

## Structure of a Ditanodecatungstophosphate

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**Abstract.** Tetrakis(diethylammonium) sodium dititanodecatungstophosphate undecahydrate,  $[(C_2H_5)_2NH_2]_4Na[H_2PTi_2W_{10}O_{40}] \cdot 11H_2O$ ,  $M_r = 3124.9$ , orthorhombic,  $P2_12_12_1$ ,  $a = 17.934$  (3),  $b = 18.699$  (5),  $c = 20.461$  (6) Å,  $V = 6861$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 3.16$ ,  $D_x = 3.03$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 173.9$  mm<sup>-1</sup>,  $F(000) = 5656$ ,  $T = 298$  K,  $R = 0.056$  for 6524 unique reflections. The  $[H_2PTi_2W_{10}O_{40}]^{5-}$  anion has a Keggin structure with two metal atom sites occupied with Ti atoms. The anion keeps the preferred orientation in the crystal and the site occupancy refinement revealed the substituted sites. The  $C_2$  isomer was found to be predominant. The W—Ti distances are *ca* 0.05 Å shorter than the corresponding W—W distances.

**Introduction.** Much of the attention on the heteropoly compounds has been focused on their redox chemistry because of their catalytic activities for the oxidation reactions. The Keggin  $[X^{n+}M_{12}O_{40}]^{(8-n)-}$  anions are the most extensively studied as there are many isomorphs with different central heteroatoms. The charge of the central heteroatom determines the net charge of the anion, which influences its reduction potential (summarized by Pope, 1983). In contrast with this isotropic effect, substituting the peripheral metal atoms (Mo or W) changes not only the net charge but the charge distribution on the surface of the polyanion, where the chemical reaction takes place.

However, these substituted anions tend to be disordered in the crystal since they retain the highly symmetric structure of their original Keggin anion. The  $[CoW_{11}Co(H_2O)O_{39}]^{8-}$  (Barrett, 1972) and  $[VW_8V_4O_{40}]^{7-}$  anions (Nishikawa, Kobayashi & Sasaki, 1975) are located at the  $\bar{4}3m$  sites, giving no structural information about the substituted sites. Although the W<sup>IV</sup> and W<sup>VI</sup> sites were resolved and independently refined in the  $C_{3v}$   $H_8[H_2W_9^{VI}W_3^{IV}O_{40}]^{4-}$  anion located at the  $\bar{4}3m$  site, the O atoms bonded to the W<sup>IV</sup> atoms and those bonded to the W<sup>VI</sup> atoms were not resolved and refined as single atoms (Jeannin, Launay & Sedjadi, 1980). They showed very anisotropic thermal parameters, indicating the displacement of the O atoms bonded

to the W<sup>IV</sup> atoms from those bonded to the W<sup>VI</sup> atoms. In the  $\beta_1$  isomer of the  $[SiW_{11}MoO_{40}]^{4-}$  anion (Robert, Tézé, Hervé & Jeannin, 1980), the Mo atom is in the rotated  $M_3O_{13}$  unit of the  $\beta$  Keggin structure. However, the Mo atom was disordered in the three equivalent positions and no structural deviations caused by the metal substitution was revealed. In the two structure analyses of  $\alpha$ - $XM_{11}$  Keggin anions ( $SiW_{11}O_{39}^{6-}$ : Matsumoto & Sasaki, 1976;  $PW_{11}O_{39}^{7-}$ : Fuchs, Thiele & Palm, 1981), the lacunary sites were disordered. In this work, we carried out the X-ray crystal structure analysis of the diethylammonium sodium salt of the dititanodecatungstophosphate. This compound was found to preserve the preferred orientation in its crystal and the substituted sites were distinguishable. The predominant configuration has  $C_2$  symmetry, which confirms the result of the <sup>183</sup>W NMR work by Domaille & Knoth (1983). The Ti substitution reduces the original  $T_d$  symmetry of the  $M_{12}$  skeleton to  $C_2$ . The  $MO_6$  octahedra are also deformed. The terminal O atoms attached to the Ti atoms were found to be protonated to form the terminal OH groups.

**Experimental.** The  $[PTi_2W_{10}O_{40}]^{7-}$  anion was prepared according to the procedure described by Domaille & Knoth (1983).  $(C_2H_5)_2NH_2Cl$  powder was added to the resulting solution. Colourless crystals of the title compound were obtained after 24 h.  $D_m$  by flotation method in  $CH_2I_2/C_2H_4Br_2$ . Single crystal with the dimension of  $0.27 \times 0.08 \times 0.08$  mm, elongated along the  $a$  axis, was sealed in a glass capillary. Rigaku AFC5R four-circle diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). Cell parameters from  $2\theta$  values of 22 reflections with  $20 \leq 2\theta \leq 27^\circ$ . A total of 10 846 independent reflections were collected with  $2\theta$  ranging from 5 to  $60^\circ$ , of which 6524 with  $I_{obs} > 3\sigma(I_{obs})$  were used for the structure determination.  $\omega$ - $2\theta$  scan,  $\Delta\omega = (0.8 + 0.14\tan\theta)^\circ$ , scan speed  $8^\circ \text{ min}^{-1}$  in  $\omega$ . Range of indices  $0 \leq h \leq 26$ ,  $0 \leq k \leq 27$ ,  $0 \leq l \leq 29$ ,  $(\sin\theta/\lambda)_{max} = 0.704$  Å<sup>-1</sup>. Lp and absorption corrections (de Meulenaer & Tompa, 1965). Transmission factors from 0.239 to 0.336. Three standard reflec-

tions 10,0,0, 0,10,0 and 008 monitored every 150 reflections, intensity variations within  $\pm 2\%$  in  $F_{\text{obs}}$ .

The positions of the W and Ti atoms were obtained from the direct method using *MITHRIL* (Gilmore, 1984). Difference Fourier syntheses located the remaining non-H atoms. Anisotropic temperature factors were applied to W, Ti and P atoms. The occupancies of the Ti(A) and Ti(B) sites were refined with the constraint that the total of the W and Ti occupancies is 1.0 at each site. The full-matrix least-squares refinement on  $F$  converged to  $R = 0.056$  and  $wR = 0.064$  for 408 parameters and 6524 independent reflections. Function minimized was  $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ . Weighting scheme employed was  $w^{-1} = \sigma^2(F_{\text{obs}})$ , where  $\sigma^2(F_{\text{obs}}) = \sigma^2(I_{\text{obs}}) + (0.05I_{\text{obs}})^2$ .  $S = 1.40$ ,  $(\Delta/\sigma)_{\text{max}} = 0.02$ , the maximum positive and negative peaks in the final difference Fourier map were  $+4.2$  and  $-3.2 \text{ e } \text{\AA}^{-3}$ . The complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the calculations were carried out on a MicroVAX II computer using the *TEXSAN* (Molecular Structure Corporation, 1989) software package. The final atomic parameters are given in Table 1.\*

\* Lists of structure factors, anisotropic thermal parameters and complete lists of interatomic distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53619 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^3$ ;  $\times 10^4$  for Ti, P and Na;  $\times 10^5$  for W) and equivalent or isotropic thermal parameters ( $\text{\AA}^2$ )

	x	y	z	$B_{\text{eq}}^*/B_{\text{iso}}$
W(1)	32669 (8)	14956 (7)	12342 (8)	1.52
W(2)	23197 (8)	6713 (6)	24791 (7)	1.30
W(3)	44939 (7)	24070 (7)	24254 (7)	1.40
W(4)	35763 (7)	15684 (7)	36874 (7)	1.49
W(5)	37089 (7)	33877 (7)	36642 (7)	1.42
W(6)	15873 (8)	36027 (7)	13099 (8)	1.61
W(7)	27100 (8)	44637 (6)	24120 (7)	1.38
W(8)	5549 (7)	27324 (7)	26598 (7)	1.42
W(9)	16636 (8)	36025 (8)	37801 (8)	1.88
W(10)	15283 (8)	17818 (7)	38193 (7)	1.57
Ti(A)†	1386 (2)	1650 (2)	1362 (2)	1.52
Ti(B)‡	3468 (2)	3456 (2)	1210 (2)	1.46
P	2225 (5)	2567 (4)	2500 (4)	1.09
O <sub>v</sub> (1)	382 (1)	106 (1)	66 (1)	1.9 (4)
O <sub>v</sub> (2)	226 (1)	-21 (1)	266 (1)	2.1 (4)
O <sub>v</sub> (3)	542 (1)	229 (1)	226 (1)	1.4 (4)
O <sub>v</sub> (4)	390 (1)	98 (1)	425 (1)	2.4 (5)
O <sub>v</sub> (5)	415 (1)	393 (1)	420 (1)	1.3 (4)
O <sub>v</sub> (6)	96 (1)	402 (1)	78 (1)	1.7 (4)
O <sub>v</sub> (7)	280 (1)	535 (1)	256 (1)	1.1 (3)
O <sub>v</sub> (8)	-42 (1)	282 (1)	260 (1)	2.7 (5)
O <sub>v</sub> (9)	144 (1)	421 (1)	440 (1)	2.0 (4)
O <sub>v</sub> (10)	118 (1)	123 (1)	442 (1)	2.6 (5)
O <sub>v</sub> (A)	72 (1)	136 (1)	78 (1)	2.0 (4)
O <sub>v</sub> (B)	405 (1)	372 (1)	56 (1)	2.3 (5)
O <sub>v</sub> (12)	303 (1)	68 (1)	181 (1)	1.3 (4)
O <sub>v</sub> (1A)	233 (1)	140 (1)	88 (1)	1.6 (4)
O <sub>v</sub> (2A)	154 (1)	76 (1)	188 (1)	1.2 (3)
O <sub>v</sub> (3A)	440 (1)	170 (1)	315 (1)	1.3 (4)
O <sub>v</sub> (35)	456 (1)	309 (1)	311 (1)	1.2 (3)
O <sub>v</sub> (45)	381 (1)	248 (1)	407 (1)	2.0 (4)
O <sub>v</sub> (67)	190 (1)	444 (1)	183 (1)	1.6 (4)
O <sub>v</sub> (6B)	250 (1)	371 (1)	85 (1)	1.2 (4)

Table 1 (cont.)

	x	y	z	$B_{\text{eq}}^*/B_{\text{iso}}$
O <sub>v</sub> (7B)	338 (1)	435 (1)	172 (1)	1.5 (4)
O <sub>v</sub> (89)	73 (1)	344 (1)	333 (1)	1.9 (4)
O <sub>v</sub> (80)	63 (1)	207 (1)	337 (1)	1.4 (4)
O <sub>v</sub> (90)	150 (1)	268 (1)	424 (1)	1.4 (4)
O <sub>v</sub> (13)	401 (1)	172 (1)	191 (1)	1.6 (4)
O <sub>v</sub> (1B)	331 (1)	248 (1)	101 (1)	1.4 (3)
O <sub>v</sub> (3B)	420 (1)	311 (1)	186 (1)	1.2 (3)
O <sub>v</sub> (24)	313 (1)	96 (1)	306 (1)	1.6 (4)
O <sub>v</sub> (20)	172 (1)	107 (1)	313 (1)	2.1 (4)
O <sub>v</sub> (40)	259 (1)	175 (1)	401 (1)	1.6 (4)
O <sub>v</sub> (68)	90 (1)	342 (1)	207 (1)	1.7 (4)
O <sub>v</sub> (6A)	148 (1)	263 (1)	111 (1)	2.3 (4)
O <sub>v</sub> (8A)	77 (1)	202 (1)	205 (1)	1.6 (4)
O <sub>v</sub> (57)	344 (1)	402 (1)	300 (1)	1.7 (4)
O <sub>v</sub> (59)	270 (1)	345 (1)	396 (1)	1.4 (4)
O <sub>v</sub> (79)	201 (1)	421 (1)	310 (1)	2.4 (5)
O <sub>v</sub> (12A)	244 (1)	188 (1)	210 (1)	1.3 (4)
O <sub>v</sub> (345)	324 (1)	251 (1)	289 (1)	0.7 (3)
O <sub>v</sub> (67B)	256 (1)	323 (1)	206 (1)	0.9 (3)
O <sub>v</sub> (890)	188 (1)	264 (1)	299 (1)	0.7 (3)
N(1)	248 (2)	511 (2)	499 (2)	2.9 (6)
C(1)	293 (3)	451 (2)	530 (2)	3.5 (9)
C(2)	255 (3)	411 (3)	583 (2)	4.4 (10)
C(3)	287 (3)	534 (3)	447 (3)	4.5 (11)
C(4)	245 (3)	597 (3)	419 (2)	4.4 (10)
N(2)	456 (3)	498 (3)	752 (3)	7.3 (13)
C(5)	415 (3)	420 (3)	787 (3)	5.7 (13)
C(6)	370 (4)	381 (3)	746 (3)	7.6 (16)
C(7)	509 (3)	477 (3)	693 (3)	5.6 (13)
C(8)	548 (3)	536 (2)	671 (2)	3.4 (8)
N(3)	488 (2)	266 (2)	991 (2)	4.8 (9)
C(9)	518 (4)	213 (3)	1037 (3)	6.5 (15)
C(10)	589 (5)	223 (5)	1079 (4)	12.3 (29)
C(11)	439 (2)	222 (2)	952 (2)	3.3 (8)
C(12)	408 (3)	255 (3)	897 (3)	6.0 (13)
N(4)	453 (2)	15 (2)	254 (2)	4.6 (8)
C(13)	491 (4)	2 (4)	185 (4)	9.7 (24)
C(14)	544 (2)	53 (2)	166 (2)	2.6 (7)
C(15)	442 (4)	-43 (3)	300 (3)	6.2 (14)
C(16)	392 (3)	-97 (3)	265 (2)	4.6 (10)
Na	169 (8)	1007 (8)	5105 (7)	2.3 (3)
O <sub>w</sub> (1)§	514 (1)	85 (1)	478 (1)	0.9 (3)
O <sub>w</sub> (2)	493 (1)	19 (1)	998 (1)	2.7 (5)
O <sub>w</sub> (3)	214 (1)	227 (1)	639 (1)	3.3 (5)
O <sub>w</sub> (4)	333 (2)	242 (2)	544 (1)	4.1 (6)
O <sub>w</sub> (5)	450 (2)	338 (2)	568 (1)	3.9 (6)
O <sub>w</sub> (6)	457 (2)	138 (2)	569 (2)	4.8 (7)
O <sub>w</sub> (7)	157 (2)	340 (2)	704 (2)	4.7 (7)
O <sub>w</sub> (8)	75 (2)	163 (2)	600 (2)	5.0 (8)
O <sub>w</sub> (9)	64 (2)	448 (2)	634 (2)	5.3 (8)
O <sub>w</sub> (10)	307 (2)	172 (2)	737 (2)	6.3 (9)
O <sub>w</sub> (11)	204 (3)	31 (2)	993 (2)	7.2 (11)

$$* B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

† Occupied 72.0 (7)% by Ti and 28.0% by W.

‡ Occupied 69.8 (7)% by Ti and 30.2% by W.

§ O<sub>w</sub> denote O atoms of water of crystallization.

**Discussion.** The [H<sub>2</sub>PTi<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>5-</sup> anion has the Keggin structure. Three metal atoms share one O atom (O<sub>c</sub>), which also coordinates to the central P atom. Each two of these three metal atoms share another O atom (O<sub>e</sub>) to form an edge-shared M<sub>3</sub>O<sub>13</sub> triad. Four M<sub>3</sub>O<sub>13</sub> units share two O atoms (O<sub>v</sub>) with each other to make up the PM<sub>12</sub>O<sub>40</sub> framework. Each metal atom is octahedrally coordinated by one O<sub>c</sub>, two O<sub>e</sub>, two O<sub>v</sub> and one O<sub>t</sub> (terminal O) atoms. Two metal atom sites have lower electron densities than the other ten sites. These atoms are assigned as the Ti atoms. Subsequent refinement led to their negative temperature factors. Therefore, the occupancies of these sites were refined with the full-matrix least-squares program assuming that the sum of the Ti and W occupancies is unity at each site.



Fig. 2 shows the packing diagram of the unit cell. The intermolecular contacts are illustrated by the thin lines. The N(3) atom is connected to the O<sub>i</sub>(A) (2.77 Å) and O<sub>i</sub>(B) (2.82 Å) atoms which belong to the two anions related to each other by the screw axis along *a*. This is the major reason why the highly symmetric [H<sub>2</sub>PTi<sub>2</sub>W<sub>10</sub>O<sub>40</sub>]<sup>3-</sup> anion is not completely disordered in this crystal unlike the other substituted Keggin anions. The elongated shape along the *a* axis of the crystal is due to the same reason. This is the first X-ray structure analysis which has succeeded in identifying the substituted sites of an  $\alpha$ -Keggin anion and observing the structural deviations caused by the metal substitution.

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## Structure of LaCuO<sub>3</sub> by Powder Neutron Diffraction

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**Abstract.** Lanthanum copper oxide, LaCuO<sub>3</sub>, *M<sub>r</sub>* = 250.46, hexagonal, *P*6<sub>3</sub>, *a* = 5.50195 (1), *c* = 13.2124 (4) Å, *V* = 346.4 Å<sup>3</sup>, *Z* = 6, *D<sub>x</sub>* = 7.20 g cm<sup>-3</sup> at room temperature; *a* = 5.49219 (1), *c* = 13.1545 (2) Å, *V* = 346 Å<sup>3</sup> at 5 K, *R<sub>p</sub>* = 6.2%. The structure of the title compound, synthesized at 5 × 10<sup>9</sup> Pa, was refined using time-of-flight powder neutron diffraction methods. The structure is perovskite based with octahedral copper(III), Cu—O 1.9511 (3) Å, and a strongly distorted 12-coordinated lanthanum, La—O 2.483 (2)–3.019 (2) Å.

**Introduction.** Ternary oxides containing copper(III) in association with alkali metals are well known and are readily prepared at around 673 K in oxygen. Some evidence exists for ternary oxides of copper with alkaline earths, particularly barium in the compounds BaCuO<sub>2+x</sub> and Ba<sub>2</sub>CuO<sub>3+x</sub>, though no pure copper(3+) compound with these elements is known. LaCuO<sub>3</sub> was first described by Demazeau, Parent, Pouchard & Hagenmuller (1972) who synthesized it rapidly under very high oxygen pressures; the material is isomorphous with LaNiO<sub>3</sub>, having rhombohedrally distorted perovskite structure. Webb *et al.* (1989) have studied this compound more

recently and describe an irreversible transformation to a tetragonal phase above about 673 K.

As a result of the high pressures required for the synthesis of LaCuO<sub>3</sub>, only milligram quantities are generally available. Such quantities are sufficient for powder X-ray work and allowed Demazeau *et al.* to define a structure by comparison with LaNiO<sub>3</sub>; a more accurate structure refinement, particularly of the oxygen position, occupancy and temperature factors could be obtained from neutron diffraction data. However, this technique normally requires multi-gram quantities. In this article we describe the struc-

Table 1. *Experimental data*

Instrument	POLARIS, ISIS Rutherford-Appleton Laboratory
Sample container	Vanadium can 5 mm diameter
Time-of-flight range	4000–18000 μs (0.7 < 3.2 Å)
Number of points	1303
Number of reflections	150
Absorption correction	None
Geometric constriction	None
Number of cycles in final refinement	5
Number of structural parameters	10
Number of profile parameters	15
Maximum shift/e.s.d. for final cycle	0.0009