Hydrothermal Synthesis and Characterization of a Novel Two-Dimensional Tellurite of Molybdenum(VI), $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$

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Received January 28, 1999

A novel, two-dimensional tellurite of molybdenum(VI), $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$, has been isolated as single crystals in a hydrothermal reaction and characterized by single-crystal X-ray diffraction, infrared spectroscopy, and thermal analysis. Pertinent crystal data are as follows: trigonal space group $P\bar{3}$, $a = 12.124(4)$ Å, $c = 8.130(3)$ Å, $Z = 1$. Its strucrure consists of $(Mo_8Te_8O_{43})^{6-}$ layers interleaved with ammonium ions. The novel feature of the anionic layer is that it contains two anions, discrete $[Mo_2O_7]^{2-}$ anions residing in an extended framework of $(Mo_6Te_8O_{36})^{4-}$ anions made by corner connection of edge-shared bi-octahedral Mo_2O_{10} units, TeO_3 pyramids, and TeO_4 units with SF_4 geometry. Its decomposition temperature is 371 °C.

Introduction

We have earlier reported the hydrothermal synthesis and characterization of two novel, low-dimensional tellurites of molybdenum of the quaternary NH_4/Mo/Te/O system, namely, $(NH_4)_2Mo_3TeO_{12}$[1] and $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$.[2] Whereas the first compound has a layered, hexagonal tungsten oxide related structure, the second one is a one-dimensional compound with linear, polyoxometalate anionic chains. It is the hydrothermal method that led to the isolation of these two compounds in the form of single crystals, enabling the unambiguous characterization by single-crystal X-ray diffraction study. These two compounds are some of the new phases isolated in the course of our synthetic and structural investigation of new tellurites with novel structural features in the quaternary A/Mo/Te/O (A = NH_4, Cs, Rb, K, Na, Tl) system. The choice of this quaternary system is based on two reasons. One is that the number of tellurites with extended structures known to date in these quaternary systems is limited, and the other 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.

As a part of a continuing study of tellurites, we have investigated the composition and structure of the colorless platelike crystals isolated, along with $(NH_4)_2Mo_3TeO_{12}$[1] and $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$.[2] Our preliminary investigation, involving X-ray powder diffraction and chemical analysis, of these hand-picked crystals revealed that it is a hexagonal phase with a Mo:Te ratio of 1:1, and the structure seemed to be quite new. We have therefore resorted to a single-crystal X-ray diffraction study of these crystals and identified them as those of a novel layered tellurite, $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$. Here we report the full characterization of this new heteropolymolybdate phase with a unique feature of containing discrete anions in an extended anionic framework. Only a few examples of compounds of this type, containing discrete ions within another ion, are known. For example, $[N(C_3H_7)_4][H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]$[3] has the $[N(C_3H_7)_4]^+$ ion in a spherical anionic cage of $[H_{12}(VO_2)_{12}(C_6H_5PO_3)_8]^-$. It has been reported that similar interactions of $[W_3S_4(SCN)_9]^{5-}$ (anionic host) and $SnCl_3^-$ (anionic guest) are present in the cluster anion of $[(SCN)_9W_3S_4SnCl_3]$.[4]

Experimental Section

Synthesis. A mixture of 1.5 g (1.214 mmol) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 0.452 g (2.832 mmol) of TeO_2, and 0.151 g (2.823 mmol) of NH_4Cl with NH_4:Mo:Te ratio of 3.57:3:1 was heated along with 4.2 mL of water in a 23-ml capacity Teflon-lined acid degestion bomb from Parr (U.S.) at 225 °C for 7 days and then cooled to room temperature over a period of 2 days. About 0.1 g (approximately 10% yield, based on TeO_2) of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ was obtained as colorless hexagonal blocks of crystals, along with bright yellow chunky crystals of $(NH_4)_2Mo_3TeO_{12}$[1] and white needlelike crystals of $(NH_4)_4Mo_6TeO_{22}\cdot 2H_2O$.[2] The crystals of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ were so distinct that they were manually separated by hand-picking.

X-ray Diffraction and Crystal Structure. The powder X-ray diffraction pattern was recorded on a Rigaku Miniflex (Table model) instrument using Co Kα radiation ($\lambda = 1.7902$ Å). The powder X-ray diffraction pattern compared well with that simulated on the basis of the single-crystal data by using the LAZY-PULVERIX program.[5] The indexed powder X-ray diffraction pattern, along with refined cell parameters, is given in Table 1.

A single crystal suitable for X-ray diffraction study was mounted on a thin glass fiber with epoxy glue. The data set was gathered from the crystal on an Enraf-Nonius CAD4 automated four circle diffractometer at 293 K by a $2\theta-\omega$ method. Pertinent crystallographic data and data collection parameters are summarized in Table 2. Twenty-five reflections with $20° \le 2\theta \le 30°$ were located and centered. Their least-squares refinement resulted in a hexagonal unit cell. Intensities of two check reflections monitored throughout the entire period of data collection at regular intervals of 1 h changed by only 2%, indicating no sign of decay or decomposition of the crystal. The data set was reduced by routine computational procedure. Absorption correction based on azimuthal scans of reflections with χ angle near 90° was applied to the data sets. The minimum and maximum transmission factors from those ψ-scans were found to be 0.41 and 0.98, respectively.

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10.1021/ic9901160 CCC: $18.00

Table 1. X-ray Powder Diffraction Pattern of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$

h k l	d_{calcd}[a] (Å)	d_{obs} (Å)	I/I_o
0 0 1	8.141	8.136	100
1 0 1	6.438	6.431	6
2 0 0	5.259	5.253	5
1 1 1	4.867	4.863	3
2 0 1	4.417	4.412	12
0 0 2	4.071	4.068	4
1 0 2	3.796	3.791	3
1 1 2	3.381	3.380	6
2 0 2	3.219	3.217	62
2 2 0	3.036	3.034	27
2 2 1	2.845	2.845	16
3 0 2	2.656	2.657	3
0 1 3	2.627	2.627	6
2 0 3	2.411	2.410	13
0 4 2	2.209	2.209	13
2 2 3	2.023	2.023	3
0 1 4	1.998	1.999	6
4 2 1	1.931	1.932	3
0 2 4	1.898	1.897	11
4 2 2	1.786	1.787	11
6 0 0	1.753	1.755	6
6 0 1	1.714	1.713	3
3 1 4	1.669	1.669	3
4 2 3	1.603	1.603	8
0 2 5	1.555	1.554	16
4 4 0	1.518	1.519	3

[a] $\alpha = 12.1439(47)$ and $c = 8.1403(37)$ Å of the hexagonal cell.

Table 2. Crystallographic Data for $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$

empirical formula	$N_6Mo_8Te_8O_{44}H_{26}$
a (Å)	12.124(4)
c (Å)	8.130(3)
V (Å^3)	1034.9(6)
Z	1
fw	2602.57
T (°C)	25
space group	$P\bar{3}$
λ (Mo Kα) (Å)	0.710 73
ρ_{calcd} (g/cm^3)	4.176
μ (Mo Kα) (mm^{-1})	8.002
R[a]	0.0646
R_w[b]	0.1635

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

Table 3. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$

atom	*x*	*y*	*z*	U_{eq}[a]
Te(1)	3333	6667	3468(3)	10(1)
Te(2)	3300(1)	1626(1)	4332(2)	10(1)
Mo(1)	131(2)	5234(2)	3023(2)	10(1)
Mo(2)	0	0	2705(4)	13(1)
O(1)	4264(12)	6113(13)	2163(17)	16(3)
O(2)	4803(12)	3892(12)	4729(16)	14(3)
O(3)	2759(14)	4244(14)	4022(19)	23(3)
O(4)	6332(13)	5733(14)	2359(19)	22(3)
O(5)	4044(13)	3736(12)	1566(18)	18(3)
O(6)	222(13)	2223(13)	4283(17)	17(3)
O(7)	0	0	5000	11(6)
O(8)	1463(15)	1164(14)	1884(20)	28(4)
O(9)[b]	6667	3333	1535(130)	81(28)
N(1)	1749(18)	3515(18)	579(23)	29(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atom refined with site occupancy of 0.1667.

Table 4. Bond Lengths (Å) and Selected Angles (deg) for $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$

Mo(1)−O(5)	1.708(13)	Te(2)−O(6)	1.942(14)
Mo(1)−O(4)	1.732(14)	Te(2)−O(6)′	1.993(14)
Mo(1)−O(2)	1.862(13)	Te(2)−O(2)	2.442(13)
Mo(1)−O(1)	1.983(13)	N(1)−O(1)	2.93(2)
Mo(1)−O(2)′	2.237(14)	N(1)−O(3)	3.01(2)
Mo(1)−O(3)	2.30(2)	N(1)−O(5)	2.76(3)
Mo(2)−O(8) × 3	1.75(2)	N(1)−O(5)′	2.78(3)
Mo(2)−O(7)	1.866(3)	N(1)−O(8)	2.89(3)
Te(1)−O(1) × 3	1.899(14)	N(1)−O(8)′	2.99(2)
Te(2)−O(3)	1.82(2)		

O(1)−Mo(1)−O(2)	81.8(5)	O(8)−Mo(2)−O(8) × 3	106.4(6)
O(1)−Mo(1)−O(2)′	150.0(6)	O(1)−Te(1)−O(1)′ × 3	91.8(6)
O(1)−Mo(1)−O(3)	73.4(5)	O(3)−Te(2)−O(2)	81.8(6)
O(2)−Mo(1)−O(3)	83.1(6)	O(3)−Te(2)−O(6)	97.1(6)
O(2)′−Mo(1)−O(3)	78.3(5)	O(3)−Te(2)−O(6)′	95.1(6)
O(2)−Mo(1)−O(2)′	75.4(6)	O(6)−Te(2)−O(2)	82.6(5)
O(4)−Mo(1)−O(1)	96.3(6)	O(6)′−Te(2)−O(2)	173.1(5)
O(4)−Mo(1)−O(2)	103.7(6)	O(6)−Te(2)−O(6)′	91.7(7)
O(4)−Mo(1)−O(2)′	92.5(6)	Mo(1)−O(2)−Mo(1)′	104.6(6)
O(4)−Mo(1)−O(3)	166.9(6)	Mo(2)−O(7)−Mo(2)′	180.0
O(5)−Mo(1)−O(1)	98.4(6)	Mo(1)−O(1)−Te(1)	121.6(7)
O(5)−Mo(1)−O(2)	98.5(6)	Mo(1)−O(2)−Te(2)	112.9(6)
O(5)−Mo(1)−O(2)′	164.3(6)	Mo(1)−O(2)−Te(2)	130.1(6)
O(5)−Mo(1)−O(3)	86.7(6)	Mo(1)−O(3)−Te(2)	141.5(8)
O(5)−Mo(1)−O(4)	103.1(7)	Te(2)−O(6)−Te(2)	134.6(8)
O(7)−Mo(2)−O(8) × 3	112.4(6)		

The programs SHELXS-86 and SHELXL-93 were used for structure solution and structure refinement, respectively.[6] The graphic programs[7] ATOMS and ORTEP were used to draw the structures. As there were no systematic absences observed in the data set, we initially attempted solving the structure using the space groups, trigonal *P*3 and hexagonal *P*6. No meaningful structure could be established in the *P*6 space group, and thus the choice of any hexagonal space groups was ruled out. With *P*3, however, structure solution and refinement were possible. The choice of any of the other six possible trigonal space groups belonging to $\bar{3}m$ and $\bar{3}1m$ Laue classes with no systematic absence condition was ruled out from the poor values of agreement factors for data merging and unsuccessful structure solutions and refinements. Therefore, the choice was narrowed down to Laue class $\bar{3}$. The structure solution and refinement were also found possible in higher symmetry $P\bar{3}$, and therefore $P\bar{3}$ was chosen as the correct space group.

The heavy metal molybdenum and tellurium atoms were located by direct methods. Refinement of these positions and subsequent difference Fourier maps led to the location of the remaining lighter non-hydrogen atoms, namely, one nitrogen and oxygen atoms O(1)−O(9) of the asymmetric unit. O(9) represents the water of crystallization, and the remaining oxygen atoms along with the molybdenum and tellurium atoms of the asymmetric unit constitute only one-sixth of the anion, $(Mo_8Te_8O_{43})^{6-}$. The equivalent isotropic displacement parameter, U_{eq}, of O(9) was found to be as large as 0.2 Å^2 and indicated the possibility of its partial site occupancy. The variation of its site occupancy in the subsequent refinements led to a marked decrease of its U_{eq} to 0.0818 Å^2 with a concomitant decrease of its site occupancy factor to a value of 0.1676 from 0.3333. Therefore, the site occupancy of O(9) was fixed at 0.1667, and the composition is represented as $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$. All of the atoms were refined anisotropically, and the final difference Fourier map contained ghost peaks (≤2.524 e/Å^3) very close to the heavy metal atoms, indicating a severe absorption problem. The refined positional and equivalent isotropic thermal parameters are given in Table 3. The bond lengths and selected bond angles are presented in Table 4.

Thermal Studies. Thermogravimetric analytical (TGA) and differential scanning calorimetric (DSC) data were collected on a Perkin-Elmer Delta series TG instrument. The sample was heated under flowing N_2 gas at a rate of 20 °C/min to about 500 and 550 °C for TGA and DSC experiments, respectively.

Spectroscopic Data. The sample was ground with dry KBr and

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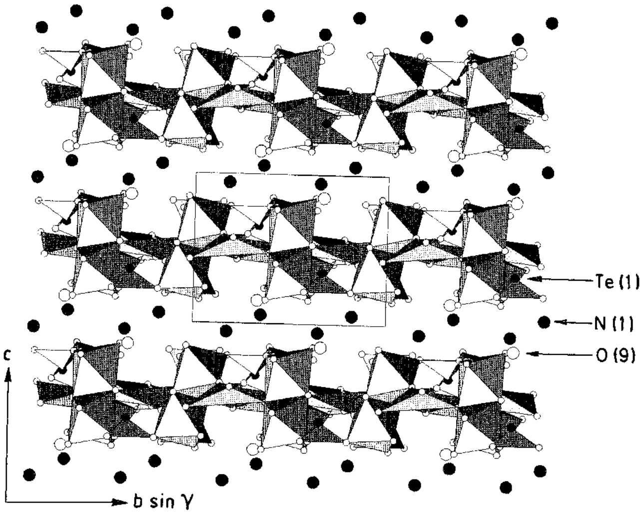

Figure 1. Unit cell diagram of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$, with the polyhedral representation of the $(Mo_8Te_8O_{43})^{6-}$ layer, viewed along the *a*-axis. All atoms are represented by spheres of arbitrary radii. Empty spheres of smaller radius represent oxygen atoms O(1)−O(8).

pressed into a transparent disk. The infrared spectra was measured on this transparent disk from 400 to 4000 cm^{-1} on a Bruker 17S, 66V FT-IR spectrometer.

Results and Discussion

As we reported earlier,[1] platelike crystals of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ could be obtained as one of the products even in hydrothermal reactions that do not employ NH_4Cl as a reactant. However, the crystals thus obtained were mosaic and of poor quality for single-crystal X-ray diffraction study. This inherent mosaicity and cleaving of crystals into thin plates could be attributed to the type of layered structure it possesses. Use of NH_4Cl as a reactant in the hydrothermal reaction, as given in the Experimental Section, yields slightly better quality crystals. In all of our hydrothermal synthetic attempts made so far with different ratios of reactants and different temperatures and durations of heating, we could only prepare this compound, with poor yield, as one of the products and not as a single phase. The hydrothermal condition is found to be necessary for this synthesis, as the product could not be prepared by simple stirring and/or refluxing of an aqueous solution of reactants. Our limited number of hydrothermal attempts to prepare alkali metal analogues of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ have not been successful.

Crystal Structure. $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ is a novel two-dimensional compound containing $(Mo_8Te_8O_{43})^{6-}$ layers interleaved with NH_4^+ ions (Figure 1). The $(Mo_8Te_8O_{43})^{6-}$ layers (Figure 2) are perpendicular to the *c*-axis, and each layer consists of two types of anions, namely, an extended framework anion of composition, $(Mo_6Te_8O_{36})^{4-}$, in which discrete $(Mo_2O_7)^{2-}$ pyromolybdate anions reside. Thus it is one of the rare examples of a discrete ion within another ion. The tellurium-rich heteropolymolybdate anion, $(Mo_6Te_8O_{36})^{4-}$, with extended framework structure, is made of edge-shared bi-octahedral Mo_2O_{10} units, TeO_3 pyramids, and TeO_4 units with SF_4 geometry. TeO_3 pyramids sitting on 3-fold axes are each corner connected to three Mo_2O_{10} moieties. Each Mo_2O_{10} unit is corner connected to two TeO_3 pyramids and four TeO_4 units and has four unshared oxygen atoms. More specifically, each molybdenum with octahedral coordination has two cis terminal oxygen atoms. The TeO_4 unit is corner connected to two each of Mo_2O_{10} moieties and TeO_4 units. Thus TeO_4 units, connected to one another, form a hexagonal ring (Figure 3) in which the discrete $(Mo_2O_7)^{2-}$ anion resides. The hexagonal ring around the Mo_2O_7 unit is like a collar, and this arrangement is pictorially similar to the d_z2 orbital. The water molecules are found within the layers and are present over pyramidal TeO_3. The entire unit cell consists of only one formula unit, $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$. This new compound constitutes the first example of a low-dimensional phase containing discrete anions within an extended anionic framework.

The two molybdenum atoms Mo(1) and Mo(2), two tellurium atoms Te(1) and Te(2), and eight oxygen atoms O(1)−O(8) of the asymmetric unit constitute the two-dimensional $(Mo_8Te_8O_{43})^{6-}$ framework. Mo(2) sitting on a 3-fold *c*-axis is tetrahedrally coordinated to three equivalent O(8) atoms and the oxygen atom O(7) that sits on $\bar{3}$ center. This $Mo(2)O_4$ tetrahedron with C_{3v} symmetry and its inversion related $Mo(2)'O_4$ tetrahedron are corner connected through O(7) and rotated along the crystallographic *c*-axis in a staggered fashion to form the discrete $(Mo_2O_7)^{2-}$ unit with D_{3d} symmetry (Figure 4, top). The

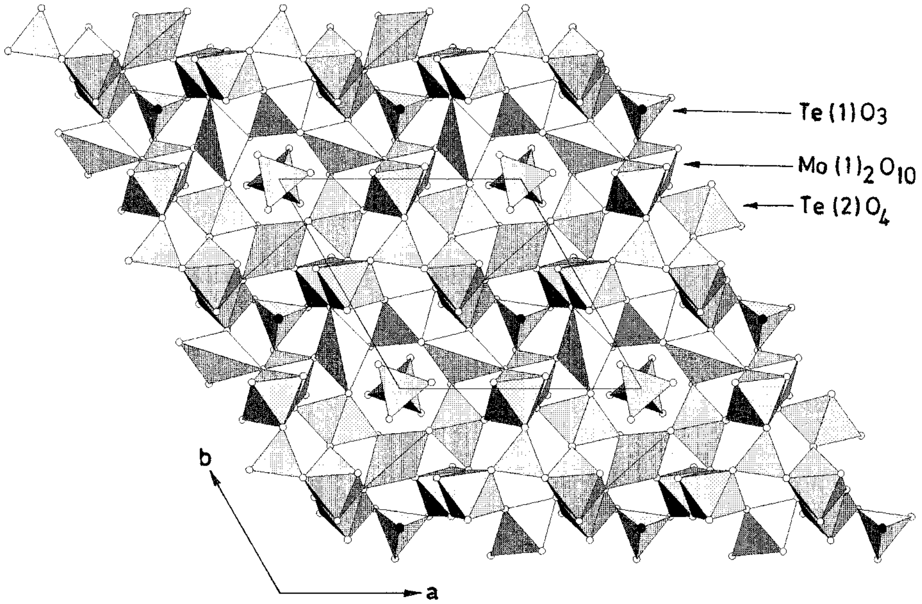

Figure 2. Polyhedral representation of the $(Mo_8Te_8O_{43})^{6-}$ layer viewed along the *c*-axis. Filled and empty spheres of arbitrary radii represent pyramidal Te(1) and oxygen atoms O(1)−O(8), respectively. Discrete Mo_2O_7 pyromolybdate units are along the *c*-axis.

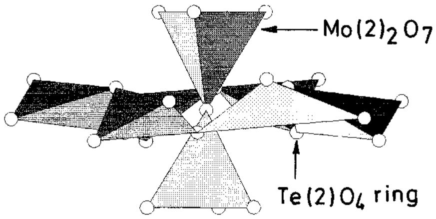

Figure 3. Polyhedral representation of the discrete $(Mo_2O_7)^{2-}$ anion and its surrounding "TeO_4" hexagonal ring. Empty spheres of arbitrary radius represent oxygen atoms O(2), O(3), and O(6)−O(8).

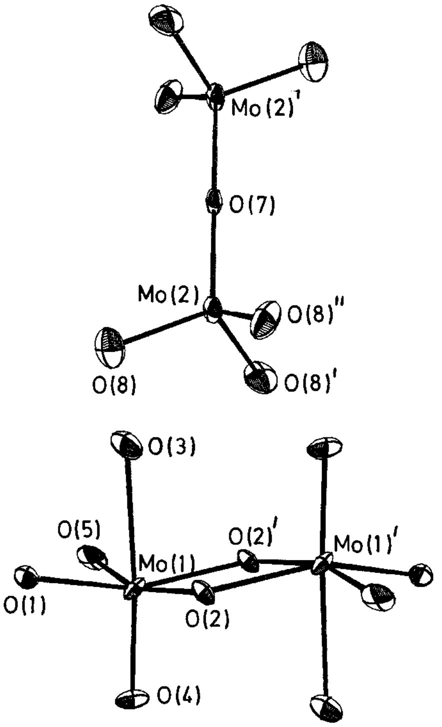

Figure 4. ORTEP view of the $(Mo_2O_7)^{2-}$ anion (top) and the Mo_2O_{10} moiety (bottom) showing the atom labeling scheme (50% thermal ellipses).

Mo(2)−O(7) bond is longer than the Mo(2)−O(8) bonds, and the bond angles are closer to the ideal value (Table 4).

Mo(1) and the five oxygen atoms O(1)−O(5) represent, as shown in the ORTEP plot[7] (Figure 4, bottom), half of the edge-shared bi-octahedral Mo_2O_{10} unit, which sits on the crystallographic inversion center. The halves are thus related by inversion symmetry. Mo(1) is octahedrally coordinated to these five oxygen atoms and O(2)′, and the edge O(2)···O(2)′ is shared by the two octahedra, $Mo(1)O_6$ and $Mo(1)'O_6$. These units are corner connected through O(1) to TeO_3 pyramids and through O(2) and O(3) oxygen atoms to TeO_4 units. The two cis oxygen atoms, O(4) and O(5), are exclusively bonded to molybdenum. Thus molybdenum forms short (<1.74 Å) molybdyl Mo(1)−O(4) and Mo(1)−O(5) bonds that are trans to long (>2.2 Å) Mo(1)−O(3) and Mo(1)−O(2) bonds, respectively. The O−Mo−O bond angles deviate by as much as 17° from the ideal value of 90°. The molybdenum is displaced from the best center[8] of its octahedron by 0.386 Å toward the O(4)−O(5) edge. The O···O nonbonding distances vary from 2.523 to 2.887 Å. All of these data clearly indicate the distortion of the MoO_6 octahedron.This type of distortion and bond length distribution of metal−oxygen MO_6 octahedra is also known for MoO_6 octahedra in MoO_3[9] and VO_6 octahedra in $NH_4V_3Se_2O_{12}$.[10]

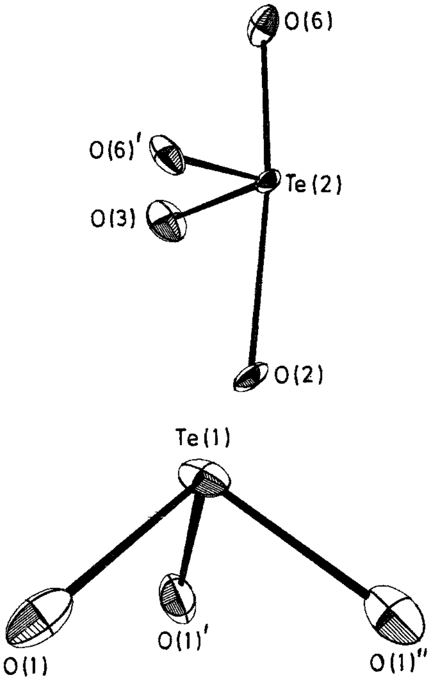

Figure 5. ORTEP view of $(TeO_4)^{2-}$ (top) and TeO_3 (bottom) units showing the atom labeling scheme (50% thermal ellipses).

Te(2) is coordinated to O(2), O(3), and two O(6) atoms, 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 5, top). The Te−O bond lengths vary from 1.82(2) to 2.442(13) Å, and the two axial bonds are longer than the two equatorial ones (Table 4). Six of these TeO_4 units are corner connected to one another through O(6) oxygen atoms to form the corrugated hexagonal ring around the O(7) oxygen atom of the $(Mo_2O_7)^{2-}$ unit. The 3.508 Å distance of O(7) to Te(2) is too long to consider any bonding interactions between them.

Te(1) sitting on a 3-fold axis is pyramidally coordinated to three O(1) oxygen atoms (Figure 5, bottom) with Te−O bond lengths of 1.899(14) Å, and thus these dimensions compare well with other pyramidal TeO_3 moieties of tellurites.[11,12] Furthermore, the edge length of the triangular oxygen base of pyramidal TeO_3 is 2.73 Å, and the height of tellurium from this triangular oxygen base is 1.061 Å. These dimensions, when compared with the corresponding values for the layered and zero-dimensional tellurites,[1] indicate that the TeO_3 pyramid is more elongated in the title compounds. The bond valence sum calculations[13] give values of 6.02 and 5.70 for Mo(1) and Mo(2) and 3.70 and 3.87 for Te(1) and Te(2), respectively.

In a sphere of 3.5 Å radius around N(1) of the ammonium ion, there are 10 oxygen atoms with N−O distances varying from 2.76(3) to 3.47(2) Å. However, N(1) could be considered as six-coordinated as only six of these 10 oxygen atoms are found at a distance of ≤3.01 Å from it, indicating hydrogen bonding[14] of the ammonium ion with the oxygen atoms of the

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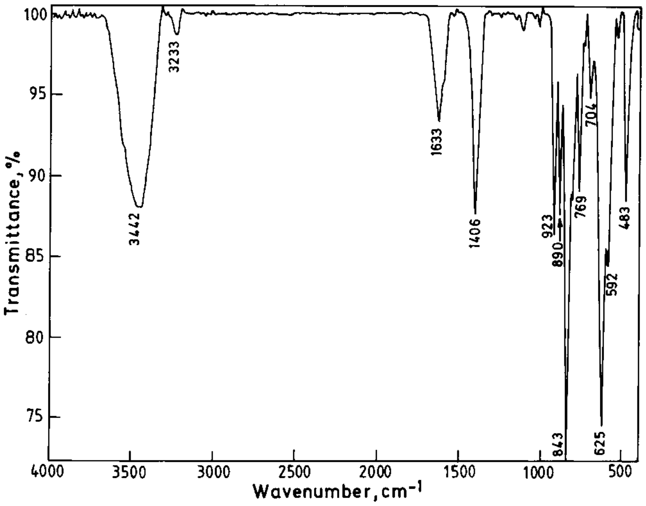

Figure 6. Infrared spectra of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$.

framework. In particular, the short N(1)−O(5) distance of 2.76(3) Å indicates strong hydrogen bonding. It is probably the hydrogen bonding of the ammonium ion that stabilizes this unique layered structure. O(9), the oxygen atom of the water molecule, is found to be at distances of 3.77 Å from N(1) and >3.2 Å from the oxygen atoms O(1), O(4), and O(5) of the framework, indicating no or very weak hydrogen bonding.

Thermal Studies. Thermogravimetric analysis of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ shows that it undergoes a weight loss of 10.63% and the decomposition is complete by about 400 °C. The endothermic peak observed at 371 °C in its DSC measurement corresponds to this decomposition. The observed weight loss, which is greater than the expected value of 6.69% for the loss of ammonia and water molecules, involves not only this loss but also the reduction of part of the tellurium and/or molybdenum. We have heated bulk sample of the title compound in a furnace under flowing N_2 atmosphere at 400 °C. The dark blue-black product of decomposition, as adjudged from its powder X-ray diffraction patteren, contains Mo_5TeO_{16}[15] and other poorly crystalline, unidentified products. Thus, this hydrothermally prepared compound, $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$, with such a low decomposition temperature, could be considered as a metastable phase.

Spectroscopic Studies. On the basis of the limited literature available on the spectral characteristics of tellurites, we assigned only selected frequencies of the infrared spectra of $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ (Figure 6). The band around 3442 cm^{-1} could be assigned to the asymmetric and symmetric O−H stretching modes of lattice water, whereas the peak around 1633 cm^{-1} corresponds to the H−O−H bending modes.[16] The peaks around 3233 and 1400 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the tetrahedral ammonium ion.[16] The peaks at 923, 890, 843, 592, and 536 cm^{-1} could be ascribed to Mo−O vibrations.[17] The peaks at 769, 704, and 625 cm^{-1} could be due to one or more of the vibrations of Mo−O, Mo−O−Te, and Te−O, all of which fall in this range.[17−19]

Concluding Remarks

This work, along with the earlier reports[1,2] clearly demonstrates the utility of the hydrothermal technique in the synthesis of new molybdotellurite phases with novel structural features. Additionally, this method has yielded some of these phases in the form of single crystals, enabling X-ray structural characterization. The new, layered $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ compound is indeed of an unprecedented type, containing discrete pyromolybdate, $(Mo_2O_7)^{2-}$, anions in the tellurium-rich heteropolymolybdate, $(Mo_6Te_8O_{36})^{4-}$, anion, with extended framework structure. To study its ion exchange behavior, we are continuing our synthetic efforts to obtain this compound with better yields as a single or at least a major phase.

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: The X-ray crystallographic file, in CIF format, for $(NH_4)_6Mo_8Te_8O_{43}\cdot H_2O$ is available free of charge via the Internet at http://pubs.acs.org.

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