1394 *Inorg. Chem.* **1999,** *38,* 1394−1400

Hydrothermal Synthesis and Characterization of Novel One-Dimensional Tellurites of Molybdenum(VI), $A_4Mo_6TeO_{22}\cdot 2H_2O$ (A = NH_4, Rb)

Vidyavathy Balraj and K. Vidyasagar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

Received August 11, 1998

Two novel, isostructural, one-dimensional tellurites of molybdenum(VI), $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$, have been synthesized by hydrothermal method. They contain linear $(Mo_6TeO_{22})^{4-}$ anionic chains, parallel to one another and held together by NH_4^+/Rb^+ ions. "Mo_6O_{22}" moieties, formed by edge-sharing of six MoO_6 octahedra, are connected through tellurium resulting in the $(Mo_6TeO_{22})^{4-}$ anionic chain. Tellurium is four-coordinated with SF_4 geometry. The water of crystallization occupies the rest of the lattice. Both compounds have been structurally characterized by single-crystal X-ray diffraction studies. Pertinent crystal data are as follows: for $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$, monoclinic space group $C2/c$, $a = 21.354(10)$ Å, $b = 7.761(2)$ Å, $c = 15.508(10)$ Å, $\beta = 119.34(5)°$, $Z = 4$; for $Rb_4Mo_6TeO_{22}\cdot 2H_2O$, monoclinic space group $C2/c$, $a = 21.410(5)$ Å, $b = 7.757(2)$ Å, $c = 15.507(7)$ Å, $\beta = 119.68(3)°$, $Z = 4$. Hydrothermal syntheses, structure, powder X-ray diffraction, spectroscopy, and thermal studies of these compounds are described.

Introduction

Many new compounds with novel structures and interesting properties have been reported to be synthesized by employing low-temperature methods such as hydrothermal technique. This method, apart from being employed widely for the synthesis of microporous materials like zeolites, has recently found broader application in the synthesis of a wide variety of inorganic solids.[1−4] The compounds so synthesized have been found to possess novel low-dimensional as well as three-dimensional framework structures.

As a part of our ongoing research on low-temperature synthetic routes for oxide materials, we have employed the hydrothermal technique, to explore the A−Mo−Te−O "phase space" for tellurites. The choice of this quaternary system is based on two reasons. One is that the number of tellurites with extended structures in these quaternary systems is limited, and the other reason is the possible rich structural chemistry of tellurites, as Te^{4+} is known to exhibit a variety of coordinations such as pyramidal "TeO_3", "TeO_4" with SF_4 geometry, and "TeO_5" with square-pyramidal geometry. We have initially attempted the synthesis of layered hexagonal tungsten bronze related tellurites of molybdenum(VI), namely, $A_2Mo_3TeO_{12}$ (A = monovalent ion). We have succeeded in the preparation of the cesium and ammonium compounds. We have also isolated two new zero-dimensional compounds, $A_4Mo_6Te_2O_{24}\cdot 6H_2O$ (A = Rb, K) with discrete $(Mo_6Te_2O_{24})^{4-}$ anions. It is noteworthy that all four compounds have the anions with the same empirical formula.[5] During these synthetic investigations for tellurites, we have isolated two new isostructural, one-dimensional compounds, $A_4Mo_6TeO_{22}\cdot 2H_2O$ (A = NH_4, Rb), with novel structural features. These compounds contain hexanuclear molybdenum−oxygen clusters linked by the heteroatom tellurium, resulting in a one-dimensional $(Mo_6TeO_{22})^{4-}$ anionic chain. The majority of polynuclear molybdenum−oxygen clusters containing heteroatom M, such as P, Te, Si, and Se, are known to exist as discrete $[Mo_xM_yO_z]^{n-}$ anions with Keggin, Anderson−Evans, Dexter−Silverton, and Dawson structures.[6] Polyoxometalates with chainlike, layerlike, or three-dimensional extended anionic framework structures have rarely been observed. Recently, heteropolymolybdates, $K_2[Se_2MoO_8]\cdot 3H_2O$[7] and $Na_{0.5}K_{6.5}[Mo_8V_7O_{42}]\cdot 12.5H_2O$,[8] with novel chainlike anions have been reported. In the former case, distorted MoO_6 octahedra are linked to two SeO_3 pseudo-tetrahedra, resulting in a sinusoidally corrugated anionic chain, $[Se_2MoO_8]_n^{2n-}$, whereas in the latter, capped α-Keggin fragments are linked to form a chain, $[Mo_8V_4O_{36}(VO_4)(VO)_2]_n^{7n-}$. In this paper, we report the synthesis and characterization of two such rare one-dimensional molybdenum(VI) tellurites, $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$.

Experimental Section

Synthesis. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, MoO_3, Rb_2CO_3, and TeO_2 of high purity were used for the synthesis. 23-mL capacity Teflon-lined acid digestion bombs of Parr make were employed for hydrothermal synthesis.

---

(1) Soghomonian, V.; Chen, Q.; Zhang, Y.; Haushalter, R. C.; O'Connor, C. J.; Tao, C.; Zubieta, J. *Inorg. Chem.* **1995**, *34*, 3509. (b) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 5603. (c) Cao, G.; Haushalter, R. C.; Strohmaier, K. G. *Inorg. Chem.* **1993**, *32*, 127.

(2) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2924.

(3) (a) Zhang, Y.; Haushalter, R. C.; Clearfield, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1149. (b) Khan, M. I.; Chen, Q.; Goshorn, D. P.; Hope, H.; Parkin, S.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 3341. (c) Khan, M. I.; Chen, Q.; Goshorn, D. P.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 672. (d) Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *206*, 131.

(4) (a) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1995**, *34*, 4774. (b) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1996**, *35*, 1461. (c) Vaughey, J. T.; Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1994**, *33*, 4370. (d) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1994**, *33*, 6043. (e) Harrison, W. T. A.; Dussack, L. L.; Vogt, T.; Jacobson, A. J. *J. Solid State Chem.* **1995**, *120*, 112.

(5) Vidyavathy, B.; Vidyasagar, K. *Inorg. Chem.* **1998**, *37*, 4764.

(6) (a) Pope, M.; Muller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (b) Pope, M. *Heteropoly and Isopoly Oxometalates, Inorganic Chemistry Concepts*; Springer: Berlin, 1983. (c) Evans, H. T. *J. Am. Chem. Soc.* **1948**, *70*, 1291.

(7) Robl, C.; Haake, K. *J. Chem. Soc., Chem. Commun.* **1992**, 1786.

(8) Muller, A.; Koop, M.; Schiffels, P.; Bogge, H. *J. Chem. Soc., Chem. Commun.* **1997**, 1715.

10.1021/ic980957r CCC: $18.00

Table 1. X-ray Powder Diffraction Patterns of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$

			$(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$			$Rb_4Mo_6TeO_{22}\cdot 2H_2O$		
h	*k*	*l*	d_{cal} (Å)	d_{obs} (Å)	I/I_0	d_{cal} (Å)	d_{obs} (Å)	I/I_0
2	0	0	9.307	9.300	15	–	–	–
1	1	0	7.164	7.161	100	7.159	7.157	100
1	1	−1	–	–	–	6.890	6.894	19
3	1	0	4.846	4.843	13	4.843	4.839	13
0	2	0	3.881	3.875	6	3.878	3.881	68
2	2	−1	3.636	3.632	11	3.636	3.640	46
2	2	0	3.582	3.577	13	3.580	3.580	85
0	2	2	–	–	–	3.361	3.354	14
5	1	0				3.354		
4	2	−2	–	–	–	3.114	3.117	30
6	0	0	3.102	3.102	16	–	–	–
4	2	0	–	–	–	2.978	2.984	71
5	1	1	2.966	2.967	31	–	–	–
4	2	1	2.735	2.729	5	2.731	2.733	14
2	2	−4	2.728			2.726		
6	2	−2	–	–	–	2.625	2.624	9
6	2	−1	–	–	–	2.562	2.562	15
1	3	0				2.561		
7	1	0	2.516	2.514	10	2.514	2.513	18
1	1	5	2.385	2.384	5	–	–	–
5	3	0	2.124	2.121	10	2.123	2.125	59
5	3	1	2.014	2.012	4	2.012	2.015	24
2	4	−1	–	–	–	1.907	1.909	14
5	1	−8	–	–	–	1.878	1.877	21
2	4	−2				1.877		
6	4	−1	–	–	–	1.686	1.688	14

$(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$. A mixture of 2.0 g (1.62 mmol) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.3013 g (1.89 mmol) of TeO_2 with Mo:Te ratio of 6:1 was heated along with 4.2 mL of water in an acid digestion bomb at 175 °C for 4 days and then cooled to room temperature over a period of 36 h. White powder (1.939 g, 88.3% yield) of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ was obtained as the only product. It was filtered, washed with distilled water, and air-dried. Colorless, transparent, needlelike crystals of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ were obtained in a mixture of products when a reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2 g, 1.62 mmol), TeO_2 (0.909 g, 5.695 mmol), and 4.2 mL of water, with the 2:1 ratio of Mo:Te, was carried out by heating at 225 °C for 7 days and by cooling to room temperature over a period of 2 days. Crystals suitable for single-crystal X-ray diffraction studies were hand picked.

$Rb_4Mo_6TeO_{22}\cdot 2H_2O$. A reaction of Rb_2CO_3 (0.436 g, 1.89 mmol), MoO_3 (0.544 g, 3.78 mmol), and TeO_2 (0.151 g, 0.946 mmol) with the Rb:Mo:Te ratio of 4:4:1 was carried out by heating them together with 4.2 mL of water in an acid digestion bomb at 175 °C for 4 days and then by cooling to room temperature over a period of 36 h. $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ was obtained as the major phase (0.937 g, 69.3% yield) in the form of microcystalline solid along with small amounts (about 0.073 g) of $Rb_4Mo_6Te_2O_{24}\cdot 6H_2O$ [5] in the form of blocks of crystals which were removed by hand picking. The title compound was filtered, washed with distilled water, and air-dried. However, single crystals suitable for X-ray diffraction studies were obtained when the same reaction was carried out at 175 °C for a longer duration of 7 days and cooled to room temperature over 36 h.

X-ray Diffraction and Crystal Structure. The powder X-ray diffraction patterns were recorded on Rigaku Miniflex (table model) instrument using Co Kα radiation ($\lambda = 1.7902$ Å) and also on a Seifert automated powder diffractometer using Cu $K\alpha_1$ radiation (germanium single crystal was used as a monochromator, Cu $K\alpha_1$, $\lambda = 1.5406$ Å). Silicon was used as an external standard. The indexed powder X-ray diffraction patterns of the two title compounds are given in Table 1. The observed powder X-ray diffraction patterns agree well with those simulated based on their single-crystal structural data using the LAZY-PULVERIX program,[9] indicating the monophasic nature of the materials.

Table 2. Crystallographic Data for $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$

compd	$(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$	$Rb_4Mo_6TeO_{22}\cdot 2H_2O$
empirical formula	$N_4Mo_6TeO_{24}H_{20}$	$Rb_4Mo_6TeO_{24}H_4$
fw	1163.43	1433.15
space group	$C2/c$	$C2/c$
a (Å)	21.354(10)	21.410(5)
b (Å)	7.761(2)	7.757(2)
c (Å)	15.508(10)	15.507(7)
β (deg)	119.34(5)	119.68(3)
V (Å^3)	2240(2)	2237.4(12)
Z	4	4
T (°C)	25	25
λ(Mo Kα) (Å)	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	3.449	4.255
μ(Mo Kα) (mm^{-1})	4.643	13.291
R^a	0.0187	0.0496
$R_w{}^b$	0.0546	0.0926

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b\ R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$.

The crystal structures of the ammonium and rubidium compounds were determined by single-crystal X-ray diffraction studies. Colorless, transparent, needlelike crystals of both compounds were mounted on a thin glass fiber with epoxy glue. The single-crystal X-ray data were collected from an Enraf-Nonius CAD4 automated four-circle diffractometer by standard procedures. Pertinent crystallographic data and data collection parameters are summarized in Table 2. About 25 reflections with $20° \leq 2\theta \leq 30°$ were located and centered. Their least-squares refinement resulted in monoclinic unit cells. The data sets were reduced by routine computational procedures. Absorption corrections based on azimuthal scans of reflections with χ angle near 90° were applied to the data sets. Intensities of two check reflections monitored at regular intervals remained invariant, indicating no sign of decay or decomposition of the crystals. The observed systematic absences indicated $C2/c$ and Cc as the possible space groups. The choice of space group $C2/c$ was proved to be correct from successful structure solution and refinements for both compounds. The programs SHELXS-86 and SHELXL-93 were used for structure solutions and structure refinement, respectively.[10]

For the ammonium compound, the positions of one tellurium and three crystallographically distinct molybdenum atoms were located by direct methods. Refinement of these positions and subsequent difference Fourier maps led to the location of the remaining 14 atoms of the asymmetric unit. The final difference Fourier map, after successful anisotropic refinement of all atoms, did not show any chemically significant feature.

The isostructural nature of these two compounds was inferred from their similar lattice parameters and X-ray powder diffraction patterns. Therefore the rubidium compound was modeled, starting with the refined positional parameters of the ammonium compound, and only nitrogen atoms were replaced by rubidium atoms. In the final cycles of refinement, four oxygen atoms, O(1), O(3), O(4), and O(6), were refined isotropically and the rest of the atoms anisotropically. The final difference Fourier map contained ghost peaks (<1.7 e/Å^3) very close to existing atoms. The refined positional and equivalent isotropic thermal parameters for $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ are given in Tables 3 and 4, respectively. The bond lengths and selected bond angles are presented in Table 5.

Thermal Studies. Thermogravimetric analytical (TGA) and differential scanning calorimetric (DSC) data for the two compounds were collected on a Perkin-Elmer Delta series TG instrument. The samples were heated to about 550 °C under flowing N_2 gas at the rates of 10 and 20 °C/min for TGA and DSC studies, respectively.

Spectroscopic Data. The samples were ground with dry KBr and pressed into transparent disks. The infrared spectra were measured on

---

(9) Yvon, K.; Jeitschko, W.; Parthe, E. *J. Appl. Crystallogr.* **1977**, *10*, 73.

(10) (a) Sheldrick, G. M. *SHELXS-86 User Guide*; Crystallography Department, University of Gottingen: Gottingen, Germany, 1985. (b) Sheldrick, G. M. *SHELXL-93 User Guide*; Crystallography Department, University of Gottingen: Gottingen, Germany, 1993.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$

atom	*x*	*y*	*z*	$U_{eq}{}^{a}$
Te(1)	5000	3771(1)	2500	12(1)
Mo(1)	4941(1)	2796(1)	4763(1)	10(1)
Mo(2)	1392(1)	356(1)	1783(1)	12(1)
Mo(3)	3582(1)	4359(1)	280(1)	12(1)
O(1)	4322(1)	4697(3)	4776(2)	12(1)
O(2)	455(1)	2475(4)	1045(2)	17(1)
O(3)	4424(1)	2339(4)	673(2)	14(1)
O(4)	4385(1)	4025(4)	3235(2)	14(1)
O(5)	4330(1)	1134(4)	4353(2)	19(1)
O(6)	2987(2)	3725(4)	2840(2)	23(1)
O(7)	1690(2)	1652(4)	2801(2)	21(1)
O(8)	1758(1)	1609(4)	1022(2)	15(1)
O(9)	3197(1)	2989(4)	764(2)	21(1)
O(10)	3053(1)	3839(4)	4949(2)	21(1)
O(11)	650(1)	345(4)	3431(2)	14(1)
O(12)	785(2)	4039(5)	3545(3)	42(1)
N(1)	3027(2)	249(5)	4392(3)	25(1)
N(2)	3379(2)	326(5)	2264(3)	29(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Rb_4Mo_6TeO_{22}\cdot 2H_2O$

atom	*x*	*y*	*z*	$U_{eq}{}^{a}$
Te(1)	5000	3763(2)	2500	11(1)
Mo(1)	4933(1)	2786(2)	4763(1)	8(1)
Mo(2)	1386(1)	377(2)	1799(1)	11(1)
Mo(3)	3588(1)	4338(2)	257(1)	10(1)
O(1)*	4319(5)	4690(13)	4758(7)	8(2)
O(2)	457(5)	2449(13)	1057(7)	11(2)
O(3)*	4433(5)	2355(13)	668(7)	10(2)
O(4)*	4376(5)	4034(13)	3225(7)	12(2)
O(5)	4322(5)	1119(14)	4336(8)	15(2)
O(6)*	2979(6)	3798(15)	2802(8)	19(3)
O(7)	1662(6)	1691(14)	280(8)	17(3)
O(8)	1744(5)	1628(14)	1036(7)	13(2)
O(9)	3194(6)	2954(15)	722(8)	20(3)
O(10)	3055(5)	3875(15)	4915(8)	16(2)
O(11)	652(5)	322(14)	3439(7)	12(2)
O(12)	780(7)	4047(17)	3527(9)	33(3)
Rb(1)	3026(1)	243(2)	4432(1)	21(1)
Rb(2)	3344(1)	385(2)	2225(1)	24(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. Atoms marked with an asterisk were refined isotropically.

these transparent disks from 400 to 4000 cm^{-1} for both the compounds on a Bruker 17S, 66V FT-IR spectrometer. Raman spectra were recorded on an RFS 100 FT Raman spectrometer with FRA 106 FT-Raman accessory provided with a CaF_2 beam splitter. Nd:YAG laser operating at an output of 200 mW for a 1064 nm line was used as the excitation source.

Results and Discussion

Synthesis. The yield and purity of the title compounds, in the hydrothermal reactions, are affected by the ratio of reactants, temperature, and duration of heating. A number of hydrothermal experiments have been carried out for the optimization of the synthetic procedure, and only the standardized reaction conditions are presented in the Experimental Section. The crystals of ammonium compound could be prepared by heating at higher temperatures and longer durations, whereas single crystals of the rubidium compound could be obtained by carrying out the reaction for longer durations. Thus higher temperatures and/or longer reaction periods seem to give the product in the form of single crystals, but sometimes at the expense of the yield and purity of the desired products. It might also lead to entirely different products, as we have observed in some of our earlier hydrothermal studies[5] in the A−Mo−Te−O system.

Crystal Structure. $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ are novel, one-dimensional compounds containing linear chains of $(Mo_6TeO_{22})^{4-}$ anions and NH_4^+/Rb^+ cations and water of crystallization. The one-dimensional anionic chain can be described as being built from "Mo_6O_{22}" moieties connected to one another in the linear fashion through tellurium. The three molybdenum atoms, Mo(1) to Mo(3), and eleven oxygen atoms, O(1) to O(11), of the asymmetric unit account for only a half of the "Mo_6O_{22}" moiety. This Mo_6O_{22} moiety sits on crystallographic inversion center, and the two halves are thus related by inversion symmetry. These moieties have six MoO_6 octahedra fused together by edge sharing, as shown in its ORTEP plot[11] and polyhedral representation (Figure 1). Here the MoO_6 octahedra of Mo(1), Mo(2), and Mo(3) share four, three, and two edges, respectively. It is evident from the figure that O(1) is bonded to four molybdenum atoms, whereas each of the four oxygen atoms, O(2), O(3), O(4), and O(8), bridge two molybdenum atoms. The remaining six oxygen atoms, each bonded to only one molybdenum, are distributed among Mo(1), Mo(2), and Mo(3). Such moieties are connected to tellurium through O(4) and O(11) oxygen atoms to result in the linear $(Mo_6TeO_{22})^{4-}$ anionic chain. Therefore, the five oxygen atoms, O(5), O(6), O(7), O(9), and O(10), are terminal ones, and the rest of them are each bonded to more than one metal center. Mo(1) has one terminal oxygen atom, namely, O(5), whereas Mo(2) and Mo(3) have two each.

The MoO_6 octahedra are all distorted. The Mo−O bond lengths span a considerable range from 1.701 to 2.403 Å. The terminal Mo−O bond lengths are smaller than other Mo−O bond lengths for both compounds. The O−Mo−O bond angles vary from 70 to 107°, differing from the ideal value of 90° by as much as 20°. However, the deviation of these bond angles from the ideal value of 180°, as given in Table 5, is maximum in Mo(1)O_6 octahedra and minimum in Mo(3)O_6 octahedra, indicating that the extent of distortion is maximum in Mo(1)O_6 octahedra which shares a maximum number of four edges. The values of O$\cdots$O nonbonding edge lengths of these distorted MoO_6 octahedra vary widely from 2.486 to 3.149 Å. The unshared O(3)$\cdots$O(4) edge of Mo(1)O_6 octahedra and the five shared edges, O(1)$\cdots$O(8), O(1)$\cdots$O(4), O(1)$\cdots$O(3), O(1)$\cdots$O(2), and O(1)$\cdots$O(1)′, have shorter lengths than the remaining unshared edges. Mo(1), Mo(2), and Mo(3) are displaced from the centers of their octahedra by 0.457, 0.447, and 0.396 Å for the ammonium compound and 0.472, 0.442, and 0.387 Å for the rubidium compound, respectively, toward the peripheral O$\cdots$O edges, O(2)$\cdots$O(5), O(6)$\cdots$O(7), and O(9)$\cdots$O(10), which contain mostly terminal oxygen atoms. The centers of the octahedra, calculated by averaging the coordinates of oxygen atoms, are not significantly different from the "best centers[12]". While the displacement of molybdenum atoms from the centers of MoO_6 octahedra is due to the second-order Jahn−Teller effect associated with such octahedrally coordinated d° metal cations, the observed direction[13] of the displacement, namely, toward the peripheral edges, is only to minimize the repulsion between the highly charged six Mo^{6+} ions in the moiety.

Generally the Mo−O bonds are shorter, the fewer the metal atoms that share the oxygen atoms. In the ammonium phase, the mean Mo−O distances are 1.716 Å for terminal oxygen

---

(11) Johnson, C. K. *ORTEP*; Oak Ridge National Laboratory: Oak Ridge, TN, 1970.

(12) Zunic, T. B.; Makovicky, E. *Acta Crystallogr.* **1996**, *B52*, 78.

(13) Kunz, M.; Brown, I. D. *J. Solid State Chem.* **1995**, *115*, 395.

Table 5. Bond Lengths (Å) and Selected Bond Angles (deg) for $A_4Mo_6TeO_{22}$·$2H_2O$ (A = NH_4, Rb) Compounds

	NH_4	Rb		NH_4	Rb		NH_4	Rb
Mo(1)−O(5)	1.719(3)	1.723(10)	A(2)-O(6)′	3.102(5)	3.069(11)	O(1)−Mo(3)-O(3)	73.06(10)	73.5(4)
Mo(1)−O(2)	1.750(3)	1.758(10)	A(2)-O(8)	3.186(5)	3.131(10)	O(8)−Mo(3)-O(1)	74.05(11)	74.1(4)
Mo(1)−O(3)	1.824(3)	1.816(10)	A(2)-O(10)	3.489(6)	3.393(11)	O(8)−Mo(3)-O(3)	81.47(12)	81.7(4)
Mo(1)−O(1)	1.987(3)	1.975(10)	A(2)-O(2)	3.401(5)	3.479(10)	O(8)−Mo(3)-O(11)	152.97(11)	153.5(4)
Mo(1)−O(4)	2.275(3)	2.287(10)	A(2)-O(4)	3.458(5)	3.451(10)	O(9)−Mo(3)- O(1)	159.54(12)	160.3(5)
Mo(1)−O(1)′	2.383(3)	2.402(10)	O(1)−Mo(1)-O(1)′	74.65(11)	74.5(4)	O(9)−Mo(3)-O(3)	86.57(12)	86.9(5)
Mo(2)−O(7)	1.711(3)	1.701(10)	O(1)- Mo(1)−O(4)	71.87(11)	71.2(4)	O(9)−Mo(3)-O(8)	101.57(14)	100.9(5)
Mo(2)−O(6)	1.716(3)	1.702(11)	O(2)−Mo(1)-O(1)	97.37(13)	97.4(4)	O(9)−Mo(3)-O(11)	97.6(14)	97.7(5)
Mo(2)−O(4)	1.943(3)	1.922(10)	O(2)−Mo(1)-O(1)′	78.61(12)	77.3(4)	O(10)−Mo(3)-O(1)	95.99(13)	95.5(4)
Mo(2)−O(8)	1.963(3)	1.955(11)	O(2)−Mo(1)-O(3)	103.35(13)	103.3(4)	O(10)−Mo(3)-O(3)	168.65(12)	168.6(4)
Mo(2)−O(1)	2.194(3)	2.186(10)	O(2)−Mo(1)-O(4)	161.80(12)	160.6(4)	O(10)−Mo(3)-O(8)	98.62(14)	98.5(5)
Mo(2)−O(2)	2.403(3)	2.367(10)	O(3)−Mo(1)-O(1)	76.53 (11)	76.0(4)	O(10)−Mo(3)-O(9)	104.45(14)	104.2 (5)
Mo(3)−O(10)	1.710(3)	1.705(11)	O(3)−Mo(1)-O(1)	140.11(12)	138.9(4)	O(10)−Mo(3)-O(11)	94.81(13)	95.0(5)
Mo(3)−O(9)	1.724(3)	1.728(11)	O(3)−Mo(1)-O(4)	78.37(12)	78.1(4)	O(11)−Mo(3)-O(1)	81.32(12)	82.0(4)
Mo(3)−O(8)	1.932(3)	1.917(10)	O(4)−Mo(1)-O(1)	84.30(10)	84.3(3)	O(11)−Mo(3)-O(3)	80.84(11)	80.5(4)
Mo(3)−O(11)	2.014(3)	2.015(11)	O(5)−Mo(1)-O(1)	100.0(12)	100.5(4)	O(4)−Te(1)-O(4)′	169.4(2)	168.7(6)
Mo(3)−O(1)	2.204(3)	2.193(10)	O(5)−Mo(1)-O(1)′	173.69(11)	173.9(4)	O(11)−Te(1)-O(4)	86.89(12)	86.9(4)
Mo(3)−O(3)	2. 233(3)	2.214(10)	O(5)−Mo(1)-O(3)	106.52(14)	106.6(5)	O(11)−Te(1)-O(4)′	86.21(12)	85.8(4)
Te(1)−O(11) × 2	1.881(3)	1.875(10)	O(5)−Mo(1)-O(2)	105.7(2)	107.1(5)	O(11)′-Te(1)-O(4)	86.21(12)	85.8(4)
Te(1)−O(4) × 2	2.128(3)	2.139(10)	O(5)−Mo(1)-O(4)	90.88(13)	90.7(4)	O(11)′-Te(1)-O(4)′	86.89(12)	86.9(4)
A(1)-O(5)	2.896(5)	2.930(10)	O(1)−Mo(2)-O(2)	70.65(10)	71.0(3)	O(11)−Te(1)-O(11)′	99.0(2)	99.7(7)
A(1)-O(10)	2.910(5)	2.908(11)	O(4)−Mo(2)-O(1)	74.53(12)	74.4(4)	Mo(1)−O(1)-Mo(1)′	105.35(11)	105.5(4)
A(1)-O(7)	2.919(5)	2.979(11)	O(4)−Mo(2)-O(2)	81.45(11)	81.8(4)	Mo(1)−O(2)-Mo(2)	111.78(14)	113.0(5)
A(1)-O(8)	2.982(5)	2.997(11)	O(4)−Mo(2)-O(8)	147.55(12)	147.3(4)	Mo(1)−O(1)-Mo(2)	105.57(13)	106.3(4)
A(1)-O(12)	3.004(6)	2.973(13)	O(6)−Mo(2)-O(1)	101.98(13)	102.5(5)	Mo(1)−O(1)-Mo(3)	147.79(14)	147.7(5)
A(1)-O(10)	3.029(5)	3.028(10)	O(6)−Mo(2)-O(2)	172.62(13)	173.4(4)	Mo(1)−O(3)-Mo(3)	114.13(14)	114.8(5)
A(1)-O(9)	3.057(5)	3.069(12)	O(6)−Mo(2)-O(4)	97.16(13)	97.8(5)	Mo(2)−O(1)-Mo(1)	98.08(11)	97.6(4)
A(1)-O(9)′	3.197(5)	3.093(12)	O(6)−Mo(2)-O(8)	95.83(13)	95.5(5)	Mo(2)−O(4)-Mo(1)	104.09(12)	104.4(4)
A(1)-O(6)	3.274(6)	3.241(11)	O(7)−Mo(2)-O(1)	153.79(12)	153.1(5)	Mo(2)−O(1)-Mo(3)	94.69(11)	94.7(4)
A(1)-O(3)	3.327(5)	3.330(10)	O(7)−Mo(2)-O(2)	83.26(13)	82.2(4)	Mo(3)−O(1)-Mo(1)	96.05(10)	95.4(4)
A(2)-O(12)	2.819(6)	2.849(12)	O(7)−Mo(2)-O(4)	104.73(13)	104.5(5)	Mo(3)−O(8)-Mo(2)	112.3(14)	112.6(5)
A(2)-O(7)	2.854(5)	2.866(11)	O(7)−Mo(2)-O(6)	104.1(2)	104.2(5)	Mo(1)−O(4)-Te(1)	112.04(12)	111.6(4)
A(2)-O(5)	2.927(6)	2.939(11)	O(7)−Mo(2)-O(8)	100.71(14)	101.1(5)	Mo(2)−O(4)-Te(1)	142.0(2)	142.1(5)
A(2)-O(9)	2.991(5)	2.960(11)	O(8)−Mo(2)-O(1)	73.73(11)	73.5(4)	Mo(3)−O(11)-Te(1)	116.8(2)	117.1(5)
A(2)-O(6)	3.032(5)	3.019(12)	O(8)−Mo(2)-O(2)	81.88(11)	81.7(4)			

atoms which remain unshared, 2.017 Å for oxygen atoms shared by two metal centers, 2.109 Å for oxygen atoms shared by three metal centers, and 2.192 Å for oxygen atoms shared by four metal centers. The corresponding values in the isostructural rubidium compound are 1.712, 2.006, 2.104, and 2.189 Å, respectively. For Mo(2) and Mo(3), the terminal oxygen atoms are found to occur in pairs, namely, O(6), O(7) and O(9), O(10), respectively, forming V-shaped MoO_2 groups with mean angles of 104.3 and 104.2° for the ammonium and rubidium compounds, respectively. The values of these angles compare well with those listed for various molybdates by Evans et al.[14] The Mo(1)···Mo(2), Mo(2)···Mo(3), and Mo(1)···Mo(3) nonbonding distances are 3.332, 3.235, and 3.412 Å for the ammonium compound and 3.333, 3.222, and 3.401 Å for the rubidium compound, respectively. These values are comparable to those reported for edge-shared MoO_6 octahedra in the molybdates such as $(C_3H_{10}N)_6[H_2Mo_8O_{28}]$·$2H_2O$,[15] $Eu_2(H_2O)_{12}[Mo_8O_{27}]$·$6H_2O$,[16] $Cs_2Mo_5O_{16}$, and $Cs_2Mo_7O_{22}$,[17] wherein the values range from 3.25 to 3.50 Å. The dimensions of the Mo_6O_{22} moiety in these two compounds are influenced only to a smaller extent, by the nature of countercations, NH_4^+/Rb^+. The terminal Mo−O bond lengths and O···O nonbonding distances span a wider range in the rubidium phase than in the ammonium compound. However, the O−Mo−O angles do not differ much between the two compounds.

Tellurium sits on a 2-fold axis and connects two such Mo_6O_{22} moieties through two oxygen atoms, namely, O(4) and O(11), to give rise to the linear $(Mo_6TeO_{22})^{4-}$ anionic chain. Tellurium is thus four-coordinated, and the coordination of tellurium in this "TeO_4" moiety can be described as a trigonal bipyramid with one of the equatorial positions occupied by the Te(IV) lone pair of electrons (Figure 2). The two equivalent axial Te−O(4) bonds are longer than the two equivalent equatorial Te−O(11) bonds (Table 5). The equatorial bonds in the rubidium compound are shorter than those in the ammonium phase, whereas the converse is true with respect to the axial bonds. The O_{ax}−Te−O_{ax} and O_{eq}−Te−O_{eq} angles (Table 5) deviate from the ideal values of 180 and 120° by as much as 21° in both compounds. These values of bond lengths and angles of the TeO_4 moiety are comparable to those found in α-TeO_2 [18] and various other tellurites, such as $Te_3Nb_2O_{11}$ [19] and $Zn_2Te_3O_8$.[20] In these compounds, also, tellurium sits on a 2-fold axis having equivalent axial and equatorial bonds. The axial Te−O bonds are longer and the equatorial Te−O bonds are shorter than the corresponding ones in α-TeO_2. Both types of bonds, on the other hand, are found to be longer than those in $Te_3Nb_2O_{11}$ and $Zn_2Te_3O_8$. The BVS calculation by the Brese and O'Keeffe method[21] have given values of 5.86 to 6.08 and 3.92 closer to the expected values of 6 and 4 for molybdenum and tellurium, respectively, in both compounds. As shown in the unit cell diagram (Figure 3), the anionic linear chains are parallel to the

---

(14) Evans, H. T., Jr.; Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1975**, 505.

(15) Isobe, M.; Marumo, F.; Yamase, T.; Ikawa, T. *Acta Crystallogr.* **1978**, *B34*, 2728.

(16) Yamase, T.; Naruke, H. *J. Chem. Soc., Dalton Trans.* **1991**, 285.

(17) Gatehouse, B. M.; Miskin, B. K. *Acta Crystallogr.* **1975**, *B31*, 1293.

(18) Lindqvist, O. *Acta Chem. Scand.* **1968**, *22*, 977.

(19) Galy, J.; Lindqvist, O. *J. Solid State Chem.* **1979**, *27*, 279.

(20) Hanke, K. *Naturwissenschaften* **1966**, *53*, 273.

(21) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

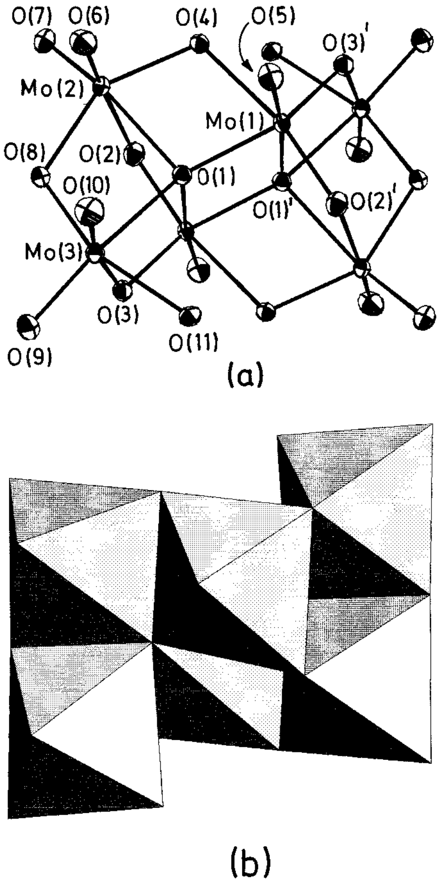


Figure 1. Mo_6O_{22} moiety of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$: (a) ORTEP view showing the atom labeling scheme (50% thermal ellipses) and (b) polyhedral representation.

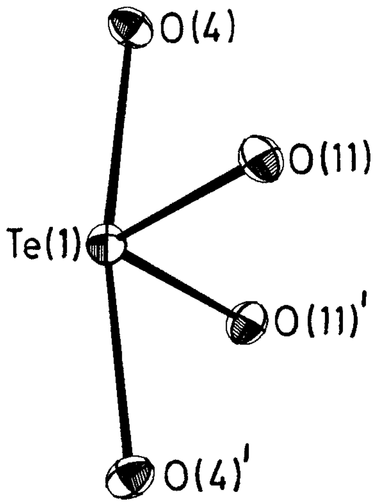
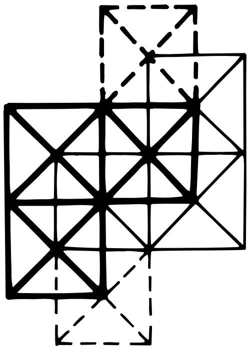


Figure 2. ORTEP view of the TeO_4 moiety of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ showing the atom labeling scheme (50% thermal ellipses).

c-axis. The NH_4^+/Rb^+ ions and water of crystallization fill the rest of the lattice, and the water molecules are parallel to the *c*-axis.

The structural motif of this novel hexanuclear Mo_6O_{22} moiety built from edge-sharing of six MoO_6 octahedra is unprecedented. Hexamolybdate clusters of the type Mo_6O_x with different modes of connectivity of six MoO_6 octahedra have been known, as, for example, in Mo_6O_{24}[5] of $(Mo_6Te_2O_{24})^{4-}$ and Mo_6O_{27} [22] of $[Mo_6O_{18}(H_2O)_6(MeAsO_3)]^{2-}$. The present Mo_6O_{22} moiety can be conceived as being derived from the Mo_8O_{28}[15,23] cluster of the $[H_2Mo_8O_{28}]^{6-}$ anion, as shown in the following schematic representation by removing those two octahedra indicated by dotted lines.



These two MoO_6 octahedra in Mo_8O_{28} can be considered as having been fused to the present Mo_6O_{22} by sharing its three oxygen atoms, O(4), O(11), and O(3). It is noted that only two of these oxygen atoms, namely, O(4) and O(11), are bonded to tellurium to form the extended framework of the $(Mo_6TeO_{22})^{4-}$ anionic chain. The majority of these sorts of heteropolymolybdates are known to exist as discrete anions. But, in these two compounds, the connectivity of Mo_6O_{22} moieties by heteroatom tellurium to result in an extended linear anionic chain is a rare feature.

$K_2[SeMo_3O_{13}]\cdot 3.5H_2O$, $K_2[SMo_3O_{13}]\cdot 4H_2O$, and $Rb_2[SMo_3O_{13}]$ are other known heteropolymolybdates containing linear anionic chains, namely, isostructural $[XMo_3O_{13}]^{2-}$ (X = Se, S) polyanions[24] with MoO_6 octahedra and XO_4 tetrahedra. Their structure could be described as follows. A string of composition MoO_5 is built by trans-corner connection of each octahedron to two such octahedra. Two such strings are fused together to form Mo_3O_{12} chains so that each octahedron shares its two cis edges with two octahedra of the other string. XO_4 tetrahedra, each corner connected to three different octahedra, alternate above and below the chain. There are three types of similar polyanionic chains known in isopolymolybdates such as $Na_2Mo_2O_7$, $K_2Mo_2O_7$, and $Ag_2Mo_2O_7$ containing $[Mo_2O_7]^{2-}$ polyanions.[25] In the first two compounds, half of the molybdenum is present in octahedral coordination and the other half in tetrahedral coordination. The $[Mo_2O_7]^{2-}$ chain of the sodium compound consists of a MoO_5 string of corner connected MoO_6 octahedra, and each octahedron is further linked to its neighbor via MoO_4 tetrahedron by corner-sharing. In the potassium compound, on the other hand, two octahedra share an edge to form Mo_2O_{10} units which are linked to one another through MoO_4 tetrahedra to form a one-dimensional chain. The $[Mo_2O_7]^{2-}$ chain of the silver compound, built exclusively from MoO_6 octahedra, is formed by blocks of four edge-shared octahedra, joined by further edge-sharing.

There are two crystallographically distinct A atoms, A(1) and A(2). If 3.5 Å is considered as the cutoff limit for the A−O bond length, both A(1) and A(2) are ten-coordinated. O(12), the oxygen atom of the water molecule, is one of the oxygen atoms in these polyhedra. In a sphere of radius of 3.2 Å around

---

(22) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284.

(23) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 1993.

(24) (a) Fuchs, J.; Kreusler, H. U.; Forster, A. *Z. Naturforsch.* **1979**, *34b*, 1683. (b) Robl, C.; Haake, K. *Z. Naturforsch.* **1993**, *48b*, 399.

(25) (a) Seleborg, M. *Acta Chem. Scand.* **1967**, *21*, 499. (b) Magarill, S. A.; Klevtsova, R. F. *Sov. Phys. Cryst.* **1972**, *16*, 645. (c) Gatehouse, B. M.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1316.

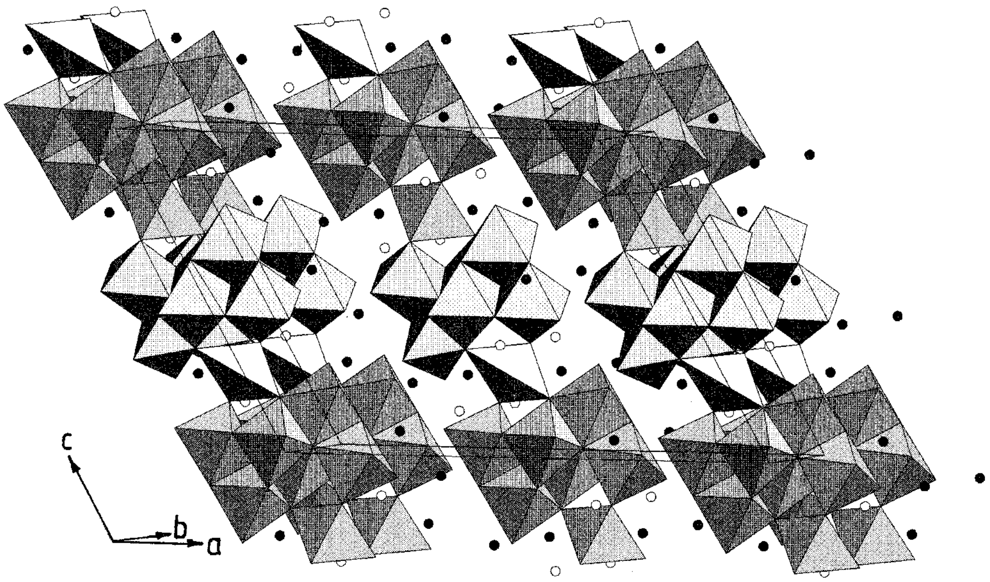


Figure 3. Unit cell diagram of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ with the polyhedral representation of the $(Mo_6TeO_{22})^{4-}$ anionic chain. Isolated, empty, and filled spheres of arbitrary radii represent oxygen atoms of water molecules and nitrogen atoms, respectively.

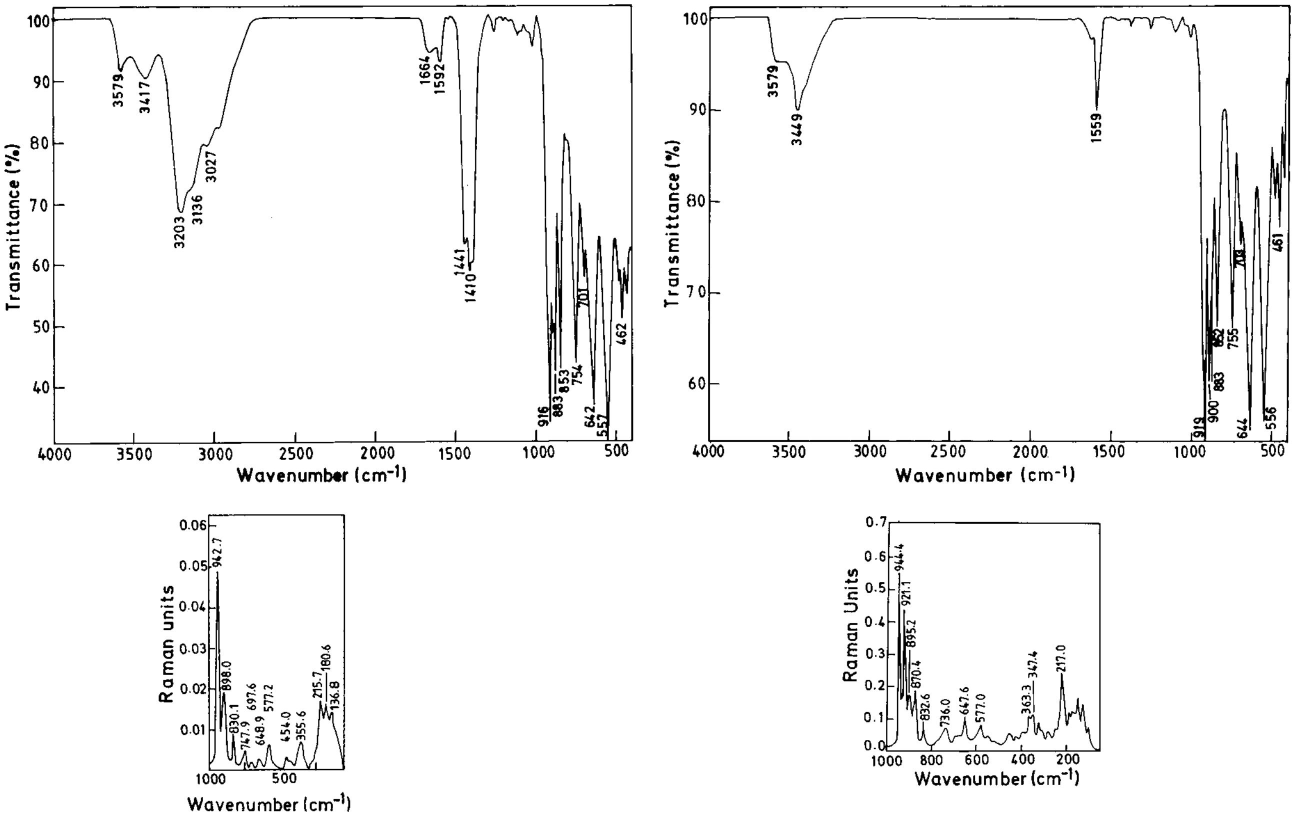


Figure 4. Infrared (top) and Raman (bottom) spectra of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ (left) and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ (right).

O(12), in $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$, only N(1), N(2), O(3), and O(11) are found at distances of 3.004, 2.819, 2.960, and 2.878 Å, respectively. These short O(12)—N(1) and O(12)—N(2) bond lengths and O(12)···O(3) and O(12)···O(11) nonbonding distances are indicative of hydrogen-bonding interactions[23,26] of O(12) with these four atoms. However, the arrangement of these four atoms around O(12) is not tetrahedral because two of the three dihedral angles are found to be 99.9 and 69.4°, quite deviated from the ideal value of 90°. Similarly, in $Rb_4Mo_6TeO_{22}\cdot 2H_2O$, the values of O(12)···O(3) and O(12)···O(11) nonbonding distances are 2.986 and 2.900 Å, respectively, indicating hydrogen-bonding.

Thermal Studies. Thermogravimetric analysis of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ has shown that it undergoes a total weight loss of 15% in two stages and the decomposition is complete by about 450 °C. The two endothermic peaks at 310 and 378 °C observed in its DSC measurement correspond to these two decomposition stages. The first stage decomposition seems to be immediately followed by the second stage. The observed total weight loss, which is greater than the expected value of 12.05% for the loss of ammonia and water molecules, involves not only this loss

---

(26) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination*; W. A. Benjamin, Inc.: New York, 1968.

but also the reduction of part of tellurium and/or molybdenum. We have heated a bulk sample of this compound in a furnace under flowing N_2 atmosphere at 400 °C, and the blue colored product of decomposition, as adjudged from its powder X-ray diffraction pattern, contains mostly MoO_3.[27]

The rubidium compound undergoes a weight loss of 2.8% starting at 300 °C, corresponding to the loss of two water molecules, and this decomposition gives rise to a small endothermic peak at 300 °C in its DSC measurement. This compound when heated in bulk quantity in a furnace, under flowing N_2 atmosphere, at 400 °C, has given a product whose powder X-ray diffraction pattern has shown that it contains mostly $Rb_2Mo_3O_{10}$.[28]

Spectroscopic Studies. The infrared and Raman spectra of the two compounds are given in Figure 4. Here we assign only selected frequencies on the basis of the limited literature available on the spectral characteristics of tellurites. The infrared spectra of the two compounds are very much similar except for the absence, in the rubidium phase, of bands corresponding to ammonium ions. The bands around 3579 and 3417 cm^{-1} of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and 3579 and 3449 cm^{-1} of $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ could be assigned to the antisymmetric and symmetric O−H stretching modes of lattice water, whereas the peaks at 1664 and 1592 cm^{-1} of the ammonium compound and that around 1599 cm^{-1} of the rubidium compound correspond to the H−O−H bending modes.[29] The bands in the 3203 to 3027 cm^{-1} range and those around 1441 and 1410 cm^{-1} in the infrared spectrum of the ammonium phase are due to the symmetric and asymmetric stretching vibrations of the tetrahedral ammonium ion.[29] The intense peaks at 916, 883, 853, and 557 cm^{-1} in the infrared spectrum of this compound can be ascribed to Mo−O vibrations.[30] The peaks at 754, 701, and 642 cm^{-1} could be due to one or more of the vibrations of Mo−O, Te−O, and Mo−O−Te, all of which fall in this range.[30−32] The peaks in the range 919 to 556 cm^{-1} in the infrared spectrum of the rubidium compound could be assigned similarly. The Raman spectra (Figure 4) of the two compounds are similar. The peaks in the 945 to 830 cm^{-1} in the Raman spectra of these two compounds could be assigned to Mo−O vibrations, whereas the bands in the 748 to 647 cm^{-1} range could be due to either Mo−O or Te−O vibrations or both.

Concluding Remarks

Two new, isostructural, one-dimensional compounds, $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$, have been synthesized by hydrothermal method. These compounds are novel in the sense that they contain extended framework anionic chains of composition, (Mo_6TeO_{22}),$^{4-}$ built by connecting hexanuclear Mo_6O_{22} moieties through tellurium, which is four-coordinated with SF_4 geometry. These compounds are thus rare examples of heteropolymolybdates with extended anionic structural frameworks. The mode of connectivity of six MoO_6 octahedra in this Mo_6O_{22} moiety is of unprecedented type. The present work thus demonstrates the utility of hydrothermal method to isolate heteropolyoxometalates with extended structural frameworks. The title compounds with low decomposition temperatures are metastable phases.

Acknowledgment. We thank the Regional Sophisticated Instrumentation Centre at our institute for single-crystal X-ray data collection. We also thank the Department of Science and Technology, Government of India, for financial support.

Supporting Information Available: X-ray crystallographic files, in CIF format, for $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$ and $Rb_4Mo_6TeO_{22}\cdot 2H_2O$ compounds are available free of charge via the Internet at http://pubs.acs.org.

IC980957R

---

(27) JCPDS Powder Diffraction File, Card No. 5-508.

(28) JCPDS Powder Diffraction File, Card No. 36-337.

(29) Nakamato, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley-Interscience: New York, 1970.

(30) Bart, J. C. J.; Cariati, F.; Sgamellotti, A. *Inorg. Chim. Acta* **1979**, *36*, 105.

(31) Dimitriev, Y.; Bart, J. C. J.; Dimitrov, V.; Arnaudov, M. *Z. Anorg. Allg. Chem.* **1981**, *479*, 229.

(32) Arnaudov, M.; Dimitrov, V.; Dimitriev, Y.; Markova, L. *Mater. Res. Bull.* **1982**, *17*, 1121.