

# Molybdenum(V) Chloromonophosphates with a Layer Structure: $AMoOPO_4Cl$ ( $A = K, Rb$ )

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Two new pentavalent molybdenum chloromonophosphates,  $KMoOPO_4Cl$  and  $RbMoOPO_4Cl$ , have been synthesized. They crystallize in the  $P4/nmm$  space group with  $a = b = 6.4340(5)$  and  $c = 7.2715(9)$  Å for the potassium compound and  $a = b = 6.4551(8)$  and  $c = 7.4612(8)$  Å for the rubidium compound. Their original structure consists of  $[MoPO_5Cl]_{\infty}$  layers parallel to (001), whose cohesion is ensured by  $K^+$  or  $Rb^+$  ions. The chloride ions and the alkali metal cations form a puckered rock salt layer. © 1998 Academic Press

## INTRODUCTION

The exploration of transition metal phosphates has allowed numerous original compounds, characterized by a mixed valence or an unusual valence of the transition elements, to be synthesized. This is the case for the pentavalent molybdenum phosphates, whose crystal chemistry has been extensively studied over the past 10 years (for review, see refs 1–3). Mo(V), owing to its particular electronic configuration, which imposes the presence of a molybdenyl ion, favors the formation of open frameworks so that large cations can be intercalated in those structures.

In contrast, the chemistry of Mo(V) oxychlorides has not yet been developed. To our knowledge, only one Mo(V) chlorophosphate,  $(MoOCl_3 \cdot POCl_3)_2$  (4), has been synthesized, whereas two oxychlorides,  $MoOCl_3$  (5) and  $K_2MoOCl_5$  (6), are known. These compounds resemble the oxides in that, whatever the structure, one observes  $MoX_6$  octahedra ( $X = O, Cl$ ) characterized by a short Mo–O bond of 1.6 Å. This suggests that it should be possible to generate new Mo(V) chlorophosphates with an open structure by introducing large cations other than the P(V) and Mo(V) species. For this reason, we have studied the systems  $ACl$ –“ $Mo_2O_5$ ”– $P_2O_5$  ( $A = K, Rb$ ). We report herein two new Mo(V) chloromonophosphates,  $AMoOPO_4Cl$  ( $A = K, Rb$ ), that exhibit a layer structure.

## SYNTHESIS AND CRYSTAL GROWTH

The systems  $ACl$ –“ $Mo_2O_5$ ”– $P_2O_5$  ( $A = K, Rb$ ) were explored by mixing various compositions using a two-step synthesis method. In the first step mixtures of  $H(NH_4)_2PO_4$ ,  $ACl$ , and  $MoO_3$  were heated at 700 K in air in a platinum crucible to decompose the ammonium phosphate. In the second step, an adequate amount of metallic molybdenum was added to the products to obtain the required Mo(V) phosphate formula; the mixtures were then sealed in evacuated silica ampoules and heated at various temperatures. This method gave biphasic samples of black and yellow crystals. The black crystals were identified as the already known phosphate  $A_xMo_2O_2(PO_4)_2 \cdot H_2O$  (7), whereas the yellow crystals correspond to a new Mo(V) chloromonophosphate  $AMoOPO_4Cl$  whose composition  $AMoPO_4Cl$  was determined by microprobe analysis.

Using the foregoing experimental method allowed single crystals of  $AMoPO_5Cl$  of good quality to be grown for the following second heat treatment: heating at 923 K for 24 hr, cooling at  $15 K hr^{-1}$  to 573 K, and finally quenching to room temperature.

Attempts to prepare a single phase from a starting nominal composition  $AMoPO_5Cl$  were unsuccessful. They always led to biphasic samples. Thus, for magnetic characterization yellow crystals of  $KMoPO_5Cl$  were picked out with the aid of a tweezers and a binocular.

## X-RAY DIFFRACTION STUDY

Single crystals, obtained in the form of yellow plates, were selected for the potassium and rubidium phases; the dimensions of the crystals were  $0.154 \times 0.128 \times 0.008$  mm and  $0.077 \times 0.038 \times 0.008$  mm, respectively. The cell parameters were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based on 25 reflections with  $18^\circ < \theta < 22^\circ$ . The data were collected on an Enraf Nonius CAD4 diffractometer with the parameters reported Table 1. The reflections were corrected for Lorentz

**TABLE 1**  
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for  $\text{KMoOPO}_4\text{Cl(I)}$  and  $\text{RbMoOPO}_4\text{Cl(II)}$

	I	II
Crystal Data		
Cell dimensions ( $\text{\AA}$ )	$a = b = 6.4340(5)$ $c = 7.2715(9)$	$a = b = 6.455(5)$ $c = 7.4612(8)$
Volume ( $\text{\AA}^3$ )	301.01(6)	310.9(1)
Space group	$P4/mmm$ (No. 129)	$P4/mmm$ (No. 129)
Z	2	2
Data Collection		
$\lambda(\text{MoK}\alpha)$ ( $\text{\AA}$ )	0.71073	0.71073
Scan mode	$\omega-\theta$	$\omega-\frac{2}{3}\theta$
Scan width (deg)	$1.2 + 0.35 \tan \theta$	$1.1 + 0.35 \tan \theta$
Slit aperture (mm)	$1.1 + \tan \theta$	$1 + \tan \theta$
Maximum $\theta$ (deg)	45	45
Standard reflections	3 measured every hour	3 measured every hour
Measured reflections	781	808
Reflections with $I > 3\sigma(I)$	335	143
$\mu$ ( $\text{mm}^{-1}$ )	3.52	10.5
Refinement		
Parameters refined	20	20
Agreement factors	$R = 0.026$ $R_w = 0.029$	$R = 0.043$ $R_w = 0.043$
Weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$
$\Delta/\sigma_{\text{max}}$	0.0004	0.0001
$\Delta\rho$ ( $\text{e}\text{\AA}^{-3}$ )	0.99	1.5

and polarization effects and for absorption. The structure was solved by the heavy-atom method.

The Laue symmetry is  $P4/mmm$  and the systematic extinctions  $h + k = 2n + 1$  for  $hk0$  are characteristic of the space group  $P4/mmm$ . The refinement of the structures led to the atomic parameters listed in Table 2, with reliability factors  $R = 0.026$  and  $R_w = 0.029$  for  $A = \text{K}$  and  $R = 0.043$  and  $R_w = 0.043$  for  $A = \text{Rb}$ .

The structure of these two compounds is simple and original: it consists of  $\text{MoO}_5\text{Cl}$  octahedra and  $\text{PO}_4$  tetrahedra sharing their apices such that they can be formulated  $A\text{MoOPO}_4\text{Cl}$ .

The projection of this structure along  $\bar{a}$  shows its layered character (Fig. 1). One recognizes  $[\text{MoPO}_5\text{Cl}]_\infty$  layers parallel to (001), whose cohesion is ensured through a (001) layer of  $\text{K}^+$  or  $\text{Rb}^+$  ions.

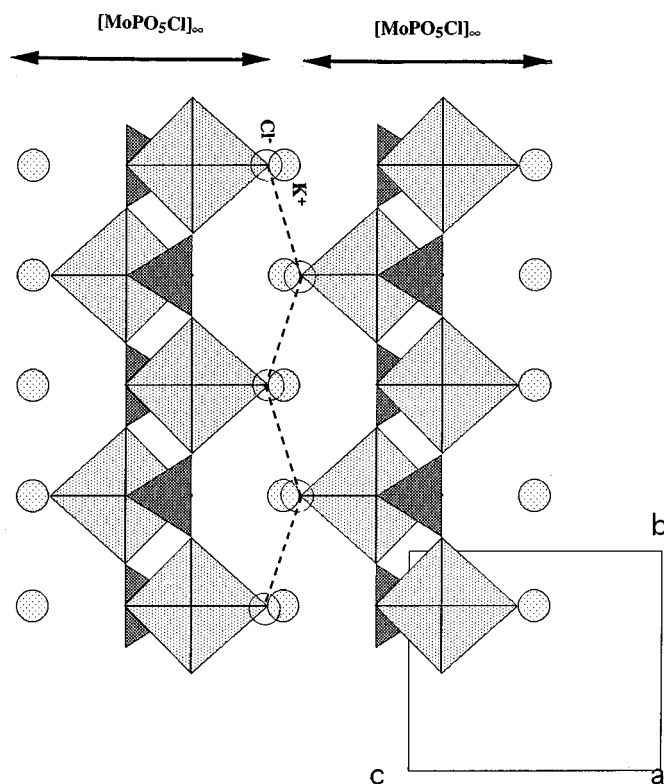
The projection of the  $[\text{MoPO}_5\text{Cl}]_\infty$  layer along  $\bar{c}$  (Fig. 2) shows that it consists of  $[\text{MoPO}_7\text{Cl}]_\infty$  chains in which a  $\text{MoO}_5\text{Cl}$  octahedron alternates with a  $\text{PO}_4$  tetrahedron. Such chains run along  $[100]$  and  $[010]$  such that each  $\text{PO}_4$  tetrahedron shares its four apices with four  $\text{MoO}_5\text{Cl}$  octahedra, whereas each  $\text{MoO}_5\text{Cl}$  octahedron shares its four equatorial oxygen atoms O(2) with four  $\text{PO}_4$  tetrahedra, the apical oxygen atom O(1) being free and the opposite apical chlorine atom forming four ionic bonds with  $\text{K}^+$  or  $\text{Rb}^+$

**TABLE 2**  
Atomic Parameters for  $\text{KMoOPO}_4\text{Cl}$  and  $\text{RbMoOPO}_4\text{Cl}^a$

Atom	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )	Site	Occup
$\text{KMoOPO}_4\text{Cl}$						
Mo	0.25	0.25	0.0936(1)	0.696(8)	2c	1.00
Cl	0.25	0.25	0.4495(3)	1.47(3)	2c	1.00
P	0.25	0.75	0.0	0.77(3)	2a	1.00
K	0.25	0.75	0.5	2.17(4)	2b	1.00
O(1)	0.25	0.25	-0.132(1)	2.5(2)	2c	1.00
O(2)	0.25	0.5617(4)	0.1292(4)	1.36(6)	8i	1.00
$\text{RbMoOPO}_4\text{Cl}$						
Mo	0.25	0.25	0.0885(6)	0.56(8)	2c	1.00
Cl	0.25	0.25	0.436(2)	1.92(3)	2c	1.00
P	0.25	0.75	0.0	0.80(3)	2a	1.00
Rb	0.25	0.75	0.5	1.60(4)	2b	1.00
O(1)	0.25	0.25	-0.137(4)	1.84(2)	2c	1.00
O(2)	0.25	0.561(2)	0.130(1)	1.28(3)	8i	1.00

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as  $B = \frac{1}{3} \sum_i \sum_j \bar{a}_i \cdot \bar{a}_j \cdot \beta_{ij}$ .

ions. Consequently, the  $\text{MoO}_5\text{Cl}$  octahedron exhibits the specific geometry of Mo(V) (Table 3): the four equatorial Mo–O(2) distances are normal (2.02–2.03  $\text{\AA}$ ), the apical Mo–O(1) bond is abnormally short (1.64–1.68  $\text{\AA}$ ), and the



**FIG. 1.** Projection of the structure of  $\text{KMoOPO}_4\text{Cl}$  along  $\bar{a}$ .

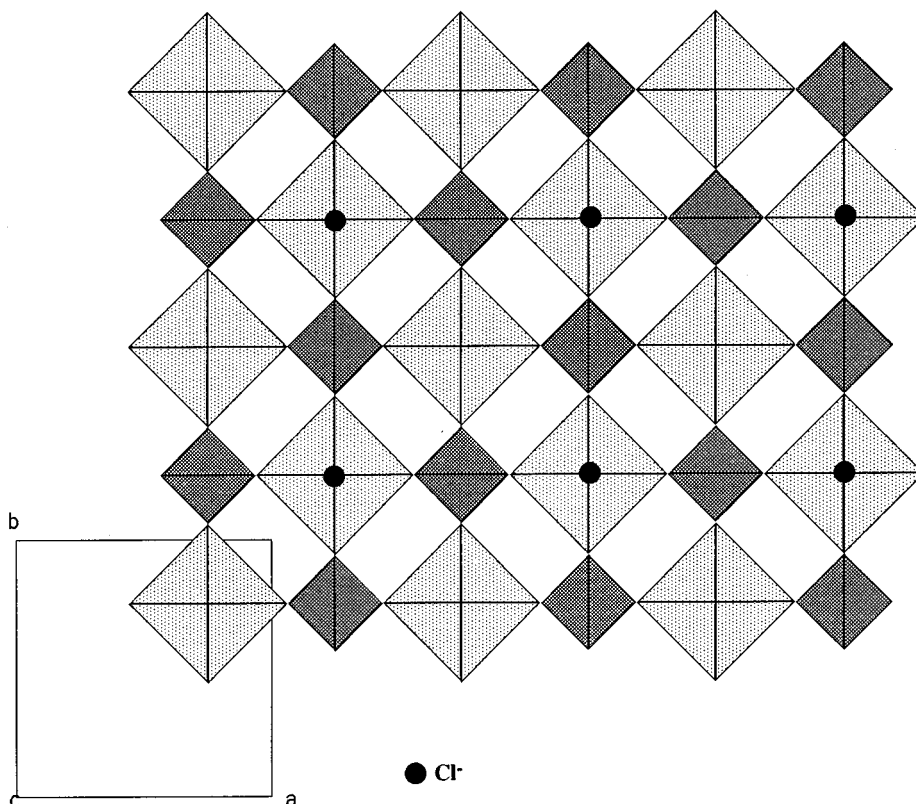


FIG. 2. Projection of a  $[\text{MoPO}_5\text{Cl}]_\infty$  layer along  $\vec{c}$ .

opposite Mo–Cl bond is much longer (2.60 Å), i.e., greater than the value usually observed for Mo–Cl distances (8) (2.20–2.35 Å). The  $\text{PO}_4$  tetrahedra are regular (Table 3), with P–O(2) distances ranging from 1.53 to 1.56 Å, which is in the range usually observed in monophosphates.

Note that the arrangement of the  $\text{PO}_4$  tetrahedra and  $\text{MoO}_5\text{Cl}$  octahedra within a layer can be derived from that of an octahedral perovskite layer in which one octahedron of two would be replaced by one  $\text{PO}_4$  tetrahedron. Such a geometry has previously been observed between  $\text{VO}_6$  octahedra and  $\text{PO}_4$  tetrahedra in the vanadium phosphate  $\text{Ca}(\text{VO})_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (9).

An interesting feature of this structure deals with the arrangement of the  $\text{Cl}^-$  and  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions. Between two  $[\text{MoPO}_5\text{Cl}]_\infty$  layers the Cl atoms of one layer are shifted by  $(\vec{a} + \vec{b})/2$  with respect to each other (see Fig. 1, circles connected by dashed line). As a result, they form a puckered layer parallel to (001) in which the  $\text{Cl}^-$  ions exhibit a slightly distorted face-centered arrangement (Fig. 3). The  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions are then located between the  $\text{Cl}^-$  ions along  $\vec{a}$ . As a result, the  $\text{Cl}^-$  and  $\text{K}^+$  (or  $\text{Rb}^+$ ) ions form a puckered rock salt layer (Fig. 3). Taking into consideration such  $[\text{KCl}]_\infty$  or  $[\text{RbCl}]_\infty$  layers, the structure can also be described as a stacking along  $\vec{c}$  of puckered rock salt type layers  $[\text{KCl}]_\infty$

with  $[\text{MoPO}_5]_\infty$  layers in which molybdenum adopts the pyramidal coordination.

The  $\text{K}^+$  (or  $\text{Rb}^+$ ) cations are surrounded by eight atoms (four Cl + four O(1)), forming a dodecahedron. The four K(Rb)–Cl distances, ranging from 3.23 to 3.26 Å, are larger than those observed for KCl (3.14 Å) and RbCl (3.26 Å) structures (10, 11). In the same way the four K–O or Rb–O

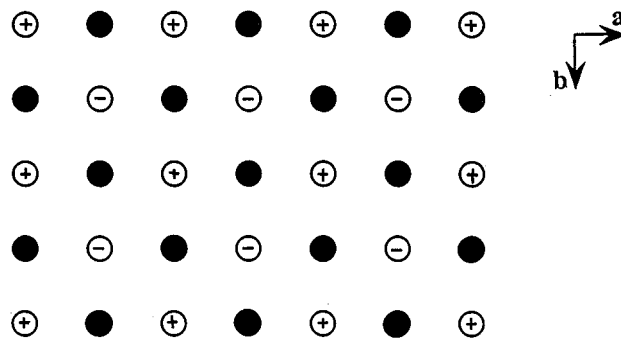


FIG. 3. Rock salt type arrangement of a "KCl" (001) layer in  $\text{KMoOPO}_4\text{Cl}$ . The filled circles represent the  $\text{K}^+$  ions ( $z = \frac{1}{2}$ ), and the unfilled circles represent the  $\text{Cl}^-$  ions ("+" corresponds to  $z = 0.5505$  and "–" to  $z = 0.4495$ ).

**TABLE 3**  
Distances (Å) and Angles (Deg) in the Polyhedra in  
KMoOPO<sub>4</sub>Cl and RbMoOPO<sub>4</sub>Cl<sup>a</sup>

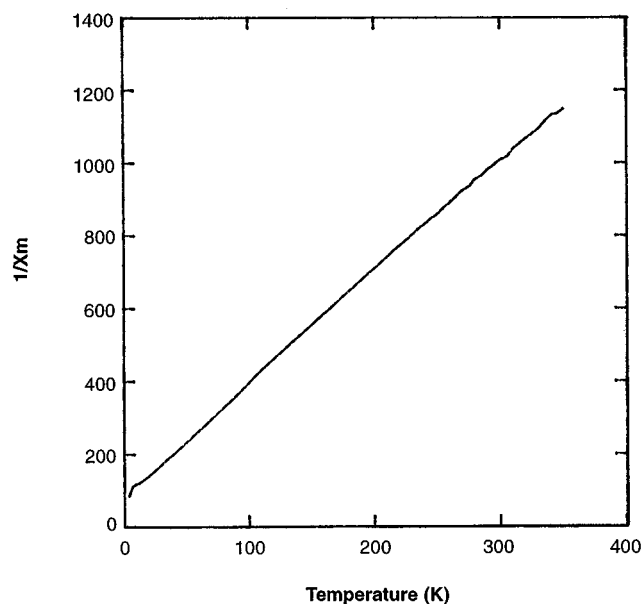
KMoOPO <sub>4</sub> Cl						
Mo	Cl	O(1)	O(2)	O(2) <sup>i</sup>	O(2) <sup>ii</sup>	O(2) <sup>iii</sup>
Cl	<b>2.588(2)</b>	4.226(6)	3.074(6)	3.074(6)	3.074(6)	3.074(6)
O(1)	180.0(5)	<b>1.638(8)</b>	2.760(6)	2.760(6)	2.760(6)	2.760(6)
O(2)	82.66(8)	97.34(8)	<b>2.022(3)</b>	4.011(6)	2.836(6)	2.836(6)
O(2) <sup>i</sup>	82.66(8)	97.34(8)	165.3(1)	<b>2.022(3)</b>	2.836(6)	2.836(6)
O(2) <sup>ii</sup>	82.66(8)	97.34(8)	89.06(2)	89.06(2)	<b>2.022(3)</b>	4.011(6)
O(2) <sup>iii</sup>	82.66(8)	97.34(8)	89.06(2)	89.06(2)	165.3(1)	<b>2.022(3)</b>
RbMoOPO <sub>5</sub> Cl						
Mo	Cl	O(1)	O(2)	O(2) <sup>i</sup>	O(2) <sup>ii</sup>	O(2) <sup>iii</sup>
Cl	<b>2.60(1)</b>	4.28(2)	3.04(2)	3.04(2)	3.04(2)	3.04(2)
O(1)	180.0(8)	<b>1.68(3)</b>	2.83(2)	2.83(2)	2.83(2)	2.83(2)
O(2)	81.2(3)	98.8(3)	<b>2.03(1)</b>	4.02(2)	2.84(2)	2.84(2)
O(2) <sup>i</sup>	81.2(3)	98.8(3)	162.4(5)	<b>2.03(1)</b>	2.84(2)	2.84(2)
O(2) <sup>ii</sup>	81.2(3)	98.8(3)	88.66(7)	88.66(7)	<b>2.03(1)</b>	4.02(2)
O(2) <sup>iii</sup>	81.2(3)	98.8(3)	88.66(7)	88.66(7)	162.4(5)	<b>2.03(1)</b>
P						
O(2)	O(2) <sup>iv</sup>	O(2) <sup>v</sup>	O(2) <sup>vi</sup>			
O(2)	<b>1.533(3)</b>	2.42(8)	2.54(8)	2.54(8)		
O(2) <sup>iv</sup>	104.4(2)	<b>1.533(3)</b>	2.54(8)	2.54(8)		
O(2) <sup>v</sup>	112.05(8)	112.05(8)	<b>1.533(3)</b>	2.42(8)		
O(2) <sup>vi</sup>	112.05(8)	112.05(8)	104.4(2)	<b>1.533(3)</b>		
RbMoOPO <sub>5</sub> Cl						
Mo	Cl	O(1)	O(2)	O(2) <sup>i</sup>	O(2) <sup>ii</sup>	O(2) <sup>iii</sup>
Cl	<b>2.60(1)</b>	4.28(2)	3.04(2)	3.04(2)	3.04(2)	3.04(2)
O(1)	180.0(8)	<b>1.68(3)</b>	2.83(2)	2.83(2)	2.83(2)	2.83(2)
O(2)	81.2(3)	98.8(3)	<b>2.03(1)</b>	4.02(2)	2.84(2)	2.84(2)
O(2) <sup>i</sup>	81.2(3)	98.8(3)	162.4(5)	<b>2.03(1)</b>	2.84(2)	2.84(2)
O(2) <sup>ii</sup>	81.2(3)	98.8(3)	88.66(7)	88.66(7)	<b>2.03(1)</b>	4.02(2)
O(2) <sup>iii</sup>	81.2(3)	98.8(3)	88.66(7)	88.66(7)	162.4(5)	<b>2.03(1)</b>
P						
O(2)	O(2) <sup>iv</sup>	O(2) <sup>v</sup>	O(2) <sup>vi</sup>			
O(2)	<b>1.56(1)</b>	2.43(2)	2.59(2)	2.59(2)		
O(2) <sup>iv</sup>	102.8(6)	<b>1.56(1)</b>	2.59(2)	2.59(2)		
O(2) <sup>v</sup>	112.9(3)	112.9(3)	<b>1.56(1)</b>	2.43(2)		
O(2) <sup>vi</sup>	112.9(3)	112.9(3)	102.8(6)	<b>1.56(1)</b>		

<sup>a</sup>Symmetry codes: i =  $\frac{1}{2} - x, \frac{1}{2} - y, z$ ; ii =  $y, \frac{1}{2} - x, z$ ; iii =  $\frac{1}{2} - y, x, z$ ; iv =  $x, \frac{3}{2} - y, z$ ; v =  $-\frac{1}{2} + y, \frac{1}{2} + x, -z$ ; vi =  $1 - y, 1 - x, -z$ ; vii =  $x, 1 + y, z$ ; viii =  $-\frac{1}{2} + x, 1 + y, 1 - z$ ; ix =  $\frac{1}{2} + x, 1 - y, 1 - z$ ; x =  $-\frac{1}{2} + y, \frac{1}{2} + x, 1 - z$ ; xi =  $1 - y, 1 - x, 1 - z$ .

distances of 2.956 and 3.02 Å, respectively (Table 3), are much longer than the sum of the ionic radii of K<sup>+</sup> (or Rb<sup>+</sup>) and O<sup>2-</sup>. These large distances are in agreement with the rather high thermal factors observed for these cations (Table 2), i.e., 2.17 and 1.60 Å<sup>2</sup> for K<sup>+</sup> and Rb<sup>+</sup>, respectively.

### MAGNETIC MEASUREMENT

The magnetic susceptibility of small yellow crystals extracted from a biphasic preparation was measured by SQUID magnetometry from 4.5 to 350 K under 0.3 T after



**FIG. 4.** Inverse molar magnetic susceptibility  $1/\chi_m$  versus temperature for a sample made of small crystals picked out from a biphasic preparation.

zero-field cooling. Due to the small amount of material the sample holder signal was carefully subtracted. From the slope of the  $1/\chi_m$  versus temperature curve (Fig. 4) in the range 100–350 K a magnetic moment of 1.63  $\mu_B$  per Mo(V) was obtained. This value is somewhat lower than the theoretical value (1.73  $\mu_B$ ) expected for a Mo<sup>5+</sup>. It must be pointed out that the second phase of the biphasic sample (7) has a lower magnetic signal (3) and one cannot exclude that a very small amount of this phase has been mixed when picking out the KMoOPO<sub>4</sub>Cl crystals, leading to a slightly smaller moment per Mo(V).

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