Chem. Mater. **2000,** *12,* 2239−2243

A Series of Mo(VI) Monophosphates Involving the Lone Pair Cation Te(IV): $A_2TeMo_2O_6(PO_4)_2$ (A = K, Rb, Tl, Cs)

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Received January 14, 2000. Revised Manuscript Received May 9, 2000

A new series of Mo(VI) monophosphates containing Te(IV), $A_2TeMo_2O_6(PO_4)_2$ with A = K, Rb, Tl, Cs, has been synthesized. Their crystal structure, determined from single crystals in the *Pbcn* space group ($a \approx 12.55-12.37$ Å, $b \approx 8.63-9.49$ Å, $c \approx 11.13-11.51$ Å), consists of corner-sharing PO_4 tetrahedra, MoO_6 octahedra, and TeO_4E trigonal bipyramids (E being the electronic lone pair of Te(IV)). The original $[TeMo_2P_2O_{14}]_\infty$ framework is remarkable by its layered character forming $[Mo_2P_2O_{14}]_\infty$ layers interconnected through TeO_4E bipyramids. The existence of intersecting tunnels running along the [100], [010], [110], and [001] directions is also an interesting feature of this new structural type.

Introduction

Lone pair cations are of great interest for the generation of anisotropic structures with particular physical properties. The stereoactivity of the electronic lone pair of such elements was evidenced and studied a long time ago (see for a review refs 1−3). Their role for the creation of original properties is exemplified by the Bi^{3+}-based oxides, with a layered structure such as the Aurivillius phases which are extensively studied for their ferroelectric properties (see for a review refs 4 and 5) and the high T_C superconducting cuprates (see for a review ref 6). Owing to its interesting lone pair stereoactivity, Te(IV) is susceptible to develop original frameworks (see for instance refs 7 and 8). In the field of molybdenum phosphates, whose investigation has been highly carried out these last 15 years (see for a review refs 9−11), no Te(IV) molybdenophosphate has been synthesized to date to our knowledge. We present herein the original crystal structure of a new series of Te(IV) molybdenophosphates, $A_2TeMo_2O_6(PO_4)_2$, whose opened framework hosts large A cations (K^+, Rb^+, Tl^+, Cs^+).

Experimental Section

Synthesis and Crystal Growth. The single crystal used for the structure determination of $K_2TeMo_2O_6(PO_4)_2$ was grown from a mixture of nominal composition $KTeMo_2PO_{10}$, synthesized in two steps. First, K_2CO_3, TeO_2, MoO_3, and $(NH_4)_2HPO_4$ were mixed in an agate mortar, placed in a platinum crucible, and heated at 673 K in air to decompose the potassium carbonate and the ammonium phosphate. The appropriate amount of Mo was then added and the resulting mixture was sealed in an evacuated silica ampule which was then heated at 873 K for 20 h and cooled at a rate of 10 K/h^{-1} to room temperature. Colorless crystals were extracted from the resulting mixture. Their EDS analyses, performed with a Tracor microprobe mounted on a JEOL 840 scanning electron microscope, led to the approximate cationic composition "$K_2TeMo_2P_2$", which was confirmed by the structure determination.

The growth of the other $A_2TeMo^{VI}_2O_6(PO_4)_2$ crystals with A = Rb, Tl, Cs was performed in a similar way but starting from the stoichiometric composition and without any metal addition in the second step. The heating temperatures were 923, 853, and 793 K for Rb, Tl, and Cs compounds, respectively.

Note that the four $A_2Te^{IV}Mo^{VI}_2O_6(PO_4)_2$ phases (A = K, Rb, Tl, Cs) can easily be prepared as monophasic powder samples in platinum crucibles heated in air at 873 K for 12 h, leading to a pale yellow powder.

X-ray Diffraction Studies and Structure Determination. Single-crystal studies were performed on $A_2TeMo_2O_6(PO_4)_2$ for A = K, Rb, Tl, Cs. For each phase, several parallelepipedic colorless crystals were selected optically and tested by the oscillation and Weissenberg methods using Cu Kα radiation. The dimensions of the single crystals chosen for the structure determinations are reported in Table 1. The cell parameters given in Table 1 were determined and refined by diffractometric techniques at 293 K using a least-squares method based upon 25 reflections in the range $18° < \theta < 22°$. The data were collected on a CAD4 Enraf-Nonius diffractometer using Mo Kα radiation. The reflections were corrected for Lorentz and polarization effects and for absorption and secondary extinction. The structures were solved in the *Pbcn* space group (deduced from the systematic absences $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$, and $h + k = 2n+1$ for $hk0$) using the heavy-atom method. The refinement of the atomic coordinates and of the anisotropic thermal factors of all atoms led to the reliability factors given in Table 1 and to the atomic parameters listed in Table 2. The calculations were performed on a SPARK station with the XTAL 3.2 package.[12]

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Table 1. Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $A_2TeMo_2O_6(PO_4)_2$ Crystals

	A = K	A = Rb	A = Tl	A = Cs
	(1) Crystal Data			
crystal dimensions (mm^3)	0.128 × 0.128 × 0.019	0.103 × 0.103 × 0.077	0.064 × 0.058 × 0.039	0.154 × 0.045 × 0.019
space group	*Pbcn*	*Pbcn*	*Pbcn*	*Pbcn*
cell dimensions	a = 12.553(1) Å b = 8.6284(5) Å c = 11.1338(5) Å	a = 12.544(1) Å b = 8.9340(4) Å c = 11.3222(9) Å	a = 12.503(2) Å b = 8.912(2) Å c = 11.300(2) Å	a = 12.3670(8) Å b = 9.4907(6) Å c = 11.515(4) Å
volume $(c)^3$	1205.9(1)	1268.8(2)	1259.1(4)	1351.5(4)
Z	4	4	4	4
ρ_{calc} (g·cm^{-3})	3.765	4.064	5.350	4.282
	(2) Intensity Measurements			
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
scan mode	$\omega-{}^4/_3\theta$	$\omega-\theta$	$\omega-{}^2/_3\theta$	$\omega-\theta$
scan width (°)	1.0 + 0.35 tnθ	1.0 + 0.35 tnθ	1.50 + 0.35 tnθ	1.0 + 0.35 tnθ
slit aperture (mm)	1.0 + tnθ	1.0 + tnθ	1.90 + tnθ	1.0 + tnθ
max θ (°)	45	45	45	45
standard reflections	3 measured every 3600 s	3 measured every 3600 s	3 measured every 3600 s	3 measured every 3600 s
measured reflections	5490	5777	5727	6139
reflections with $I > 3\sigma$	2542	2143	831	1589
μ (mm^{-1})	5.48	12.18	30.06	9.59
	(3) Structure Solution and Refinement			
parameters refined	97	97	97	97
agreement factors	R = 0.025 R_w = 0.028	R = 0.033 R_w = 0.031	R = 0.034 R_w = 0.027	R = 0.027 R_w = 0.023
weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$	$w = 1/\sigma^2$	$w = 1/\sigma^2$
Δ/σ max	$<10^{-3}$	$<2 \times 10^{-2}$	$<4 \times 10^{-3}$	$<4 \times 10^{-3}$

Table 2. Positional Parameters and Their Estimated Standard Deviations in the $A_2TeMo_2O_6(PO_4)_2$ Structures[a]

		A = K					A = Rb		
atom	x	y	z	$U \times 100$ (Å^2)	atom	x	y	z	$U \times 100$ (Å^2)
K	0.30377(7)	0.0286(1)	0.28309(7)	2.03(2)	Rb	0.31435(4)	0.03036(6)	0.28468(5)	2.11(1)
Te	0	0.13859(3)	1/4	0.723(5)	Te	0	0.13014(5)	1/4	0.867(9)
Mo	0.12041(2)	0.26247(3)	0.52191(2)	0.721(5)	Mo	0.11993(3)	0.25492(5)	0.52006(3)	0.830(8)
P	0.13045(6)	0.1440(1)	−0.00670(7)	0.73(2)	P	0.13241(9)	0.1383(1)	−0.0029(1)	0.84(3)
O(1)	0.0712(2)	0.2828(3)	0.3448(2)	0.94(5)	O(1)	0.0711(3)	0.2681(4)	0.3441(3)	1.10(8)
O(2)	0.2687(2)	0.2738(3)	0.4454(2)	1.06(5)	O(2)	0.2696(3)	0.2761(4)	0.4505(3)	1.25(8)
O(3)	0.1209(2)	0.4565(3)	0.5484(2)	1.60(6)	O(3)	0.1121(3)	0.4424(4)	0.5429(3)	1.6(1)
O(4)	0.1619(2)	0.1898(3)	0.6567(2)	1.36(6)	O(4)	0.1600(3)	0.1909(4)	0.6542(3)	1.6(1)
O(5)	−0.0339(2)	0.2291(3)	0.5604(2)	1.21(6)	O(5)	−0.0335(3)	0.2152(4)	0.5558(3)	1.46(9)
O(6)	0.1287(2)	0.0236(3)	0.4494(2)	1.28(6)	O(6)	0.1354(3)	0.0226(4)	0.4540(3)	1.46(9)
O(7)	0.1308(2)	0.1557(3)	0.1314(2)	1.17(6)	O(7)	0.1314(3)	0.1486(4)	0.1335(3)	1.38(9)

		A = Tl					A = Cs		
atom	x	y	z	$U \times 100$ (Å^2)	atom	x	y	z	$U \times 100$ (Å^2)
Tl	0.31926(6)	0.02867(8)	0.28339(5)	2.80(2)	Cs	0.33601(3)	0.03116(4)	0.28706(3)	2.25(1)
Te	0	0.1295(2)	1/4	0.94(4)	Te	0	0.11780(5)	1/4	0.90(1)
Mo	0.1212(1)	0.2539(2)	0.5204(1)	0.92(3)	Mo	0.12183(4)	0.23889(5)	0.51931(4)	0.82(1)
P	0.1322(4)	0.1379(5)	−0.0037(3)	1.0(1)	P	0.1365(1)	0.1260(1)	0.0019(1)	0.84(3)
O(1)	0.0727(8)	0.268(1)	0.3436(7)	1.3(3)	O(1)	0.0732(3)	0.2450(4)	0.3440(3)	1.3(1)
O(2)	0.2707(8)	0.272(1)	0.4502(7)	1.8(4)	O(2)	0.2724(3)	0.2769(4)	0.4565(3)	1.1(1)
O(3)	0.1149(9)	0.444(1)	0.5421(8)	1.8(3)	O(3)	0.0966(4)	0.4127(4)	0.5384(3)	1.8(1)
O(4)	0.1605(8)	0.192(1)	0.6559(7)	1.7(4)	O(4)	0.1617(3)	0.1889(4)	0.6540(3)	1.5(1)
O(5)	−0.0336(9)	0.210(1)	0.5576(8)	1.8(4)	O(5)	−0.0300(3)	0.1778(4)	0.5522(3)	1.5(1)
O(6)	0.1374(7)	0.024(1)	0.4533(8)	1.2(3)	O(6)	0.1562(4)	0.0236(4)	0.4612(3)	1.8(1)
O(7)	0.1320(8)	0.146(1)	0.1319(7)	1.4(3)	O(7)	0.1333(3)	0.1368(4)	0.1348(3)	1.3(1)

[a] All atoms were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter defined as:

$$U_{eq} = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U^{ij} a^{*i} a^{*j} \mathbf{a}_i \mathbf{a}_j$$

Description of the Structure and Discussion

The refined atomic coordinates (Table 2) clearly show that the four compounds are isotypic. The projection of the structure of $K_2TeMo_2O_6(PO_4)_2$ along **a** (Figure 1a) and **b** (Figure 1b) shows that the $[TeMo_2P_2O_{14}]_\infty$ framework consists of corner-sharing MoO_6 octahedra, PO_4 tetrahedra, and TeO_4E trigonal bipyramids (E standing for the electronic lone pair of Te (IV)).

The important characteristic of this framework deals with its anisotropy, forming $[Mo_2P_2O_{14}]_\infty$ layers parallel to (001) interconnected through TeO_4E bipyramids. The $[Mo_2P_2O_{14}]_\infty$ layers (Figure 2) can be described as the assemblage along **b** of $[MoPO_8]_\infty$ chains running along **a**. Such $[MoPO_8]_\infty$ chains in which one octahedron

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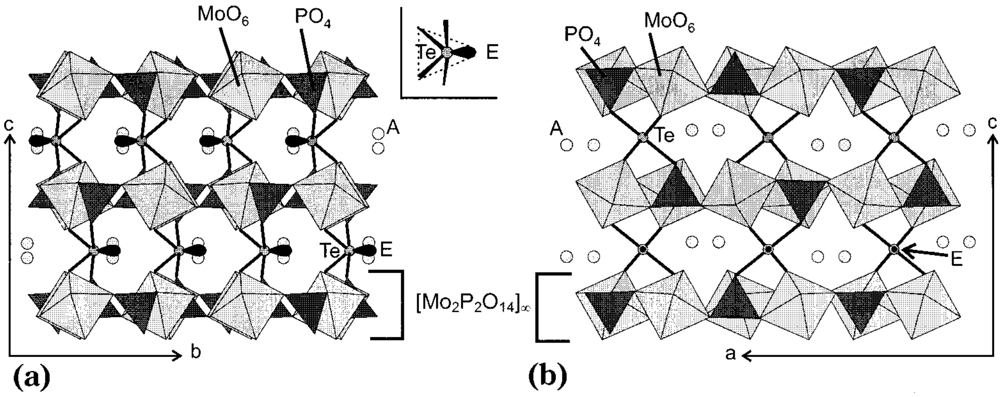

Figure 1. Projection of the structure of $K_2TeMo_2O_6(PO_4)_2$ (a) along **a** and (b) along **b.** (The PO_4 tetrahedra are shown as dark triangles, whereas the MoO_6 octahedra are gray.)

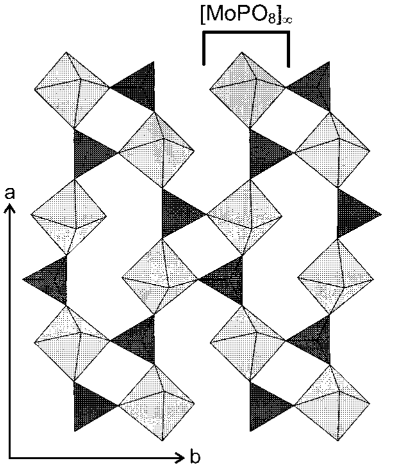

Figure 2. Projection along **c** of one $[Mo_2P_2O_{14}]_\infty$ layer, showing the $[MoPO_8]_\infty$ chains running along the **a** direction.

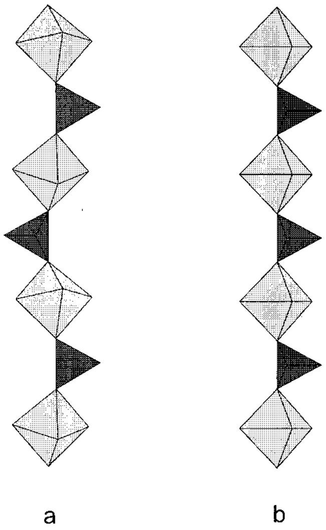

Figure 3. $[MoPO_8]_\infty$ chains (a) in $K_2TeMo_2O_6(PO_4)_2$, i.e., with a trans configuration, and (b) with a cis configuration.[15]

alternates with one tetrahedron are often encountered in molybdenum phosphates;[9,13−15] nevertheless, these chains have a particular trans configuration of the relative positions of the corners of their PO_4 tetrahedra along **a** (Figure 3a), whereas a cis configuration (Figure 3b) is more generally observed in other phosphates (see for example ref 15). Within each $[Mo_2P_2O_{14}]_\infty$ layer two successive chains are connected in such a way that a PO_4 tetrahedron of one chain shares one apex with a MoO_6 octahedron of the next chain and vice versa (Figure 2). It results in the formation of small diamond-shaped windows and large S-shaped windows. The three-dimensional $[TeMo_2P_2O_{14}]_\infty$ framework is then achieved by the TeO_4E bipyramids which sit between these layers, sharing two apexes with each of their two adjacent $[Mo_2P_2O_{14}]_\infty$ layers: one with an MoO_6 octahedron and one with a PO_4 tetrahedron (Figure 1). In fact, the $[TeMo_2P_2O_{14}]_\infty$ framework can be described as an intersecting tunnel structure with tunnels running along [010] (Figure 1b), [100] (Figure 1a), [110] (Figure 4a), and [001] (Figure 4b); note, however, that the [100] and [110] tunnels should be considered as partially obstructed by the $5s^2$ lone pair of Te(IV), whereas the [001] tunnels are partially obstructed by oxygen.

In this structure, each MoO_6 octahedron shares three apexes with three monophosphate groups and one apex with a TeO_4E trigonal bipyramid, its two remaining corners being free. The examination of the angles and distances resulting from the refinements of the four structures shows that the geometry of the MoO_6 octahedra is very similar in these compounds (Table 3) whatever the nature of the A cation (K^+ or Rb^+ or Tl^+ or Cs^+).

Each MoO_6 octahedron exhibits two short Mo−O distances of about 1.7 Å corresponding to the two free apexes, one long Mo−O bond (~2.2 Å) opposed to one of the shortest Mo−O distances, and three intermediate Mo−O distances (~2 Å). This geometry is usually observed for the Mo(VI) octahedron, and the hexavalent character of molybdenum in these phases has been confirmed by valence calculations[16] which lead to molybdenum valences of 5.99, 6.02, 5.97, and 6.09 for the $ATeMo_2O_6(PO_4)_2$ compounds with A = K, Rb, Tl, and Cs, respectively.

Each PO_4 tetrahedron is linked by corner sharing to three MoO_6 octahedra and one TeO_4E trigonal bipyramid. It presents rather homogeneous P−O distances ranging from 1.515(4) to 1.55(1) Å (Table 3).

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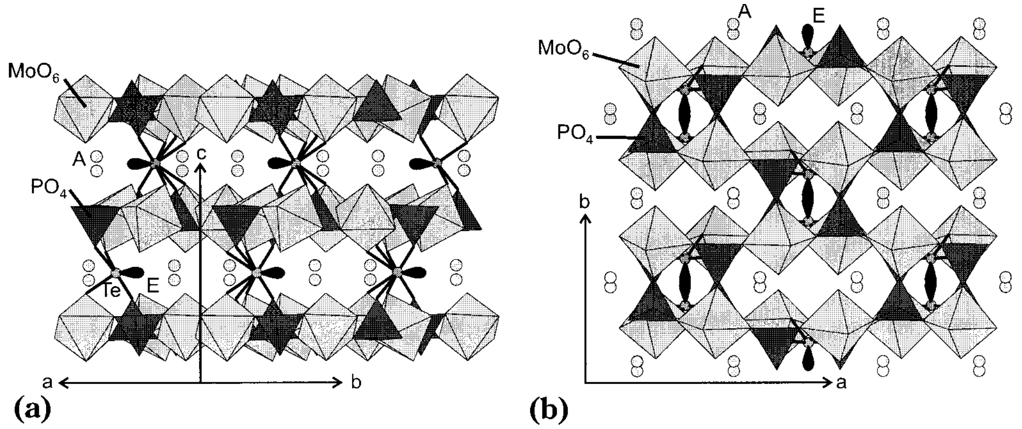

Figure 4. Projection of the structure of $K_2TeMo_2O_6(PO_4)_2$ (a) along [110] and (b) along **c**.

Table 3. Distances (Å) and Angles (°) in the $A_2TeMo_2O_6(PO_4)_2$ Structures

A	K	Rb	Tl	Cs	A	K	Rb	Tl	Cs
Mo−O(1)	2.074(2)	2.087(3)	2.091(8)	2.107(4)	O(2$^{\mathrm{i}}$)−O(5$^{\mathrm{ii}}$)	2.479(3)	2.472(5)	2.45(1)	2.484(5)
Mo−O(2)	2.050(2)	2.044(3)	2.04(1)	2.030(4)	O(2$^{\mathrm{i}}$)−O(6$^{\mathrm{iii}}$)	2.511(3)	2.505(5)	2.53(2)	2.503(5)
Mo−O(3)	1.700(3)	1.698(4)	1.71(1)	1.693(4)	O(2$^{\mathrm{i}}$)−O(7)	2.499(3)	2.508(5)	2.49(1)	2.500(5)
Mo−O(4)	1.708(2)	1.699(4)	1.700(9)	1.695(4)	O(5$^{\mathrm{ii}}$)−O(6$^{\mathrm{iii}}$)	2.486(4)	2.481(5)	2.46(2)	2.473(6)
Mo−O(5)	2.004(2)	1.998(3)	2.02(1)	2.001(4)	O(5$^{\mathrm{ii}}$)−O(7)	2.538(3)	2.541(5)	2.53(1)	2.534(5)
Mo−O(6)	2.216(2)	2.215(4)	2.19(1)	2.192(4)	O(6$^{\mathrm{iii}}$)−O(7)	2.550(3)	2.544(5)	2.53(1)	2.529(5)
O(1)−O(2)	2.722(3)	2.767(4)	2.75(1)	2.800(5)	O(2$^{\mathrm{i}}$)−P−O(5$^{\mathrm{ii}}$)	107.0(1)	106.7(2)	106.5(6)	107.3(2)
O(1)−O(3)	2.788(3)	2.784(5)	2.78(1)	2.762(5)	O(2$^{\mathrm{i}}$)−P−O(6$^{\mathrm{iii}}$)	109.6(1)	109.9(2)	110.5(6)	109.7(2)
O(1)−O(4)	3.742(3)	3.747(5)	3.76(1)	3.771(5)	O(2$^{\mathrm{i}}$)−P−O(7)	108.2(1)	108.6(2)	108.2(5)	108.4(2)
O(1)−O(5)	2.778(3)	2.772(5)	2.81(1)	2.790(5)	O(5$^{\mathrm{ii}}$)−P−O(6$^{\mathrm{iii}}$)	108.4(1)	108.5(2)	107.8(6)	108.2(2)
O(1)−O(6)	2.622(3)	2.647(5)	2.63(1)	2.701(6)	O(5$^{\mathrm{ii}}$)−P−O(7)	111.0(1)	110.8(2)	112.3(6)	111.1(2)
O(2)−O(3)	2.690(4)	2.684(5)	2.69(1)	2.698(6)	O(6$^{\mathrm{iii}}$)−P−O(7)	112.4(1)	112.2(2)	111.4(6)	112.0(2)
O(2)−O(4)	2.803(3)	2.790(5)	2.79(1)	2.783(5)	Te−O(1)	1.861(2)	1.857(3)	1.86(1)	1.857(4)
O(2)−O(5)	4.027(3)	4.021(5)	4.03(1)	4.010(5)	Te−O(1$^{\mathrm{ii}}$)	1.861(2)	1.857(3)	1.86(1)	1.857(4)
O(2)−O(6)	2.785(3)	2.822(5)	2.77(2)	2.801(5)	Te−O(7)	2.112(2)	2.118(3)	2.13(1)	2.123(4)
O(3)−O(4)	2.648(4)	2.646(5)	2.65(1)	2.633(6)	Te−O(7$^{\mathrm{ii}}$)	2.112(2)	2.118(3)	2.13(1)	2.123(4)
O(3)−O(5)	2.764(4)	2.734(5)	2.80(2)	2.729(6)	O(1)−O(1$^{\mathrm{ii}}$)	2.767(3)	2.779(4)	2.79(1)	2.822(5)
O(3)−O(6)	3.895(4)	3.894(5)	3.88(1)	3.869(6)	O(1)−O(7)	2.722(3)	2.720(5)	2.73(1)	2.721(5)
O(4)−O(5)	2.703(3)	2.679(5)	2.67(1)	2.646(6)	O(1)−O(7$^{\mathrm{ii}}$)	2.776(3)	2.767(5)	2.79(1)	2.763(5)
O(4)−O(6)	2.749(3)	2.738(5)	2.75(1)	2.719(5)	O(1$^{\mathrm{ii}}$)−O(7)	2.776(3)	2.767(5)	2.79(1)	2.763(5)
O(5)−O(6)	2.971(3)	2.962(5)	2.95(1)	2.923(6)	O(1$^{\mathrm{ii}}$)−O(7$^{\mathrm{ii}}$)	2.722(3)	2.720(5)	2.73(1)	2.721(5)
O(1)−Mo−O(2)	82.61(9)	84.1(1)	83.6(4)	85.2(1)	O(7)−O(7$^{\mathrm{ii}}$)	4.214(3)	4.222(5)	4.24(1)	4.231(5)
O(1)−Mo−O(3)	94.7(1)	94.2(2)	93.6(4)	92.6(2)	O(1)−Te−O(1$^{\mathrm{ii}}$)	95.1(1)	96.9(1)	96.9(4)	98.9(2)
O(1)−Mo−O(4)	163.2(1)	163.5(2)	164.5(5)	165.3(2)	O(1)−Te−O(7)	86.24(9)	86.1(1)	86.0(4)	86.0(2)
O(1)−Mo−O(5)	85.86(9)	85.4(1)	86.2(4)	85.5(2)	O(1)−Te−O(7$^{\mathrm{ii}}$)	88.40(9)	88.0(1)	86.6(4)	87.7(2)
O(1)−Mo−O(6)	75.30(9)	75.9(1)	75.7(4)	77.8(2)	O(1$^{\mathrm{ii}}$)−Te−O(7)	88.40(9)	88.0(1)	88.6(4)	87.7(2)
O(2)−Mo−O(3)	91.2(1)	91.2(2)	91.2(5)	92.4(2)	O(1$^{\mathrm{ii}}$)−Te−O(7$^{\mathrm{ii}}$)	86.24(9)	86.1(1)	86.0(4)	86.0(2)
O(2)−Mo−O(4)	96.0(1)	96.0(2)	96.4(4)	96.3(2)	O(7)−Te−O(7$^{\mathrm{ii}}$)	172.0(1)	171.1(1)	171.8(4)	170.3(2)
O(2)−Mo−O(5)	166.75(9)	168.1(1)	167.4(4)	168.4(2)	A−O(1$^{\mathrm{iv}}$)	2.726(3)	2.830(3)	2.77(1)	3.011(4)
O(2)−Mo−O(6)	81.42(9)	82.9(1)	81.6(4)	83.0(2)	A−O(2)	2.818(3)	2.943(3)	2.94(1)	3.141(4)
O(3)−Mo−O(4)	102.0(1)	102.3(2)	101.8(5)	102.0(2)	A−O(2$^{\mathrm{iv}}$)	2.988(3)	3.130(3)	3.17(1)	3.381(4)
O(3)−Mo−O(5)	96.2(1)	95.1(2)	96.8(5)	94.9(2)	A−O(3$^{\mathrm{i}}$)	2.782(3)	2.900(4)	2.86(1)	3.030(4)
O(3)−Mo−O(6)	168.2(1)	168.8(2)	167.7(4)	169.6(2)	A−O(3$^{\mathrm{iv}}$)	3.163(3)	3.164(4)	3.13(1)	3.214(4)
O(4)−Mo−O(5)	93.1(1)	92.5(2)	91.5(4)	91.1(2)	A−O(4$^{\mathrm{i}}$)	2.841(3)	2.914(4)	2.89(1)	3.067(4)
O(4)−Mo−O(6)	88.0(1)	87.7(2)	89.0(4)	87.8(2)	A−O(4$^{\mathrm{iii}}$)	2.949(3)	3.137(4)	3.14(1)	3.370(4)
O(5)−Mo−O(6)	89.4(1)	89.2(1)	88.7(4)	88.3(2)	A−O(6)	2.874(3)	2.953(4)	2.976(9)	2.995(4)
P−O(2$^{\mathrm{i}}$)	1.545(2)	1.541(3)	1.55(1)	1.547(4)	A−O(7)	2.962(2)	3.051(3)	3.08(1)	3.219(4)
P−O(5$^{\mathrm{ii}}$)	1.538(3)	1.540(4)	1.52(1)	1.538(4)					
P−O(6$^{\mathrm{iii}}$)	1.527(3)	1.518(4)	1.53(1)	1.515(4)					
P−O(7)	1.541(2)	1.547(4)	1.534(9)	1.535(4)					

^{a} Symmetry codes: (i) $^{1}/_{2} - x$, $^{1}/_{2} - y$, $-^{1}/_{2} + z$; (ii) $-x$, y, $^{1}/_{2} - z$; (iii) x, $-y$, $-^{1}/_{2} + z$; (iv) $^{1}/_{2} - x$, $-^{1}/_{2} + y$, z.

The tellurium cation is environed by four oxygen atoms: two of them are shared with two MoO_6 octahedra and correspond to the shortest Te−O distances (from 1.857(3) to 1.861(2) Å), whereas the two other oxygen atoms belong to two PO_4 tetrahedra with longer Te−O distances (from 2.112(2) to 2.13(1) Å) (Table 3). These four oxygen atoms form a very distorted tetrahedron, very flattened, the Te atom being nearly situed outside of this "O_4" tetrahedron. In fact, the coordination of Te(IV) can be described by a trigonal bipyramid TeO_4E, the E lone pair being the fifth apex of the pyramid (see inset Figure 1a).

In the four studied compounds, the A cation is surrounded by nine oxygen atoms, always with the same environment. The only difference concerns the A−O distances which increase (as expected) with the size of the A cation: they are ranging from 2.726(3) to 3.163(3) Å for A = K, from 2.830(3) to 3.164(4) Å for A = Rb, from 2.77(1) to 3.17(1) Å for A = Tl, and from 2.995(4) to 3.381(4) Å for A = Cs (Table 3).

In conclusion, this study shows for the first time the possibility to synthesize an opened mixed framework built up of TeO_4E bipyramids, PO_4 tetrahedra, and MoO_6 octahedra. The flexibility of this new structure is remarkable since it can host A cations with variable sizes, ranging from potassium to cesium, without any significant variation of the geometry of the different polyhedra forming the $[TeMo_2P_2O_{14}]_\infty$ framework. These results open the route to the exploration of transition metal phosphates containing Te(IV) in their host lattice to improve the structure flexibility. The research of mixed valent Mo(V)−Mo(VI) phosphates containing Te(IV) is in progress to generate new transport properties.

Acknowledgment. The authors would like to thank Dr. M.-M. Borel for the helpful discussions.

Supporting Information Available: Crystallographic data for $A_2TeMo_2O_6(PO_4)_2$ with A = K, Rb, Tl, Cs. This material is available free of charge via the Internet at http://pubs.acs.org.

CM000035Y