Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu—O(2^i)	1.894 (6)	Si(3)—O(10^i)	1.593 (4)
Cu—O(3^v)	1.961 (6)	Si(4)—O(6^{iii})	1.619 (7)
Cu—O(3^{ii})	1.965 (5)	Si(4)—O(8^{xiii})	1.551 (7)
Cu—O(8^{iii})	1.895 (7)	Si(4)—O(9^{xiii})	1.653 (6)
Si(1)—O(2^{iii})	1.574 (6)	Si(4)—O(12)	1.608 (4)
Si(1)—O(4^{xii})	1.637 (7)	Rb(1)—O(2) ×2^i	3.010 (7)
Si(1)—O(7^{iii})	1.637 (7)	Rb(1)—O(2) ×2^{iv,ix}	3.164 (7)
Si(1)—O(11^i)	1.621 (4)	Rb(1)—O(4) ×2^{v,iii}	3.111 (7)
Si(2)—O(1)	1.613 (4)	Rb(1)—O(8) ×2^{ix}	3.180 (7)
Si(2)—O(3^{xiii})	1.597 (6)	Rb(2)—O(6) ×2^{vi,vii}	3.294 (7)
Si(2)—O(7^{ix})	1.629 (6)	Rb(2)—O(7) ×2^{i,iii}	3.041 (7)
Si(2)—O(9^{xv})	1.628 (6)	Rb(2)—O(9) ×2^{x,xi}	3.131 (7)
Si(3)—O(4)	1.592 (6)	Rb(2)—O(9) ×2^{ii,viii}	3.097 (7)
Si(3)—O(5^{xiv})	1.577 (3)	Rb(2)—O(10^{xi})	3.092 (13)
Si(3)—O(6^{xvi})	1.610 (7)	Rb(2)—O(12^x)	3.246 (13)

O(2^i)—Cu—O(3^v)	95.9 (2)	O(3^{xiii})—Si(2)—O(9^{xv})	111.5 (3)
O(2^i)—Cu—O(8^{iii})	92.0 (3)	O(7^{ix})—Si(2)—O(9^{xv})	106.4 (4)
O(3^{ii})—Cu—O(3^v)	79.1 (2)	O(4)—Si(3)—O(5^{xiv})	111.3 (3)
O(3^{ii})—Cu—O(8^{iii})	94.9 (3)	O(4)—Si(3)—O(6^{xvi})	112.1 (4)
O(2^{iii})—Si(1)—O(4^{xii})	108.4 (4)	O(4)—Si(3)—O(10^i)	109.0 (5)
O(2^{iii})—Si(1)—O(7^{iii})	112.3 (3)	O(5^{xiv})—Si(3)—O(6^{xvi})	108.7 (3)
O(2^{iii})—Si(1)—O(11^i)	115.1 (5)	O(5^{xiv})—Si(3)—O(10^i)	109.7 (5)
O(4^{xii})—Si(1)—O(7^{iii})	107.8 (3)	O(6^{xvi})—Si(3)—O(10^i)	105.9 (6)
O(4^{xii})—Si(1)—O(11^i)	106.3 (4)	O(6^{iii})—Si(4)—O(8^{xiii})	114.0 (4)
O(7^{iii})—Si(1)—O(11^i)	106.6 (4)	O(6^{iii})—Si(4)—O(9^{xiii})	103.9 (3)
O(1)—Si(2)—O(3^{xiii})	113.2 (5)	O(6^{iii})—Si(4)—O(12)	106.4 (6)
O(1)—Si(2)—O(7^{ix})	107.5 (4)	O(8^{xiii})—Si(4)—O(9^{xiii})	112.1 (4)
O(1)—Si(2)—O(9^{xv})	107.4 (5)	O(8^{xiii})—Si(4)—O(12)	116.5 (6)
O(3^{xiii})—Si(2)—O(7^{ix})	110.6 (4)	O(9^{xiii})—Si(4)—O(12)	102.6 (5)

Symmetry code: (i) $1 - x$, $-\frac{1}{2} + y$, $1 - z$; (ii) x, $\frac{1}{2} - y$, $1 + z$; (iii) $1 - x$, $1 - y$, $1 - z$; (iv) $1 - x$, $2 - y$, $1 - z$; (v) $1 - x$, $\frac{1}{2} + y$, $1 - z$; (vi) $-1 + x$, $-1 + y$, z; (vii) $-1 + x$, $\frac{1}{2} - y$, z; (viii) $-x$, $1 - y$, $1 - z$; (ix) x, $\frac{3}{2} - y$, z; (x) x, y, $1 + z$; (xi) $-x$, $-\frac{1}{2} + y$, $1 - z$; (xii) $1 - x$, $-y$, $1 - z$; (xiii) x, $\frac{1}{2} - y$, z; (xiv) $1 + x$, y, z; (xv) $1 - x$, $1 - y$, $-z$; (xvi) x, $-1 + y$, z.

repeating unit along the shortest period of the cell. CuO$_4$ squares share corners with SiO$_4$ tetrahedra. Two kinds of Rb atom site have eight and ten nearest O-atom neighbours, respectively, and are located in the cavity of the six-membered rings.

The interatomic distances and bond angles are listed in Table 2. Si—O and Cu—O distances agree with previous data (Kawamura & Kawahara, 1976,

1977; Kawamura, Kawahara & Iiyama, 1978; Kawamura & Iiyama, 1981; Heinrich & Gramlich, 1982). In the SiO$_4$ double sheets, the bridging Si—O distance to other Si atoms (mean 1.626 Å) is significantly longer than those to Cu and Rb atoms (mean 1.578 Å). The average Si—O distances for the four SiO$_4$ tetrahedra are 1.617, 1.617, 1.593 and 1.608 Å, and the distortion indices, $[d(M—O)_{max} - d(M—O)_{min}]/\langle d(M—O) \rangle$, of SiO$_4$ tetrahedra (Liebau, 1985) are 3.92×10^{-2}, 1.98×10^{-2}, 2.02×10^{-2} and 6.34×10^{-2}, respectively. The bonding of SiO$_4$ tetrahedra and CuO$_4$ squares is directional and rigid compared with Rb—O polyhedra, which are irregular in shape and have ionic character. Accordingly, the latter are considered to compensate for all the strains resulting from the framework constructed by these rigid and rather covalent sp^3 tetrahedra of SiO$_4$ and the dsp^2 planar CuO$_4$ squares. Here the alkali metals may play an important role in the stabilization of the structure. In fact, the number of phases containing $A_xCu_ySi_pO_q$ (A = alkali metal) is much larger than that containing only Cu$_x$Si$_p$O$_q$.

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Structure of Potassium Paradodecatungstate 7½-Hydrate

BY HOWARD T. EVANS JR

US Geological Survey, Reston, Virginia 22092, USA

AND ULI KORTZ AND GEOFFREY B. JAMESON

Department of Chemistry, Georgetown University, Washington, DC 20057, USA

Abstract. K$_{10}$[H$_2$W$_{12}$O$_{42}$].7½H$_2$O, $M_r = 3406.3$, triclinic, $P\bar{1}$, $a = 13.126$ (2), $b = 16.274$ (7), $c = 11.756$ (4) Å, $\alpha = 96.77$ (2), $\beta = 90.04$ (2), $\gamma = 77.77$ (2)°, $V = 2436.4$ Å^3, $Z = 2$, $D_x = 4.645$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 280.5$ cm^{-1}, $F(000) = 2982$, $T = 296$ K, $R = 0.051$, $wR = 0.067$ and $S =$

2.20 for 7588 observed reflections with $2\theta < 52°$. Two independent polyanions are present centered at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The crystal is isostructural with that previously reported for $(NH_4)_6H_6W_{12}O_{42}.10H_2O$, but evidently four NH_4 groups were misidentified as H_2O molecules, and the ammonium compound should be written as $(NH_4)_{10}[H_2W_{12}O_{42}].6(or\ 7\frac{1}{2})H_2O$.

Introduction. In an approach to a metadodecatungstate synthesis (Flynn & Pope, 1973), a solution of K_2WO_4 lightly acidified with acetic acid (pH 4–5) deposited large clear tabular crystals. These have been found by crystal structure analysis to be a paradodecatungstate salt, $K_{10}[H_2W_{12}O_{42}].7\frac{1}{2}H_2O$. The structure turned out to be closely isotypic with the previously reported structure of $(NH_4)_6H_6W_{12}O_{42}.10H_2O$ (Averbuch-Pouchot, Tordjman, Durif & Guitel, 1979), indicating that the chemistry of the latter needs to be revised.

Experimental. The structure of the crystal defined in Table 1 was solved and refined independently from two different data sets, one at US Geological Survey, and the other at Georgetown University; each study was undertaken unknown to the other until after the refinements were completed. Different techniques of data collection and refinement were used in each case, but the results obtained in the latter study, which gave lower coordinate standard deviations and better internal consistency, are those reported in detail here.

The triclinic unit-cell dimensions given in Table 1 (and the orientation matrix) were obtained by least-squares refinement of the setting angles for 19 carefully centered reflections in the 2θ range 25–27°. The crystal used for structure analysis was a very thin plate, $0.25 \times 0.60 \times 0.015$ mm in dimensions. Graphite-monochromated Mo $K\alpha$ radiation was used to measure intensity data in one hemisphere of the reciprocal sphere bounded by $2\theta = 52°$. Of these intensity data, 7588 with $I > 5.0\sigma(I)$ were used for the structure analysis. Lorentz and polarization corrections were applied to the data, and anomalous-dispersion corrections were applied to the atomic scattering factors. Empirical absorption corrections were computed from ψ scans of four reflections, and also by the internal empirical method of Walker & Stuart (1983) using the program *DIFABS* during refinement. The latter method appeared to lead to improved results, which are reported here. Other diffraction parameters are listed in Table 2.

Application of *MULTAN*11/82 (Main *et al.*, 1982), as incorporated in the Enraf–Nonius *MolEN* package (Fair, 1990), led directly to a valid structure dominated by two of the familiar paradodecatungstate polyanions, one at the center of inversion at the origin, the other at the center of inversion at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

Table 1. *Crystallography of potassium and ammonium paradodecatungstates*

	$K_{10}[H_2W_{12}O_{42}].7\frac{1}{2}H_2O$	$(NH_4)_{10}[H_2W_{12}O_{42}].6H_2O$*
Formula weight	3415.3	3186.7
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell		
a (Å)	13.126 (2)	13.21 (1)
b (Å)	16.274 (7)	16.63 (1)
c (Å)	11.756 (4)	11.94 (2)
α (°)	96.77 (2)	97.31 (5)
β (°)	90.04 (2)	91.39 (5)
γ (°)	77.77 (2)	77.54 (5)
V (Å³)	2436.4 (4)	2540.4
Z	2	2
Density D, (g cm⁻³)	4.65	4.17
Data set		
Total No. of reflections	9370	5437
No. used in refinement	7588	4025
Radiation	Mo $K\alpha$	Ag $K\alpha$
Absorption		
μ (cm⁻¹)	280.5	149.1
Correction, range of A	0.12–1.00 (on F^2)†	–
	0.83–1.17 (on F^2)‡	
R	0.051	0.040
wR	0.067	–
Goodness of fit S	2.20	–

* All data for the ammonium salt were reported by Averbuch-Pouchot *et al.* (1979), who originally formulated $(NH_4)_6H_6W_{12}O_{42}.10H_2O$. Their unit cell is transformed to the K cell by the matrix: $[0,1,0/0,0,-1/-1,0,0]$.

† Based on ψ scans.

‡ From *DIFABS* (Walker & Stuart, 1983).

Table 2. *Experimental diffraction and refinement parameters*

Diffractometer	Extensively modified Picker 4-circle
Range of h	$-15\rightarrow15$
k	$-19\rightarrow20$
l	$-14\rightarrow0$
2θ (°)	$4.0\rightarrow52$
Standard reflections	500, 020, 002
Variation of standards (%)	±2
Refinement mode	Full matrix on F
Number of parameters refined	407
Quantity minimized	$\Sigma w\,\Delta F_i^2$
Weighting scheme, based on modified counting statistics	$w = 1/\sigma^2(F),\ \sigma^2(F) = \sigma_{cs}^2 + 0.04\,F^2$
Maximum shift/e.s.d.	0.07
Maximum and minimum in final difference map (e Å⁻³)	2.8, -0.8

Electron density and difference Fourier maps revealed ten sharp intermolecular peaks, which were assigned to K atoms, thus completing the charge balance within the crystal. Ten further peaks were assigned to water molecules. One, Aq(5), was very weak, so that partial occupancy was strongly suggested; it was assigned a fixed occupancy of 0.5. Four other weak peaks in neighboring pairs were assumed to represent two water molecules, Aq(7) and Aq(8), each split with one-half occupancy between two adjacent sites designated a and b. The final atomic coordinates and mean isotropic thermal vibrations are listed in Table 3.* Atomic scattering factors used

* Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55796 (90 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0197]

Table 3. *Atomic coordinates and thermal parameters* (Å^2) *for* $K_{10}[H_2W_{12}O_{42}].7\frac{1}{2}H_2O$

O atoms were refined isotropically. $\overline{U}$ is the r.m.s. thermal displacement. Non-labile H atoms H(100) and H(200) were symmetrically located between O(x08) and O(x13) ($x = 1, 2$), 0.97 Å from O(x07) (Evans & Prince, 1983). These atoms were not included in the refined model. Corresponding atom designations of Averbuch-Pouchet *et al.* (1979) for the ammonium salt are listed in the last column (NH₄).

	x	y	z	$\overline{U}$	(NH₄)
Molecule A at 0,0,0 (100 series)					
W(101)	−0.06800 (6)	0.11116 (4)	0.20593 (4)	0.122 (5)	W(12)
W(102)	0.16913	−0.00486	0.23997	0.128	W(4)
W(103)	0.13266	0.11737	0.02963	0.126	W(11)
W(104)	−0.30599	0.11050	0.02664	0.134	W(10)
W(105)	−0.04279	−0.12090	0.26977	0.130	W(1)
W(106)	−0.28314	−0.01131	0.23223	0.135	W(6)
O(101)	0.031 (1)	0.1745 (8)	0.149 (1)	0.14 (2)	O(26)
O(102)	0.057	0.0732	0.311	0.16	O(21)
O(103)	0.216	0.0765	0.168	0.16	O(25)
O(104)	−0.132	0.1881	0.311	0.16	O(8)
O(105)	0.199	0.1954	0.017	0.18	O(28)
O(106)	0.255	−0.0211	0.350	0.15	O(13)
O(107)	0.056	0.0198	0.095	0.14	O(24)
O(108)	−0.149	0.1234	0.083	0.15	O(4)
O(109)	−0.111	0.0145	0.248	0.14	O(1)
O(110)	0.089	−0.0920	0.262	0.14	O(10)
O(111)	0.239	−0.0881	0.122	0.14	O(17)
O(112)	0.227	0.0228	−0.051	0.14	O(32)
O(113)	0.040	0.1234	−0.085	0.16	O(37)
O(114)	0.320	−0.1022	−0.191	0.13	O(3)
O(115)	−0.188	−0.1168	0.240	0.15	O(35)
O(116)	−0.061	−0.1002	0.419	0.16	O(34)
O(117)	0.000	−0.2311	0.255	0.18	O(38)
O(118)	−0.341	0.2207	0.037	0.17	O(42)
O(119)	−0.419	0.0782	−0.019	0.17	O(16)
O(120)	−0.299	0.0198	0.380	0.17	O(2)
O(121)	−0.395	−0.0468	0.196	0.18	O(40)
H(100)	0.010	0.061	0.055		
Molecule B at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ (200 series)					
W(201)	0.72419 (6)	0.47496 (4)	0.47609 (5)	0.12 (1)	W(8)
W(202)	0.61148	0.67038	0.42116	0.13	W(7)
W(203)	0.54734	0.50337	0.26799	0.12	W(2)
W(204)	0.33157	0.70103	0.36477	0.13	W(5)
W(205)	0.37072	0.34989	0.26887	0.13	W(9)
W(206)	0.26451	0.54250	0.20688	0.13	W(3)
O(201)	0.311 (1)	0.5369 (8)	0.687 (2)	0.14 (2)	O(5)
O(202)	0.263	0.4031	0.560	0.14	O(36)
O(203)	0.405	0.3826	0.722	0.15	O(39)
O(204)	0.142	0.5641	0.535	0.15	O(7)
O(205)	0.435	0.5199	0.879	0.16	O(6)
O(206)	0.349	0.2405	0.611	0.17	O(33)
O(207)	0.439	0.4497	0.543	0.12	O(31)
O(208)	0.326	0.6150	0.500	0.14	O(41)
O(209)	0.290	0.4737	0.369	0.14	O(22)
O(210)	0.402	0.3080	0.411	0.16	O(20)
O(211)	0.540	0.2877	0.569	0.17	O(12)
O(212)	0.590	0.4225	0.720	0.14	O(14)
O(213)	0.503	0.5873	0.690	0.13	O(30)
O(214)	0.222	0.6429	0.313	0.14	O(18)
O(215)	0.349	0.4330	0.159	0.13	O(19)
O(216)	0.249	0.3229	0.251	0.16	O(23)
O(217)	0.450	0.2713	0.181	0.17	O(27)
O(218)	0.251	0.7790	0.456	0.16	O(11)
O(219)	0.345	0.7475	0.241	0.16	O(15)
O(220)	0.143	0.5160	0.191	0.16	O(29)
O(221)	0.279	0.5904	0.083	0.18	O(9)
H(200)	0.428	0.510	0.564		
Intermolecular cation and water molecules					
K(1)	0.1295 (4)	0.9282 (3)	0.5139 (3)	0.16 (1)	NH₄(1)
K(2)	0.1676 (4)	0.7559 (3)	0.0918 (4)	0.19 (1)	NH₄(2)
K(3)	0.1701 (5)	0.3690 (3)	0.0347 (3)	0.21 (1)	NH₄(3)
K(4)	0.0563 (4)	0.7201 (3)	0.4737 (4)	0.18 (1)	NH₄(4)
K(5)	0.3481 (5)	0.7403 (4)	0.6882 (5)	0.23 (1)	NH₄(5)
K(6)	0.0673 (4)	0.4391 (3)	0.3649 (4)	0.20 (1)	NH₄(6)
K(7)	0.4071 (5)	0.1040 (5)	0.1023 (6)	0.27 (2)	O(W6)
K(8)	0.4543 (5)	0.8718 (4)	0.2468 (5)	0.23 (1)	O(W9)
K(9)	0.2489 (4)	0.1259 (3)	0.5032 (4)	0.20 (1)	O(W5)
K(10)	0.4788 (5)	0.6428 (3)	0.0349 (4)	0.21 (1)	O(W1)
Aq(1)	0.123 (1)	0.241 (1)	0.372 (1)	0.20 (3)	O(W2)
Aq(2)	0.065 (2)	0.394 (1)	0.624 (1)	0.23 (4)	O(W3)
Aq(3)	0.360 (2)	0.254 (2)	0.878 (2)	0.30 (6)	O(W4)

Table 3. (*cont.*)

	x	y	z	$\overline{U}$	(NH₄)
Aq(4)	0.000 (2)	0.642 (1)	0.823 (2)	0.27 (5)	O(W7)
Aq(5a)*	0.190 (3)	0.509 (2)	0.889 (3)	0.23 (7)	O(W8)
Aq(6)	0.411 (2)	0.128 (1)	0.346 (2)	0.27 (5)	
Aq(7a)*	0.455 (3)	0.890 (2)	0.477 (2)	0.20 (6)	
Aq(7b)*	0.468 (3)	0.956 (2)	0.474 (3)	0.23 (7)	
Aq(8a)*	0.044 (3)	0.376 (2)	0.854 (3)	0.22 (7)	
Aq(8b)*	−0.013 (4)	0.356 (3)	0.918 (4)	0.3	

* Occupancy 0.5.
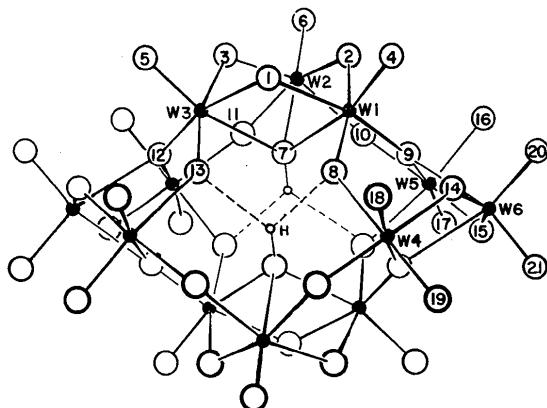
Fig. 1. Oblique view of the paradodecatungstate ion $[H_2W_{12}O_{42}]^{10-}$, showing the atom-numbering system of Allmann (1971) used in this description.

were those of Cromer & Mann (1968); anomalous-dispersion parameters and mass-absorption coefficients were taken from Cromer & Liberman (1970).

Discussion. In Table 3 the atoms are numbered and their sites (x, y, z) listed, corresponding to the two discrete paratungstate molecules in the unit cell. The numbering of atoms in the molecules (Fig. 1) follows the system of Allmann (1971). Atoms of molecule A centered at 0,0,0 are in the 100 series, and those of molecule B centered at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ are in the 200 series. The determined bond lengths are listed in Table 4, interatomic distances involving intermolecular cations and water molecules in Table 5, and principal W$\cdots$W and W$\cdots$center distances in Table 6. The variations among these various distances, all within a closely similar environment, give a good impression of the degree of flexibility and strain that the paradodecatungstate molecule can tolerate. There is still no evidence for any departure from $2/m$ symmetry for the free molecule.

The positions of the internal non-labile H atoms in the center of the paradodecatungstate molecule, which are predicted in Table 3, have been directly demonstrated by neutron diffraction in the compound $(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$ by Evans & Prince (1983).

Table 4. *Bond lengths* W—O (Å) *in* $K_{10}[H_2W_{12}O_{42}].7\frac{1}{2}H_2O$ *compared with those in the corresponding ammonium salt*

Bonds in the right-hand groups are related to those in the left-hand groups by the molecular pseudo-mirror plane. E.s.d.'s are ±0.01 Å for the K salt, ±0.02 Å for the NH₄ salt.

	K salt Molecule A $x=1$	K salt Molecule B $x=2$	NH₄ salt Molecule A $x=1$	NH₄ salt Molecule B $x=2$		K salt Molecule A $x=1$	K salt Molecule B $x=2$	NH₄ salt Molecule A $x=1$	NH₄ salt Molecule B $x=2$
W(x01)—O(x04)	1.73	1.74	1.74	1.76	W(x03)—O(x05)	1.70	1.72	1.78	1.72
—O(x08)	1.80	1.78	1.79	1.80	—O(x13)	1.82	1.86	1.84	1.84
—O(x09)	1.90	1.90	1.89	1.88	—O(x12)	1.91	1.94	1.96	1.91
—O(x01)	1.98	1.97	1.97	2.00	—O(x01)	1.95	1.93	1.97	1.95
—O(x02)	2.09	2.12	2.11	2.14	—O(x03)	2.06	2.07	2.08	2.07
—O(x07)	2.25	2.26	2.20	2.26	—O(x07)	2.26	2.28	2.27	2.28
W(x02)—O(x06)	1.72	1.72	1.73	1.77					
—O(x03)	1.86	1.83	1.89	1.85					
—O(x02)	1.85	1.85	1.89	1.85					
—O(x11)	1.91	1.96	1.91	1.98					
—O(x10)	1.98	1.96	1.97	1.94					
—O(x07)	2.28	2.28	2.25	2.26					
W(x04)—O(x18)	1.74	1.73	1.66	1.75	W(x05)—O(x17)	1.75	1.71	1.74	1.75
—O(x19)	1.74	1.74	1.77	1.73	—O(x16)	1.75	1.75	1.77	1.79
—O(x11)	1.92	1.89	1.91	1.91	—O(x10)	1.89	1.89	1.89	1.90
—O(x14)	1.96	1.94	1.91	1.91	—O(x15)	1.93	1.96	1.97	1.93
—O(x08)	2.21	2.25	2.21	2.20	—O(x13)	2.17	2.15	2.15	2.18
—O(x12)	2.25	2.18	2.16	2.23	—O(x09)	2.24	2.26	2.25	2.26
W(x06)—O(x20)	1.75	1.74	1.74	1.70					
—O(x21)	1.72	1.76	1.76	1.70					
—O(x14)	1.93	1.92	1.93	1.95					
—O(x15)	1.91	1.91	1.90	1.95					
—O(x12)	2.23	2.25	2.24	2.23					
—O(x09)	2.39	2.31	2.41	2.35					

When the potassium paradodecatungstate structure is compared with that of the ammonium salt $(NH_4)_6H_6W_{12}O_{42}.10H_2O$, whose structure was reported by Averbuch-Pouchot et al. (1979), the unit-cell parameters are found to be similar within 2% (Table 1). Furthermore, nearly all the atomic coordinates, after suitable transformation, are closely analogous. The main difference lies in the number of counterions present: Averbuch-Pouchot et al. (1979) found six NH_4^+ ions and postulated the presence of four H^+ ions to balance the charge of the polyanion $[H_2W_{12}O_{42}]^{10-}$, while in the present study a full complement of 10 K^+ ions was found. The four additional K^+ ions in this crystal correspond to four of the water molecules reported for the ammonium compound. Since it is not possible in structures of this type (dominated by the heavy W scatterers) to distinguish between N and O atoms, it must be concluded that Averbuch-Pouchot et al. (1979) misidentified four of the NH₄ groups as H₂O molecules. When this substitution is made a much more even distribution of counterions around the polyanions is found. The addition of extra H^+ ions is thus unnecessary, and the ammonium compound should probably be reformulated as $(NH_4)_{10}[H_2W_{12}O_{42}].6H_2O$ (or $7\frac{1}{2}H_2O$). The paradodecatungstate complex would hardly be stable in the presence of so many free protons.

Every atom listed for the ammonium compound by Averbuch-Pouchot et al. (1979) corresponds to an atom in the K compound except for O(W10), which could not be found in the electron density map of the K salt. Rather, five additional peaks were found which are labeled Aq(6), Aq(7a,b) and Aq(8a,b). As reported above, Aq(7) and Aq(8) were found to be split into two closely spaced pairs of peaks of half height. Aq(7a) and Aq(7b) are separated by 1.13 Å, and Aq(8a) and Aq(8b) are separated by 1.18 Å. The Aq(7b) site approaches its symmetry equivalent at 1.85 Å. The closest approach of any of these four sites to any other atoms is K(8)···Aq(7a), 2.69 Å. The K atoms all have seven to nine O-atom contacts between 2.62 and 3.25 Å, in a manner typical for this highly polarizable cation (Table 5). Several H₂O (Aq) contacts (Table 5) indicate the presence of a system of hydrogen bonds, but no attempt is made to interpret their contribution to the stability of the structure. There are six different O···O contacts less than 3.5 Å between neighboring paradodecatungstate molecules in the unit cell.

The structure of the K compound has been shifted by b/2 from that of the ammonium compound (Averbuch-Pouchot et al., 1979). Atom coordinates of Averbuch-Pouchot et al. (1979) are converted to the present setting by the formulae: $x_K = y_A$; $y_K = -z_A + 0.5$; $z_K = -x_A$, where subscript K denotes the present structure and subscript A denotes the ammonium salt. Interatomic distances in the molecules in the ammonium salt are compared with those in the K salt in Table 4.

Table 5. *Interatomic distances* (Å) *for intermolecular potassium and water in* $K_{10}[H_2W_{12}O_{42}].7\tfrac{1}{2}H_2O$

A primed atom label indicates an atom symmetrically related to a previously listed atom.

Potassium, K···O,Aq distances to 3.3 Å, ±0.01 Å except where noted

K(1)···O(218)	2.61	K(2)···O(118)	2.85 (2)	K(3)···Aq(8a)	2.69 (4)	K(4)···O(204)	2.73
···O(120)	2.79 (2)	···O(221)	2.77 (2)	···O(105)	2.75 (2)	···O(214)	2.86
···O(109)	2.84	···O(111)	2.87	···Aq(8b)	2.80 (5)	···Aq(2)	2.84 (2)
···O(116)	2.77	···O(117)	2.87 (2)	···O(220)	2.80	···O(218)	2.93 (2)
···O(106)	2.84	···O(219)	2.90	···Aq(4)	2.87 (2)	···O(117)	2.83
···O(116)'	2.84 (2)	···Aq(8b)	2.99 (6)	···O(216)	2.87	···Aq(1)	2.88 (2)
···O(104)	2.95	···O(108)	2.98	···Aq(5)	3.06 (4)	···O(104)	3.06
···O(110)	3.00	···O(110)	2.99	···O(215)	3.07	···O(116)	3.14
···O(102)	3.21	···O(113)	3.01	···Aq(3)	3.21 (3)		
K(5)···O(114)	2.73	K(6)···Aq(4)	2.68 (2)	K(7)···O(119)	2.62 (2)	K(8)···Aq(7a)	2.69 (3)
···O(213)	2.86	···O(220)	2.80	···O(103)	2.77 (2)	···O(121)	2.71 (2)
···O(208)	2.89	···Aq(2)	2.89 (2)	···Aq(6)	2.85 (2)	···O(219)	2.71 (2)
···O(104)	2.83 (2)	···O(216)	2.92	···O(217)	2.94 (2)	···O(111)	3.16
···O(217)	3.05 (2)	···O(204)	3.00	···O(119)'	2.98 (2)	···O(119)	2.90
···O(218)	3.09	···O(204)'	3.00	···O(105)	3.05 (2)	···Aq(7b)	2.88 (3)
···O(118)	3.22	···O(209)	3.09			···Aq(3)	3.08 (3)
···O(211)	3.30	···Aq(2)'	3.22 (2)			···O(106)	2.99
		···Aq(1)	3.16 (2)				
K(9)···O(116)	2.76 (2)	K(10)···O(205)	2.70				
···O(206)	2.70 (2)	···O(118)	2.77				
···O(106)	2.81	···O(205)'	2.95				
···O(120)	2.84 (2)	···O(221)	2.99 (2)				
···Aq(1)	2.83 (2)	···O(219)	3.10				
···Aq(6)	2.83 (2)	···Aq(3)	3.07 (3)				
···O(115)	3.15	···O(203)	3.27				
		···O(215)	3.15				
		···O(217)	3.27 (2)				

Water molecules, Aq—O,Aq distances to 3.3 Å

Aq(1)···O(216)	2.81 (2)	Aq(2)···O(202)	2.74 (2)	Aq(3)···O(105)	3.05 (3)	Aq(4)···O(101)	2.91 (3)
···O(102)	3.04 (2)	···Aq(8a)	2.77 (4)	···O(203)	3.09 (3)	···Aq(8b)	3.04 (5)
···O(101)	3.06 (2)	···O(204)	3.29 (2)	···O(206)	3.13 (3)	···Aq(5)	3.10 (4)
Aq(5)···O(221)	2.87 (4)	Aq(6)···O(210)	2.92 (3)	Aq(7a)···Aq(7b)	2.89 (6)	Aq(7b)···O(120)	2.74 (7)
···O(201)	2.99 (4)	···Aq(7a)	2.73 (4)	···O(120)	2.71 (4)	···O(106)	3.12 (4)
···O(205)	3.26 (4)	···Aq(7b)	2.94 (4)	···O(106)	3.18 (4)	···Aq(6)	2.94 (4)
···Aq(4)	3.10 (4)	···Aq(7b)'	3.27 (4)	···O(206)	3.06 (4)	···Aq(6)'	3.27 (4)
···Aq(8a)	3.18 (6)			···O(211)	2.86 (4)	···Aq(7a)'	2.89 (6)
Aq(8a)···O(117)	2.72 (4)	Aq(8b)···O(117)	2.68 (5)				
···O(220)	2.79 (4)	···O(220)	2.83 (5)				
···Aq(2)	2.77 (4)	···Aq(4)	3.04 (5)				
···Aq(5)	3.18 (6)						

Table 6. *Tungsten–tungsten distances to* 4.0 Å *in potassium and ammonium paratungstates*

Bonds in right-hand groups are related to those in left-hand groups by the molecular pseudo-mirror plane. E.s.d.'s are ±0.001 Å for the K salt, ± 0.002 Å for the NH_4 salt.

	K salt		NH_4 salt			K salt		NH_4 salt	
	Molecule A	Molecule B	Molecule A	Molecule B		Molecule A	Molecule B	Molecule A	Molecule B
	$x = 1$	$x = 2$	$x = 1$	$x = 2$		$x = 1$	$x = 2$	$x = 1$	$x = 2$
W(x01)···O(x02)	3.332	3.348	3.325	3.351	W(x03)···O(x02)	3.325	3.339	3.381	3.328
···O(x03)	3.378	3.375	3.383	3.375	···O(x01)	3.378	3.375	3.383	3.375
···O(x04)	3.768	3.794	3.793	3.783	···O(x05)	3.714	3.751	3.688	3.753
···O(x05)	3.883	3.893	3.881	3.892	···O(x04)	3.901	3.866	3.859	3.875
···O(x06)	3.818	3.772	3.847	3.788	···O(x06)	3.697	3.716	3.704	3.683
W(x02)···O(x03)	3.325	3.339	3.318	3.328					
···O(x01)	3.332	3.348	3.325	3.351					
···O(x04)	3.665	3.672	3.661	3.667					
···O(x05)	3.716	3.700	3.720	3.700					
W(x04)···O(x06)	3.277	3.272	3.289	3.270	W(x05)···O(x06)	3.336	3.318	3.334	3.328
···O(x02)	3.665	3.672	3.793	3.783	···O(x02)	3.716	3.700	3.720	3.700
···O(x01)	3.768	3.794	3.793	3.783	···O(x03)	3.714	3.751	3.688	3.743
···O(x03)	3.901	3.866	3.859	3.874	···O(x01)	3.882	3.893	3.882	3.892
W(x06)···O(x04)	3.277	3.272	3.289	3.270					
···O(x05)	3.336	3.315	3.334	3.328					
···O(x03)	3.697	3.716	3.704	3.788					
···O(x01)	3.818	3.772	3.847	3.683					
Center···W(x01)	2.866	2.893	2.869	2.877	Center···W(x03)	2.838	2.807	2.831	2.815
···W(x02)	3.587	3.608	3.590	3.600					
···W(x04)	4.034	4.034	4.037	4.041	···W(x05)	4.023	4.052	4.005	4.039
···W(x06)	4.661	4.642	4.689	4.636					

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Structures of Tetrakis(2-amino-6-methylpyridinium) *catena*-Bis(acetonitrile)-tetradeca-μ-chloro-pentanickelate(II) and Bis(3-picolinium) *catena*-Diaquaocta-μ-chloro-trinickelate(II)

BY MARCUS R. BOND AND ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, WA 99164, USA

Abstract. $4C_6H_9N_2^+.[Ni_5Cl_{14}(C_2H_3N)_2]^{4-}$, (I), $M_r = 1308.6$, triclinic, $P\bar{1}$, $a = 8.686$ (1), $b = 12.483$ (2), $c = 12.933$ (2) Å, $\alpha = 73.09$ (1), $\beta = 73.65$ (1), $\gamma = 70.87$ (1)°, $V = 1240.4$ (3) Å^3, $Z = 1$, $D_x = 1.75$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, graphite monochromator, $\mu = 2.670$ mm^{-1}, $F(000) = 658$, $T = 295$ K, 259 parameters refined to $R = 0.0591$ and $wR = 0.0399$ for 1506 unique observed $[F \geq 3\sigma(F)]$ reflections. $2C_6H_8N^+.[Ni_3Cl_8(H_2O)_2]^{2-}$, (II), $M_r = 684.0$, triclinic, $P\bar{1}$, $a = 7.648$ (1), $b = 8.498$ (1), $c = 9.550$ (1) Å, $\alpha = 85.15$ (1), $\beta = 83.71$ (1), $\gamma = 69.08$ (1)°, $V = 575.6$ (2) Å^3, $Z = 1$, $D_x = 1.97$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, graphite monochromator, $\mu = 3.393$ mm^{-1}, $F(000) = 343$, $T = 295$ K, 132 parameters refined to $R = 0.0246$ and $wR = 0.0339$ for 2177 unique observed $[F \geq 3\sigma(F)]$ reflections. Both structures are built up from $[Ni_nCl_{3n+1}L_2]$ oligomers which contain face-sharing NiCl$_6$ octahedra and are capped on both ends by NiCl$_5$L octahedra. Di-μ-chloride bridges link these oligomers together into the non-uniform chains characteristic of this new $A_{n-1}[Ni_nCl_{3n-1}L_2]$ family.

Introduction. We are reporting the structures of the first two members of a new family of non-uniform nickel(II) chloride chains. Uniform chains of coordination polyhedra, in which symmetrically equivalent polyhedra are typically linked to their neighbors through one, two or three shared ligands, are a familiar motif of inorganic crystal chemistry. Non-uniform chains, those containing more than one type of coordination polyhedron or more than one type of bridging arrangement, are not uncommon, but are certainly less well known. The greater complexity, both structural and physical, of the non-uniform chain systems discourages the extensive and systematic studies pursued for many uniform chain systems. There is, nevertheless, a sustained interest in non-uniform systems with alternating magnetic properties, such as alternating exchange interactions (Carlin, 1986) or one-dimensional ferrimagnetism (Coronado, Drillon, Nugteren, de Jonghe, Beltran & Georges, 1989).

The title compounds establish a series of nickel halide salts which can be formulated as $A_{n-1}[Ni_n-Cl_{3n-1}L_2]$ where A is a monopositive organoammonium cation, L is a neutral ligand and n is, to date, an odd integer. The two extreme values of n produce uniform chain structures. Infinite n yields an ANiCl$_3$-type stoichiometry consisting of tri-μ-chloro-bridged chains of NiCl$_6^{4-}$ octahedra as found in the CsNiCl$_3$ family (Bond, 1990) and $n = 1$ yields an [NiCl$_2L_2$] stoichiometry consisting of di-μ-chloro-bridged chains of [NiCl$_4L_2$]$^{2-}$ octahedra as found in [NiCl$_2$(H$_2$O)$_2$] (Morosin, 1967). Intermediate compounds of the series contain both types of bridging arrangements resulting in oligomeric segments of the tribridged CsNiCl$_3$-type chain connected by the dichloro bridge of the [NiCl$_2L_2$]-type chain. In the two systems reported here, A is a substituted pyridinium