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$Cs_6[Mo_7O_{24}].7H_2O$

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Abstract

In an attempt to crystallize a new diphosphonate complex of polyoxomolybdate at pH 7, colorless crystals of the caesium salt of heptamolybdate, $Cs_6[Mo_7O_{24}].7H_2O$, were obtained. The structure of the heptamolybdate anion was first reported by Lindqvist [*Arkiv Kemi* (1950), **2**, 325–341] and subsequently confirmed by other groups. The structure reported here is the first of a caesium salt of heptamolybdate; the coordination of the caesium counterions is of interest.

Comment

Sjöbom & Hedman (1973) reported the structure of a sodium salt of heptamolybdate, $Na_6[Mo_7O_{24}].14H_2O$, in which all six Na^+ ions are octahedrally surrounded by O atoms donated both by H_2O molecules and by the $Mo_7O_{24}^{6-}$ groups. The Na^+ ions are bound to one, two, three or four O atoms of the anion (all of which are terminal or doubly bridging). Four Na^+ cations also link $[Mo_7O_{24}]^{6-}$ ions *via* O—Na—O bridges and water molecules act as bridges for Na^+ ions. Sjöbom & Hedman (1973) suggested that particularly small cations, like Li^+ and Na^+, are more likely to be bound directly to the polyoxometallate anions than larger cations. However, structure determinations of the isomorphous ammonium and potassium salts of heptamolybdate ($A_6[Mo_7O_{24}].4H_2O$, $A = K^+, NH_4^+$) by Evans, Gatehouse & Leverett (1975) revealed that the cations with coordination numbers of 8, 9 and 10 were also directly coordinated by O atoms of the anion as well as by water molecules. All four kinds of anionic O atoms (terminal, doubly, triply and quadruply bridging) are involved in cation binding. Four water molecules act as bridges for cations and some of the cations link $[Mo_7O_{24}]^{6-}$ groups.

The Mo—O bond lengths and the Mo···Mo distances of the heptamolybdate anion in $Cs_6[Mo_7O_{24}].7H_2O$ are very similar to those of the structures reported earlier (Shimao, 1967; Evans, 1968; Gatehouse & Leverett, 1968; Sjöbom & Hedman, 1973; Evans, Gatehouse & Leverett, 1975). The Cs^+ ions are bound to anionic O atoms as well as to water molecules, each of which bridges two cations. The Cs^+ ions are bound to two, three, four or five O atoms of the same anion. In addition, they are coordinated by water molecules and O atoms of neighbouring anions, leading to coordination numbers of 9, 10 and 11 (Table 2). The distances of Cs^+ ions to water molecules [3.079 (12)–3.72 (2) Å] are approximately the same as the distances to anionic O atoms [3.034 (9)–3.779 (7) Å].

Fig. 1 shows the anion with the six independent Cs^+ cations. The Cs^+ cations are bound to terminal, doubly bridging and quadruply bridging O atoms of the anion. Cs(6), which is located on one side of the cleft of the anion, is bound to these three kinds of O atom from the same anion. The corresponding site on the other side of the cleft is occupied by a water molecule [O(1*W*), see Fig. 1]. All the O atoms of the anion except O(4*C*), O(7*B*) and O(6*A*) are bound to Cs^+ ions. Each anion is associated with a total of 18 Cs^+ ions (the six shown in Fig. 1, plus twelve which are related by symmetry).

It can be concluded that for all reported heptamolybdate salts (Na^+, K^+, NH_4^+, Cs^+), the cations are coordinated both to O atoms of the heptamolybdate anion and to O atoms of water molecules.

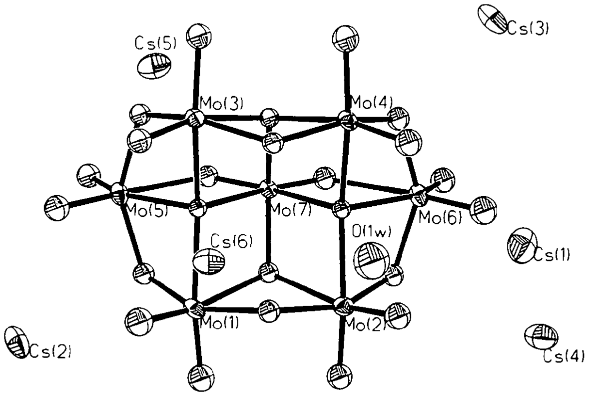

Fig. 1. Structure of the anion in $Cs_6[Mo_7O_{24}].7H_2O$ showing the position of the unique caesium cations and one of the water molecules, O(1*W*), that bridges Cs(1) and Cs(6). Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The title compound was obtained by addition of caesium chloride to a solution of sodium molybdate at pH 7.

Crystal data

$Cs_6[Mo_7O_{24}].7H_2O$	Mo $K\alpha$ radiation
$M_r = 1979.0$	$\lambda = 0.71073$ Å

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Triclinic
$P\bar{1}$
$a = 10.671$ (1) Å
$b = 11.218$ (1) Å
$c = 15.953$ (2) Å
$\alpha = 106.35$ (1)°
$\beta = 105.14$ (1)°
$\gamma = 98.66$ (1)°
$V = 1716.3$ (3) Å^3
$Z = 2$
$D_x = 3.830$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 5$–12.5°
$\mu = 8.843$ mm^{-1}
$T = 293$ K
Block
0.4 × 0.3 × 0.2 mm
Colorless

Data collection

Siemens *P4/RA* diffractometer
ω scans
Absorption correction: ψ scans [*XSCANS* (Fait, 1991) and *XEMP* (Siemens, 1989), based on the method of North, Phillips & Mathews (1968)]
6983 measured reflections
5930 independent reflections

5638 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0608$
$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.132$
$S = 1.123$
5638 reflections
243 parameters
No H atoms included
$w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 35.1P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 2.988$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.044$ e Å^{-3}
Extinction correction: (*SHELXL*93; Sheldrick, 1993)
Extinction coefficient: 0.0067 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent anisotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for O atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Mo(1)	0.8554 (1)	0.2376 (1)	0.6247 (1)	0.021 (1)
Mo(2)	0.6451 (1)	0.0912 (1)	0.7010 (1)	0.020 (1)
Mo(3)	0.6858 (1)	0.5593 (1)	0.6871 (1)	0.018 (1)
Mo(4)	0.4881 (1)	0.4082 (1)	0.7671 (1)	0.019 (1)
Mo(5)	0.9887 (1)	0.5373 (1)	0.7140 (1)	0.021 (1)
Mo(6)	0.5725 (1)	0.2247 (1)	0.8821 (1)	0.022 (1)
Mo(7)	0.8162 (1)	0.3992 (1)	0.8282 (1)	0.016 (1)
Cs(1)	0.1800 (1)	0.0128 (1)	0.6581 (1)	0.044 (1)
Cs(2)	1.1759 (1)	0.3657 (1)	0.5464 (1)	0.041 (1)
Cs(3)	0.2509 (1)	0.4436 (1)	0.9038 (1)	0.039 (1)
Cs(4)	0.4561 (1)	−0.1677 (1)	0.8496 (1)	0.051 (1)
Cs(5)	1.0723 (1)	0.7981 (1)	0.9606 (1)	0.050 (1)
Cs(6)	0.5190 (1)	0.2649 (1)	0.4580 (1)	0.029 (1)
O(1A)	1.0215 (7)	0.3689 (7)	0.6938 (5)	0.024 (2)
O(1B)	0.8286 (9)	0.2566 (8)	0.5188 (6)	0.035 (2)
O(1C)	0.9268 (9)	0.1100 (8)	0.6163 (6)	0.037 (2)
O(2A)	0.6723 (7)	0.1510 (7)	0.6039 (5)	0.023 (2)
O(2B)	0.6662 (7)	0.1035 (7)	0.8310 (5)	0.025 (2)
O(2C)	0.4782 (8)	0.0153 (8)	0.6477 (6)	0.031 (2)
O(2D)	0.7261 (8)	−0.0298 (8)	0.6866 (6)	0.033 (2)
O(3A)	0.6690 (7)	0.5481 (7)	0.5751 (5)	0.025 (2)
O(3B)	0.8772 (7)	0.6517 (7)	0.7472 (5)	0.023 (2)
O(3C)	0.6322 (8)	0.6930 (7)	0.7299 (5)	0.028 (2)
O(3D)	0.5276 (7)	0.4265 (6)	0.6596 (5)	0.019 (1)
O(4A)	0.4448 (8)	0.5490 (8)	0.8072 (6)	0.033 (2)
O(4B)	0.3369 (8)	0.2965 (8)	0.7135 (6)	0.032 (2)
O(4C)	0.7066 (7)	0.5163 (6)	0.8188 (5)	0.018 (1)
O(4D)	0.5291 (8)	0.3837 (7)	0.8896 (5)	0.027 (2)
O(5A)	1.1428 (8)	0.6304 (8)	0.7883 (6)	0.031 (2)
O(5B)	0.9876 (8)	0.5532 (8)	0.6106 (6)	0.030 (2)
O(5C)	0.7979 (6)	0.4133 (6)	0.6856 (5)	0.016 (1)
O(6A)	0.6067 (6)	0.2681 (6)	0.7642 (5)	0.016 (1)
O(6B)	0.4138 (9)	0.1226 (9)	0.8410 (6)	0.037 (2)
O(6C)	0.6332 (9)	0.2400 (8)	0.9958 (6)	0.035 (2)
O(7A)	0.9729 (7)	0.5024 (7)	0.8584 (5)	0.025 (2)
O(7B)	0.8442 (7)	0.2403 (7)	0.7634 (5)	0.022 (2)
O(7C)	0.8063 (8)	0.3727 (7)	0.9281 (5)	0.029 (2)
O(1W)	0.3049 (11)	0.1199 (10)	0.5211 (7)	0.051 (2)
O(2W)	1.2542 (13)	0.7193 (12)	0.6515 (9)	0.067 (3)
O(3W)	0.9306 (12)	0.8413 (11)	0.6639 (8)	0.061 (3)
O(4W)	1.0457 (17)	0.1460 (16)	0.8476 (12)	0.091 (4)
O(5W)	0.8175 (16)	0.9243 (15)	0.8751 (11)	0.086 (4)
O(6W)	0.2728 (20)	0.0205 (18)	0.9400 (14)	0.108 (6)
O(7W)	0.7327 (26)	0.7340 (24)	0.9610 (18)	0.149 (8)

Table 2. *Selected geometric parameters* (Å)

Mo(1)—O(1C)	1.709 (9)	Cs(2)—O(4$B^{\rm v}$)	3.137 (9)
Mo(1)—O(1B)	1.718 (9)	Cs(2)—O(1A)	3.200 (7)
Mo(1)—O(2A)	1.943 (7)	Cs(2)—O(5B)	3.262 (8)
Mo(1)—O(1A)	1.951 (7)	Cs(2)—O(3$D^{\rm v}$)	3.579 (7)
Mo(1)—O(5C)	2.192 (7)	Cs(2)—O(1B)	3.592 (9)
Mo(1)—O(7B)	2.239 (7)	Cs(2)—O(1$W^{\rm v}$)	3.236 (11)
Mo(2)—O(2D)	1.710 (8)	Cs(2)—O(3$W^{\rm iv}$)	3.281 (12)
Mo(2)—O(2C)	1.721 (8)	Cs(2)—O(2W)	3.710 (13)
Mo(2)—O(2A)	1.924 (7)	Cs(3)—O(7$A^{\rm i}$)	3.081 (8)
Mo(2)—O(2B)	1.989 (8)	Cs(3)—O(7$C^{\rm vi}$)	3.152 (8)
Mo(2)—O(6A)	2.111 (7)	Cs(3)—O(4A)	3.164 (8)
Mo(2)—O(7B)	2.278 (7)	Cs(3)—O(4D)	3.192 (8)
Mo(3)—O(3C)	1.712 (8)	Cs(3)—O(5$A^{\rm i}$)	3.302 (8)
Mo(3)—O(3A)	1.714 (8)	Cs(3)—O(4$D^{\rm vi}$)	3.335 (8)
Mo(3)—O(3D)	1.936 (7)	Cs(3)—O(6$C^{\rm vi}$)	3.337 (9)
Mo(3)—O(3B)	1.986 (7)	Cs(3)—O(1$A^{\rm i}$)	3.381 (8)
Mo(3)—O(5C)	2.167 (7)	Cs(3)—O(4B)	3.446 (8)
Mo(3)—O(4C)	2.249 (7)	Cs(3)—O(7$W^{\rm vi}$)	3.31 (3)
Mo(4)—O(4A)	1.710 (8)	Cs(3)—O(4$W^{\rm i}$)	3.44 (2)
Mo(4)—O(4B)	1.724 (8)	Cs(4)—O(4$A^{\rm vii}$)	3.034 (9)
Mo(4)—O(3D)	1.926 (7)	Cs(4)—O(6$C^{\rm viii}$)	3.125 (9)
Mo(4)—O(4D)	1.996 (8)	Cs(4)—O(3$C^{\rm vii}$)	3.271 (8)
Mo(4)—O(6A)	2.159 (7)	Cs(4)—O(6B)	3.389 (9)
Mo(4)—O(4C)	2.273 (7)	Cs(4)—O(5$A^{\rm iii}$)	3.468 (8)
Mo(5)—O(5B)	1.707 (8)	Cs(4)—O(2B)	3.628 (8)
Mo(5)—O(5A)	1.723 (8)	Cs(4)—O(2$W^{\rm iii}$)	3.099 (13)
Mo(5)—O(1A)	1.925 (8)	Cs(4)—O(6W)	3.37 (2)
Mo(5)—O(3B)	1.937 (7)	Cs(4)—O(7$W^{\rm vii}$)	3.53 (3)
Mo(5)—O(5C)	2.144 (7)	Cs(4)—O(6$W^{\rm viii}$)	3.57 (2)
Mo(5)—O(7A)	2.486 (8)	Cs(4)—O(5$W^{\rm vii}$)	3.72 (2)
Mo(6)—O(6C)	1.708 (9)	Cs(5)—O(7A)	3.127 (8)
Mo(6)—O(6B)	1.739 (9)	Cs(5)—O(7$C^{\rm ix}$)	3.157 (8)
Mo(6)—O(4D)	1.888 (8)	Cs(5)—O(6$C^{\rm ix}$)	3.158 (9)
Mo(6)—O(2B)	1.930 (8)	Cs(5)—O(5A)	3.202 (8)
Mo(6)—O(6A)	2.175 (7)	Cs(5)—O(3B)	3.277 (7)
Mo(7)—O(7C)	1.727 (8)	Cs(5)—O(2$B^{\rm ix}$)	3.496 (8)
Mo(7)—O(7A)	1.747 (7)	Cs(5)—O(6$W^{\rm x}$)	3.18 (2)
Mo(7)—O(4C)	1.897 (7)	Cs(5)—O(5$W^{\rm xi}$)	3.26 (2)
Mo(7)—O(7B)	1.902 (7)	Cs(5)—O(5W)	3.40 (2)
Mo(7)—O(6A)	2.275 (7)	Cs(5)—O(4$W^{\rm ix}$)	3.54 (2)
Mo(7)—O(5C)	2.283 (7)	Cs(5)—O(7W)	3.59 (3)
Cs(1)—O(1$C^{\rm i}$)	3.048 (9)	Cs(6)—O(3A)	3.116 (7)
Cs(1)—O(6B)	3.082 (9)	Cs(6)—O(2$C^{\rm ii}$)	3.130 (8)
Cs(1)—O(4B)	3.123 (8)	Cs(6)—O(3$A^{\rm xii}$)	3.168 (8)
Cs(1)—O(2C)	3.226 (8)	Cs(6)—O(2A)	3.169 (7)
Cs(1)—O(1$B^{\rm ii}$)	3.476 (9)	Cs(6)—O(3D)	3.186 (7)
Cs(1)—O(3$W^{\rm iii}$)	3.079 (12)	Cs(6)—O(3$C^{\rm xii}$)	3.211 (8)
Cs(1)—O(1W)	3.243 (11)	Cs(6)—O(1B)	3.215 (9)
Cs(1)—O(2$W^{\rm iii}$)	3.480 (13)	Cs(6)—O(2$D^{\rm ii}$)	3.235 (8)
Cs(1)—O(4$W^{\rm i}$)	3.71 (2)	Cs(6)—O(5C)	3.779 (7)
Cs(2)—O(5$B^{\rm iv}$)	3.101 (8)	Cs(6)—O(1W)	3.145 (11)
Cs(2)—O(3$A^{\rm iv}$)	3.111 (8)	Cs(6)—O(2$W^{\rm iv}$)	3.345 (13)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $x-1, y-1, z$; (iv) $2-x, 1-y, 1-z$; (v) $1+x, y, z$; (vi) $1-x, 1-y, 2-z$; (vii) $x, y-1, z$; (viii) $1-x, -y, 2-z$; (ix) $2-x, 1-y, 2-z$; (x) $1+x, 1+y, z$; (xi) $2-x, 2-y, 2-z$; (xii) $1-x, 1-y, 1-z$.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$K_2NiWO_2(PO_4)_2$: a New Structure Type Related to $KTiOPO_4$ (KTP)

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Abstract

Substitution of the two symmetrically unrelated Ti^{4+} ions in the structure of the well known non-linear optical crystal $KTiOPO_4$ (potassium titanyl phosphate, KTP, space group $Pna2_1$) by Ni^{2+} and W^{6+} ($2Ti^{4+} \rightarrow Ni^{2+} + W^{6+}$) leads to the new compound $K_2NiWO_2(PO_4)_2$ [dipotassium nickel bis(monophosphato)tungstate, KNiWP], which forms a new structure type. The main structural characteristic of tetragonal KNiWP (space group $P4_{1,3}2_12$) is helical chains of corner-linked alternate $[WO_6]$ and $[NiO_6]$ octahedra along [001] connected *via* phosphate groups. Structural and metric relationships exist between the KNiWP and KTP structure types.

Comment

The majority of crystal–chemical investigations carried out on the $KTiOPO_4$ (KTP) structure family during the past ten years have focused on a simple substitution of K, Ti and P by crystal–chemically related constituents. In this way, a great number of compounds have been synthesized that are isostructural with KTP. All these attempts have been made in the hope of further improving the physical properties for applications in the field of laser optics (Stucky, Phillips & Gier, 1989).

Recently, during the search for further members of the KTP group, a new family of compounds with the general formula $K_2M^{2+}M^{6+}O_2(PO_4)_2$ ($M^{2+} = Ni^{2+}, Co^{2+}, Mg^{2+}$; $M^{6+} = W^{6+}$) was found (Wostrack, 1993). These compounds can be derived from KTP by substitution of the two symmetrically unrelated Ti^{4+} ions by two cations with different valencies ($2Ti^{4+} \rightarrow M^{2+} + M^{6+}$). X-ray powder and single-crystal investigations of members of this family have shown that these compounds do not form superstructures of KTP (Wostrack, Peuchert, Schneider, Liebertz & Bohatý, 1993). As one result of our studies, the crystal structure of $K_2NiWO_2(PO_4)_2$ (KNiWP) is presented.

Both Ni^{2+} and W^{6+} occupy the special Wyckoff site 4(*a*) of space group $P4_12_12$ ($P4_32_12$) and are octahedrally surrounded by three pairs of symmetrically dependent O atoms. The $[WO_6]$ octahedra are quite distorted [W—O distance range: 1.752 (2)–2.068 (2) Å] while, by comparison, the $[NiO_6]$ octahedra differ only slightly from ideal shape [Ni—O distance range: 2.029 (2)–2.104 (2) Å]. Both types of octahedra are alternately linked with each other *via* one common O atom, O(5), forming helical chains along [001]. In the chain ...Ni—O(5)—W—O(5)—Ni... the symmetrically related O(5) atoms form short bonds with the W atom [W—O(5) = 1.752 (2), Ni—O(5) = 2.046 (2) Å]. The bridging O(5) atoms, corresponding to the titanyl O atoms of the KTP structure, are in *cis* positions relative to Ni^{2+} and W^{6+}. In contrast to this *cis–cis* arrangement in KNiWP, the titanyl O atoms of KTP are in alternating *cis–trans* positions (Fig. 1).

Quite regular phosphate tetrahedra [P—O distance range: 1.513 (2)–1.578 (2) Å] link the two octahedral chains in the unit cell to form a three-dimensional net-