (43)	-555 (29)	6 (1)
C(4)	4955 (61)	3750 (49)	-140 (34)	8 (2)

Each atom W(1,2,3) is $\text{W}_{0.72}\text{Nb}_{0.28}$, and each atom Nb(1,2,3) is $\text{Nb}_{0.72}\text{W}_{0.28}$.

of Germany). The number of solvent molecules of crystallization has been estimated from the above partial analysis and the structure determination.

Crystal sealed in a Lindemann-glass capillary; dimensions $0.35 \times 0.20 \times 0.15$ mm; Rigaku AFC6R diffractometer; initial cell dimensions from setting angles of 20 reflections in the range $15.7 \leq 2\theta \leq 21.8^\circ$, improved values from 20 strong reflections identified from rapid scan of shell $28 \leq 2\theta \leq 30^\circ$; ω - 2θ scans, speed 16°min^{-1} in ω , scan width $(1.05 + 0.30 \tan \theta)^\circ$, range $2 \leq 2\theta \leq 45^\circ$, $0 \leq h \leq 17$, $-23 \leq k \leq 23$, $-13 \leq l \leq 13$; three standard reflections every 300 reflections, no significant change; 10 990 independent reflections, $R_{\text{int}} = 0.074$ for $\pm(0kl)$, 6962 with $I \geq 3\sigma(I)$ used in refinement.

A MITHRIL E map (Gilmore, 1984) showed overlapping images of incomplete heavy-atom skeletons of the anion, in an orientation consistent with the strong Patterson vector peaks. A plausible P_2W_{11} set was shifted by the TRADIR sub-program of DIRDIF (Buerskens, 1984), and the remaining heavy atoms were revealed. The O atoms of the anion were located by further cycles of DIRDIF. Seven of the nine Na^+ ions, 21 water O atoms, and the C and N atoms of two MeCN molecules were found from difference syntheses alternating with cycles of least-squares refinement. Two Na^+ ions could not be located, presumably because of disorder, but as

Table 2. Bond lengths (Å)

W(1)—O(1)	1.70 (3)	W(14)—O(54)	1.89 (2)
W(1)—O(19)	2.34 (2)	W(14)—O(55)	1.95 (2)
W(1)—O(27)	1.90 (3)	W(14)—O(61)	1.91 (3)
W(1)—O(29)	1.95 (2)	W(15)—O(15)	1.76 (2)
W(1)—O(33)	1.91 (3)	W(15)—O(25)	2.36 (2)
W(1)—O(38)	1.90 (3)	W(15)—O(44)	1.83 (3)
W(2)—O(2)	1.72 (2)	W(15)—O(55)	1.86 (2)
W(2)—O(19)	2.37 (2)	W(15)—O(56)	1.86 (2)
W(2)—O(28)	1.94 (3)	W(15)—O(62)	1.91 (3)
W(2)—O(29)	1.93 (2)	Nb(1)—O(16)	1.78 (3)
W(2)—O(34)	1.93 (3)	Nb(1)—O(23)	2.41 (2)
W(2)—O(35)	1.92 (3)	Nb(1)—O(30)	1.96 (3)
W(3)—O(3)	1.72 (3)	Nb(1)—O(32)	1.92 (2)
W(3)—O(19)	2.38 (2)	Nb(1)—O(39)	1.98 (2)
W(3)—O(27)	1.93 (2)	Nb(1)—O(44)	2.01 (3)
W(3)—O(28)	1.90 (2)	Nb(2)—O(17)	1.76 (3)
W(3)—O(36)	1.91 (3)	Nb(2)—O(23)	2.39 (3)
W(3)—O(37)	1.87 (2)	Nb(2)—O(30)	1.96 (3)
W(4)—O(4)	1.71 (2)	Nb(2)—O(31)	1.96 (2)
W(4)—O(20)	2.32 (2)	Nb(2)—O(40)	2.00 (2)
W(4)—O(33)	1.94 (3)	Nb(2)—O(41)	2.01 (3)
W(4)—O(45)	1.91 (3)	Nb(3)—O(18)	1.75 (3)
W(4)—O(50)	1.91 (2)	Nb(3)—O(23)	2.40 (2)
W(4)—O(57)	1.88 (3)	Nb(3)—O(31)	1.92 (3)
W(5)—O(5)	1.70 (3)	Nb(3)—O(32)	1.95 (2)
W(5)—O(20)	2.38 (3)	Nb(3)—O(42)	1.97 (2)
W(5)—O(34)	1.90 (3)	Nb(3)—O(43)	1.96 (3)
W(5)—O(45)	1.94 (2)	P(1)—O(19)	1.55 (3)
W(5)—O(46)	1.90 (2)	P(1)—O(20)	1.54 (3)
W(5)—O(58)	1.88 (3)	P(1)—O(21)	1.53 (2)
W(6)—O(6)	1.76 (2)	P(1)—O(22)	1.55 (2)
W(6)—O(22)	2.39 (2)	P(2)—O(23)	1.56 (3)
W(6)—O(35)	1.89 (3)	P(2)—O(24)	1.54 (2)
W(6)—O(46)	1.89 (2)	P(2)—O(25)	1.50 (3)
W(6)—O(48)	1.86 (2)	P(2)—O(26)	1.50 (2)
W(6)—O(59)	1.89 (3)	Na(1)—O(1)	2.42 (3)
W(7)—O(7)	1.70 (2)	Na(1)—O(16)	2.45 (3)
W(7)—O(22)	2.32 (2)	Na(1)—O(63)	2.59 (3)
W(7)—O(36)	1.93 (3)	Na(1)—O(65)	2.48 (4)
W(7)—O(47)	1.91 (2)	Na(1)—O(66)	2.35 (4)
W(7)—O(48)	1.93 (2)	Na(1)—O(69)	2.37 (3)
W(7)—O(60)	1.89 (3)	Na(2)—O(67)	2.35 (3)
W(8)—O(8)	1.73 (3)	Na(2)—O(68)	2.36 (4)
W(8)—O(21)	2.33 (2)	Na(2)—O(73)	2.40 (4)
W(8)—O(37)	1.97 (3)	Na(2)—O(74)	2.52 (4)
W(8)—O(47)	1.89 (2)	Na(2)—O(79)	2.28 (6)
W(8)—O(49)	1.92 (2)	Na(2)—N(1)	2.43 (8)
W(8)—O(61)	1.90 (3)	Na(3)—O(14)	2.44 (3)
W(9)—O(9)	1.73 (2)	Na(3)—O(15)	2.35 (3)
W(9)—O(21)	2.37 (2)	Na(3)—O(68)	2.38 (4)
W(9)—O(38)	1.96 (3)	Na(3)—O(71)	2.33 (4)
W(9)—O(49)	1.87 (2)	Na(3)—O(74)	2.36 (4)
W(9)—O(50)	1.87 (2)	Na(3)—N(1)	2.82 (7)
W(9)—O(62)	1.90 (3)	Na(4)—O(49)	2.53 (3)
W(10)—O(10)	1.75 (2)	Na(4)—O(63)	2.44 (3)
W(10)—O(24)	2.37 (2)	Na(4)—O(64)	2.57 (4)
W(10)—O(39)	1.85 (3)	Na(4)—O(65)	2.42 (4)
W(10)—O(51)	1.93 (2)	Na(4)—O(66)	2.50 (4)
W(10)—O(56)	1.91 (3)	Na(4)—O(78)	2.41 (4)
W(10)—O(57)	1.93 (3)	Na(5)—O(3)	2.42 (4)
W(11)—O(11)	1.71 (3)	Na(5)—O(18)	2.47 (3)
W(11)—O(24)	2.31 (2)	Na(5)—O(63)	2.58 (4)
W(11)—O(40)	1.84 (2)	Na(5)—O(64)	2.34 (4)
W(11)—O(51)	1.90 (2)	Na(5)—O(76)	2.34 (5)
W(11)—O(52)	1.90 (2)	Na(5)—O(78)	2.59 (4)
W(11)—O(58)	1.93 (3)	Na(6)—O(2)	2.52 (3)
W(12)—O(12)	1.69 (2)	Na(6)—O(12)	2.45 (3)
W(12)—O(26)	2.38 (2)	Na(6)—O(17)	2.44 (4)
W(12)—O(41)	1.84 (3)	Na(6)—O(70)	2.40 (4)
W(12)—O(52)	1.86 (2)	Na(6)—O(72)	2.40 (5)
W(12)—O(53)	1.86 (3)	Na(6)—O(75)	2.48 (5)
W(12)—O(59)	1.92 (3)	Na(7)—O(2)	2.77 (4)
W(13)—O(13)	1.69 (2)	Na(7)—O(12)	2.51 (4)
W(13)—O(26)	2.34 (2)	Na(7)—O(17)	2.80 (5)
W(13)—O(42)	1.87 (2)	Na(7)—O(67)	2.37 (4)
W(13)—O(53)	1.94 (3)	Na(7)—O(77)	2.48 (5)
W(13)—O(54)	1.91 (2)	Na(7)—O(80)	2.40 (8)
W(13)—O(60)	1.91 (3)	N(1)—C(1)	1.1 (1)
W(14)—O(14)	1.69 (3)	N(2)—C(3)	1.14 (7)
W(14)—O(25)	2.35 (2)	C(1)—C(2)	1.7 (1)
W(14)—O(43)	1.88 (3)	C(3)—C(4)	1.35 (8)

Table 3. Non-bonded distances (Å) involving heavy atoms

W(1)···W(2)	3.406 (3)	W(8)···W(9)	3.340 (3)
W(1)···W(3)	3.404 (3)	W(8)···W(14)	3.763 (3)
W(1)···W(4)	3.695 (3)	W(9)···W(15)	3.769 (3)
W(1)···W(9)	3.708 (3)	W(10)···W(11)	3.350 (2)
W(2)···W(3)	3.389 (3)	W(10)···W(15)	3.635 (3)
W(2)···W(5)	3.696 (3)	W(10)···Nb(1)	3.712 (4)
W(3)···W(6)	3.693 (3)	W(11)···W(12)	3.649 (3)
W(3)···W(7)	3.702 (3)	W(11)···Nb(2)	3.728 (4)
W(3)···W(8)	3.702 (3)	W(12)···W(13)	3.359 (3)
W(4)···W(5)	3.348 (2)	W(12)···Nb(2)	3.727 (3)
W(4)···W(9)	3.669 (3)	W(13)···W(14)	3.639 (2)
W(4)···W(10)	3.754 (3)	W(13)···Nb(3)	3.717 (3)
W(5)···W(6)	3.664 (3)	W(14)···W(15)	3.363 (3)
W(5)···W(11)	3.778 (3)	W(14)···Nb(3)	3.733 (4)
W(6)···W(7)	3.354 (3)	W(15)···Nb(1)	3.741 (4)
W(6)···W(12)	3.755 (3)	Nb(1)···Nb(2)	3.390 (4)
W(7)···W(8)	3.669 (2)	Nb(1)···Nb(3)	3.407 (4)
W(7)···W(13)	3.760 (3)	Nb(2)···Nb(3)	3.389 (4)
W(1)···P(1)	3.47 (1)	W(10)···P(2)	3.51 (1)
W(2)···P(1)	3.47 (1)	W(11)···P(2)	3.51 (1)
W(3)···P(1)	3.47 (1)	W(12)···P(2)	3.52 (1)
W(4)···P(1)	3.51 (1)	W(13)···P(2)	3.49 (1)
W(5)···P(1)	3.52 (1)	W(14)···P(2)	3.50 (1)
W(6)···P(1)	3.53 (1)	W(15)···P(2)	3.50 (1)
W(7)···P(1)	3.49 (1)	Nb(1)···P(2)	3.53 (1)
W(8)···P(1)	3.50 (1)	Nb(2)···P(2)	3.53 (1)
W(9)···P(1)	3.53 (1)	Nb(3)···P(2)	3.53 (1)

1983) was applied after isotropic refinement (min., max. correction factors 0.635, 1.52). It was clear from the outset that the heavy atoms of the W₃ and Nb₃ caps were effectively composite as the result of orientational disorder of the anion. No evidence for separate adjacent Nb and W sites in either cap was seen in difference maps at any stage. The cap atoms were treated in the early stages of refinement as W with refined fractional site-occupancy factors, and in the later stages as three Nb_xW_{1-x} in one cap [W(1,2,3)] and three Nb_xW_{1-x} in the other [Nb(1,2,3)], with common coordinates and anisotropic thermal parameters for the Nb and W atoms at each site. The parameter *x* refined to 0.72 (1). Full-matrix least-squares refinement (on *F*) converged at *R* = 0.062, *wR* = 0.074, *S* = 2.08; 559 parameters; function minimized $\sum w(|F_o| - |F_c|)^2$; *w* = 1/*σ*²(*F*); max. Δ/σ = 0.027 in last cycle; max., min. $\Delta\rho$ = 3.3, -2.7 e Å⁻³ in final ΔF map. All computing programs were contained in the *TEXSAN* suite (Molecular Structure Corporation, 1985), and were run on a MicroVAX Series II/RC computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and isotropic or equivalent isotropic thermal parameters are given in Table 1, bond lengths in Table 2, and other distances involving heavy atoms in Table 3.* A view of the

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52901 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

expected from the elemental analysis no fragments of Bu₄N⁺ ions could be identified. An empirical absorption correction (*DIFABS*; Walker & Stuart,

anion showing the numbering of atoms is given in Fig. 1.

The crystals contain Na^+ and $(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})^{9-}$ ions and H_2O and MeCN solvent molecules, all on general positions in space group $P\bar{1}$. Although the two ends of the anion are not equivalent (see below) the cations are distributed fairly uniformly around it. All cations, except Na(2) which is bonded only to one MeCN and five water ligands, are bonded to at least one anion O atom in addition to water, while Na(1) bridges two adjacent anions and Na(6) and Na(7) each bridge three anions. There is strong evidence (Finke, Lyon, Nomiya, Sur & Mizuno, 1990) that pairing between Na^+ and the anion persists in acetonitrile and in dimethyl sulfoxide solution.

The anion has the $\alpha\text{-(P}_2\text{W}_{18}\text{O}_{62})^{6-}$ structure (Dawson, 1953; d'Amour, 1976) but with three Nb atoms replacing the W atoms in one end cap of three edge-linked WO_6 octahedra. Its non-crystallographic symmetry is close to $3m$ (C_{3v}). During the preparation of the anion under mild conditions (Edlund, Saxton, Lyon & Finke, 1988) the bond connectivity of the precursor $\alpha\text{-(P}_2\text{W}_{15}\text{O}_{56})^{12-}$ was expected to be retained. The structure of $(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})^{9-}$ is therefore further evidence that the base degradation of $\alpha\text{-(P}_2\text{W}_{18}\text{O}_{62})^{6-}$ to $\alpha\text{-(P}_2\text{W}_{15}\text{O}_{56})^{12-}$ involves the removal of one end cap, as deduced earlier from the ^{183}W NMR spectrum of the derivative $(\text{P}_2\text{W}_{15}\text{Mo}_3\text{O}_{62})^{6-}$ (Acerete, Hammer & Baker, 1984) and from studies of the derivatives $[\text{M}_4(\text{H}_2\text{O})_2\text{-(P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$ [$\text{M} = \text{Zn}$, ^{183}W NMR (Finke,

Table 4. Comparison of lengths of structurally related bonds: average [range] (\AA)

	Cap W(1,2,3)	Cap Nb(1,2,3)	$(\text{P}_2\text{W}_{18}\text{O}_{62})^{6-}$ *
$M\text{—O(terminal)}$	1.71 (1) [1.70–1.72]	1.76 (2) [1.75–1.78]	1.69 (3)
$M\text{—O}(M_{\text{cap}})$	1.93 (2) [1.90–1.95]	1.95 (2) [1.92–1.97]	1.91 (3)
$M\text{—O}(W_{\text{belt}})$ †	1.91 (2) [1.87–1.93]	1.99 (2) [1.96–2.01]	1.90 (3)
$M\text{—O}(P)$	2.37 (3) [2.34–2.39]	2.40 (1) [2.39–2.41]	2.39 (3)
	Belt W(4–9)	Belt W(10–15)	
$W\text{—O(terminal)}$	1.72 (2) [1.70–1.76]	1.72 (3) [1.69–1.77]	1.72 (3)
$W\text{—O}(M_{\text{cap}})$	1.93 (3) [1.89–1.97]	1.85 (2) [1.83–1.87]	1.94 (3)
$W\text{—O}(W_{\text{belt}})$ †	1.91 (3) [1.86–1.94]	1.91 (4) [1.86–1.95]	1.92 (3)
$W\text{—O}(W_{\text{belt}})$ ‡	1.90 (1) [1.87–1.91]	1.89 (2) [1.86–1.91]	1.91 (3)
$W\text{—O}(W_{\text{belt}})$ §	1.89 (1) [1.87–1.91]	1.92 (1) [1.90–1.93]	1.90 (3)
$W\text{—O}(P)$	2.35 (3) [2.32–2.39]	2.35 (2) [2.31–2.38]	2.36 (3)

* d'Amour (1976).

† Edge sharing, between octahedra.

‡ Corner sharing, same belt.

§ Corner sharing, between belts.

Droege & Domaille, 1987); $M = \text{Cu}$, X-ray structure (Weakley & Finke, 1990)].

The anion is disordered, occupying each site in two orientations which are essentially mirror images related by reflection in the plane of the six equatorial atoms O(57,58,59,60,61,62) linking the two halves of the anion. The reflection brings the set of anion O atoms into close self-coincidence, also the pair of P atoms and the set of W atoms in the two belts of six alternately corner- and edge-sharing WO_6 octahedra, but exchanges the cap W_3 set and the cap Nb_3 set. The relative weights of the orientations, from refined site-occupancy factors, are approximately 72:28 rather than 50:50. Therefore, a W-rich cap [W(1,2,3)] and an Nb-rich cap [Nb(1,2,3)] are present. The small differences in bond lengths appear to be real despite the partial disorder and the constraints imposed during refinement.

Average values of bond lengths in the two halves of the anion ($3m$ symmetry assumed) and in $\alpha\text{-(P}_2\text{W}_{18}\text{O}_{62})^{6-}$ (d'Amour, 1976) are compared in Table 4. All bonds around the Nb atoms are longer than corresponding bonds in the W(1,2,3) cap, in particular the terminal bonds [1.76 (2) \AA vs 1.71 (1) \AA] and the bonds of type $M_{\text{cap}}\text{—O}(W_{\text{belt}})$ [1.99 (2) vs 1.91 (2) \AA]. Parallel examples are the lengthening of terminal Nb—O bonds in $[(\text{Cp}_3\text{U})\text{-(NbW}_5\text{O}_{19})_2]^{5-}$ (Day, Klemperer & Maltbie, 1985) compared with terminal W—O in the same anion, and in $[\text{Mn}(\text{Nb}_6\text{O}_{19})_2]^{12-}$ (Flynn & Stucky, 1969) compared with terminal W—O in $(\text{W}_6\text{O}_{19})^{2-}$ (Willing, Muller & Berg, 1986). The $W_{\text{belt}}\text{—O(Nb)}$ bonds involving W(10–15) [1.85 (2) \AA] are distinctly shorter than the bonds of the more-symmetrical [1.91 (2), 1.93 (3) \AA] bridges between W(1,2,3) and W(4–9). The asymmetry in the Nb—O—W bridge is paralleled in the $[\text{Cu}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{62})_2]^{16-}$ anion (Weakley & Finke, 1990), in which each $\alpha\text{-(P}_2\text{W}_{15}\text{O}_{56})^{12-}$ group is capped by three Cu atoms; the W—O(Cu) bonds are shorter and the W—O

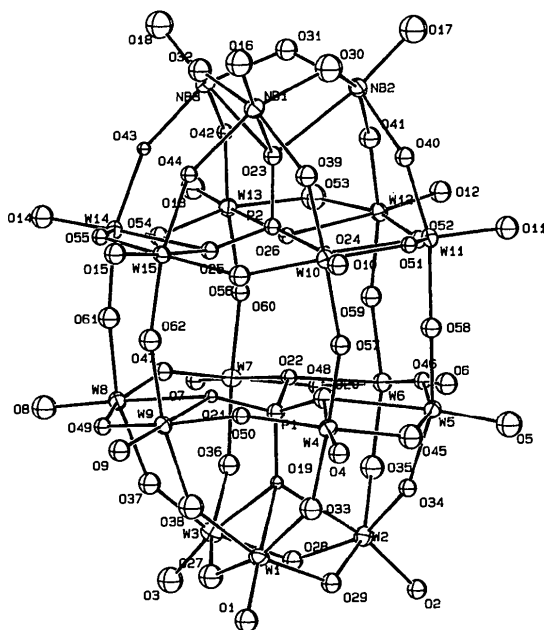


Fig. 1. The $(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})^{9-}$ anion.

bonds *trans* to Cu are longer than in the parent (P₂W₁₈O₆₂)⁶⁻. The bond-valence sums (Brown & Altermatt, 1985) are calculated from the averaged bond lengths to be 5.19 for Nb(1,2,3) and 6.02, 6.13, 6.30 for W(1,2,3), W(4-9) and W(10-15) respectively, and the bond-valence sums for O atoms in the sequence Nb—O—W_{belt}—O—W_{belt}—O—W_{cap} are 2.01, 2.07, 1.99.

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Structure of RbNaS

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Abstract. Rubidium sodium sulfide, RbNaS, $M_r = 140.524$, tetragonal, $P4/nmm$, $a = 4.696$ (1), $c = 7.559$ (1) Å, $V = 166.69$ Å³, $Z = 2$, $D_x = 2.799$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 85.12$ cm⁻¹, $F(000) = 126$, $T = 293$ K, $R = 0.0223$ for 169 unique reflections. The structure is characterized by layers of ${}^2_2[\text{NaS}_{4/4}]$ tetrahedra separated by double layers of Rb to form a PbFCl-type geometry.

Introduction. Our investigations into the existence of ternary alkali-metal oxides led to the characterization of KNaO (Sabrowsky & Schröer, 1982), RbNaO (Sabrowsky, Vogt-Mertens & Thimm, 1985), KLiO (Sabrowsky, Mertens & Thimm, 1985) and RbLiO (Sabrowsky & Vogt, 1987). Subsequently we extended our studies into the field of the interalkali-metal sulfides. Meanwhile we have succeeded in preparing NaLiS (Sabrowsky, Thimm & Vogt-Mertens, 1985a), KLiS (Sabrowsky, Thimm & Vogt-Mertens, 1985b), RbLiS (Sabrowsky, Hippler, Hitzbleck, Sitta, Thimm, Vogt & Wortmann, 1990) and KNaS (Sabrowsky, Thimm, Vogt & Harbrecht,

1987). NaLiS, KLiS and RbLiS are isotypic and crystallize in the PbFCl structure type whereas KNaS forms crystals of PbCl₂-type geometry. Here we present the results of a single-crystal structure determination of RbNaS which has been prepared recently.

Experimental. Well-shaped colourless single crystals of RbNaS were obtained by sintering equimolar mixtures of Na₂S and Rb₂S in closed silver crucibles in an argon atmosphere at 783 K. The crystals are sensitive to air and moisture. D_m was not measured. A plate-like crystal with dimensions 0.1 × 0.2 × 0.5 mm mounted in a Lindemann tube was available for the data collection. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 50 reflections ($2\theta = 16$ –27°) measured on an Enraf–Nonius CAD-4 diffractometer. The intensity measurements were carried out at 293 K with graphite-monochromated Mo $K\alpha$ radiation and the ω -2 θ scan technique. A total of 3400 reflections were collected for $2\theta = 2$ –72°