Inorg. Chem. **2004**, *43*, 4610–4614

Inorganic Chemistry
Article

Hydrothermal Synthesis and Characterization of New Pillared Layered Ethylenediphosphonates of Molybdenum(VI), $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (A = NH_4, Tl, Cs, Rb) and $K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$

K. Prabhakara Rao, Vidyavathy Balraj, M. P. Minimol, and K. Vidyasagar*

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

Received September 12, 2003

New ethylenediphosphonates of molybdenum, $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (A = NH_4 (**1**), Tl (**2**), Cs (**3**), Rb (**4**)), and $K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**5**), have been synthesized by a hydrothermal method and structurally characterized by X-ray diffraction, spectroscopic, and thermal studies. These compounds consist of pillared anionic layers $[Mo_2O_5(O_3PCH_2CH_2PO_3)]^{2-}$, with A^+, K^+, and H_3O^+ ions in the interlayer region as well as in the cavities within the anionic layers. Single-crystal X-ray structures of compounds **1** and **5** have been determined. They crystallize in the orthorhombic space group *Cmca* with $Z = 8$ and have the following unit cell parameters. For **1**, $a = 25.60(1)$, $b = 10.016(4)$, and $c = 9.635(3)$ Å and for **5**, $a = 25.63(1)$, $b = 10.007(2)$, and $c = 9.512(1)$ Å.

Introduction

Hydrothermal syntheses, using organic cations as templating agents, of several organic−inorganic hybrid phosphate materials, with open framework structures, have been well-known.[1,2] The low temperatures of 150−250 °C employed in this synthetic method ensure the retention of structure and composition of organic moieties. Their removal from these hybrid materials is necessary to create large pores and, sometimes, can lead to the collapse of the inorganic framework. To overcome this problem in synthesizing microporous solids with accessible porosity, new routes involving the use of diphosphonic acids instead of phosphoric acid have been developed. The inorganic part of the acid chelates the cationic species, while its organic part, acting as a pillar and spacer, links the inorganic parts together, frequently leading to pillared, two- or three-dimensional structures.[3−5] This method does not need any templating agent, and, therefore, the porosity becomes readily accessible.

It is noteworthy that the recent expansion of metal organophosphonate chemistry[6,7] includes phosphonates[8−10] and diphosphonates[11−18] of *p*-, *d*-, and *f*-block metals. These organic−inorganic hybrid, metal organophosphonates exhibit

---

* Author to whom correspondence should be addressed. E-mail: kvsagar@iitm.ac.in.

(1) (a) Cheetham, A. K.; Ferey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268. (b) Ferey, G.; Cheetham, A. K. *Science* **1999**, *283*, 112.

(2) (a) Finn, R. C.; Zubieta, J.; Haushalter, R. C. *Prog. Inorg. Chem.* **2003**, *51*, 421. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen. B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res*. **2001**, *34*, 319.

(3) Clearfield, A.; Wang, Z. *J. Chem. Soc., Dalton Trans.* **2002**, 2937.

(4) Clearfield, A. *Curr. Opi. Solid State Mater. Sci.* **1996**, *1*, 268.

(5) Serre, C.; Ferey, G. *Inorg. Chem.* **1999**, *38*, 5370.

(6) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371.

(7) Khan, M. I.; Zubieta, J. *Prog. Inorg. Chem.* **1995**, *43*, 1.

(8) (a) Chang, Y.-Da.; Salta, J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 325. (b) Poojary, D. M.; Grohol, D.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1508. (c) Drumel, S.; Janvier, P.; Deniaud, D.; Bujoli, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1051. (d) Khan, M. I.; Lee, Y.-S.; O'Connor, C. J.; Haushalter, R. C.; Zubieta, J. *J. Am. Chem. Soc.* **1994**, *116*, 4525.

(9) Chang, Y.-Da.; Zubieta, J. *Inorg. Chim. Acta* **1996**, *245*, 177.

(10) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, T. *J. Am. Chem. Soc.* **1989**, *111*, 381.

(11) (a) Bonavia, G.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 5603. (b) Distler, A.; Lohse, D. L.; Sevov, S. C. *J. Chem. Soc., Dalton Trans.* **1999**, 1805. (c) Cavellec, M. R.; Serre, C.; Robino, J.; Nogues, M.; Greneche, J.-M.; Ferey, G. *J. Solid State Chem.* **1999**, *147*, 122.

(12) Dumas, E.; Sassoye, C.; Smith, K. D.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 4029. (b) Kortz, U.; Pope, M. T. *Inorg. Chem.* **1995**, *34*, 2160.

(13) (a) Bonavia, G. H.; Haushalter, R. C.; Sichu, Lu.; O'Connor, C. J.; Zubieta, J. *J. Solid State Chem.* **1997**, *132*, 144. (b) Riou, D.; Baltazar, P.; Ferey, G. *Solid State Sci*. **2000**, *2*, 127. (c) Riou, D.; Serre, C.; Ferey, G. *J. Solid State Chem*. **1998**, *141*, 89. (d) Soghomonian, V.; Haushalter, R. C.; Zubieta, J. *Chem. Mater*. **1995**, *7*, 1648. (e) Riou, D.; Roubeau, O.; Ferey, G. *Microporous Mesoporous Mater*. **1998**, *23*, 23. (f) Kongshaug, K. O.; Riou, D. *J. Chem. Soc., Dalton Trans.* **2002**, 4152.

(14) (a) Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 12550. (b) Altomare, A.; Bellitto, C.; Ibrahim, S. A.; Mahmoud, M. R.; Rizzi, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3913. (c) Bellitto, C.; Federici, F.; Ibrahim, S. A. *Chem. Mater*. **1998**, *10*, 1076.

(15) (a) Bujoli-Doeuff, M.; Evain, M.; Janvier, P.; Massiot, D.; Clearfield, A.; Gan, Z.; Bujoli, B. *Inorg. Chem.* **2001**, *40*, 6694. (b) Harvey, H. G.; Teat, S. J.; Attfield. M. P. *J. Mater. Chem.* **2000**, *10*, 2632. (c) Serpaggi, F.; Ferey, G. *J. Mater. Chem.* **1998**, *8*, 2749. (d) Adair, B. A.; Delgado, G. D. de.; Delgado, J. M.; Cheetham, A. K. *Solid State Sci*. **2000**, *2*, 119.

10.1021/ic035081p CCC: \$27.50

a remarkable range of structural types, including mononuclear species, complex molecular clusters, one-dimensional structures, layered materials, and open three-dimensional frameworks. The design of metal organophosphonates with desirable bulk properties continues to be pursued by many researchers due to their potential applications.[10,19−23] For example, the vanadyl organophosphonate, $[VO(O_3PR)]\cdot H_2O$, exhibits structurally well-defined void spaces, permitting the intercalation of alcohols by substrate coordination to the vanadium centers of the V/P/O layers of the solid.[10]

Our specific interest in the diphosphonates of ternary system, A/Mo/diphosphonic acid (A = alkali metal, NH_4, and Tl), stems from our earlier successful study[24] of two-dimensional $A_2Mo_3TeO_{12}$ (A = Cs and NH_4) and zero-dimensional $A_4Mo_6Te_2O_{24}\cdot 6H_2O$ (A = Rb and K) tellurites, possessing the anions of the same empirical formula $[Mo_3TeO_{12}]^{2-}$, with pyramidal TeO_3^{2-} moieties. Layered $A_2[(MoO_3)_3(O_3PCH_3)]$ (A = Cs and Rb) and zero-dimensional $Na_4[(CH_3As)_2Mo_5O_{21}]$ compounds are, respectively, the reported[25,26] organophosphonate and organoarsonate analogoues of those tellurites of molybdenum. We have become interested in the synthetic and structural solid-state chemistry of diphosphonates of the layered- and zero-dimensional types of compounds with the empirical formula, $A_4[(MoO_3)_6(O_3P{-}R{-}PO_3)]$, to examine whether the layers or zero-dimensional moieties of $[(MoO_3)_6(O_3P{-}R{-}PO_3)]$ are pillared. So far, our synthetic efforts in this direction have led to the realization of other types of diphosphonates. For example, we recently reported[27] the isolation and characterization of isostructural, layered methylenediphosphonates, $A[MoO_2(O_3PCH_2PO_3H)]$ (A = Rb, NH_4, Tl). It is during similar synthetic attempts for diphosphonates in the "A/Mo/ethylenediphosphonic acid" system that a new type of five diphosphonates, $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (A = NH_4 (**1**), Tl (**2**), Cs (**3**), and Rb (**4**)), and $K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**5**), have been isolated. These five compounds represent the first examples of ethylenediphosphonates of molybdenum. In this paper, the hydrothermal synthesis and characterization, by X-ray diffraction, thermal, and spectroscopic studies, of these five ethylenediphosphonates with pillared layers are described.

Experimental Section

Synthesis. Teflon-lined, acid digestion bombs of 45 and 23 mL capacities and the high purity chemicals, MoO_3 (S. D. Fine Chemicals India), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Ranbaxy India), $H_2MoO_4\cdot H_2O$ (Merck), A_2CO_3 (A = K, Rb, Cs, Tl) (Aldrich), and 1,2-ethylenediphosphonic acid, $H_2O_3PCH_2CH_2PO_3H_2$ (Lancaster), were employed for the hydrothermal synthesis.

A reactant mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.33 g, 1.076 mmol) and $H_2O_3PCH_2CH_2PO_3H_2$ (0.2045 g, 1.076 mmol) was heated, along with 8.4 mL of distilled water, in a 45 mL acid digestion bomb at 200 °C for 4 days and then cooled to room temperature over a period of one and half days. The final pH of the solution was 5, and a homogeneous phase of $(NH_4)_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**1**) was obtained in the form of pale pink, flake crystals (0.2025 g, 11% yield based on $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). It was washed with water, filtered, and then air dried.

Polycrystalline samples of compounds **2**−**4** were similarly synthesized from reactant mixtures of appropriate chemicals, Tl_2CO_3 (0.3152 g, 0.667 mmol), Cs_2CO_3 (0.2172 g, 0.667 mmol), Rb_2CO_3 (0.154 g, 0.667 mmol), MoO_3 (0.1919 g, 1.33 mmol), and $H_2O_3PCH_2CH_2PO_3H_2$ (0.1287 g, 0.667 mmol). The final pH was around 3, and the yields, based on MoO_3, were 0.5537 g (96%), 0.4412 g (92%), and 0.3457 g (83%) for compounds **2**, **3**, and **4**, respectively. Compounds **2** and **3** are light green, whereas compound **4** is white.

A similar hydrothermal synthetic attempt involving a reactant mixture of K_2CO_3 (0.1382 g, 1 mmol), $H_2MoO_4\cdot H_2O$ (1.0796 g, 6 mmol), and $H_2O_3PCH_2CH_2PO_3H_2$ (0.193 g, 1 mmol) yielded compound **5** as a homogeneous phase in the form of pale pink crystals (0.5013 g, 31% yield based on $H_2MoO_4\cdot H_2O$), and the final pH was 5.

Hydrothermal synthesis, from stoichiometric mixture of reactants, is successful for only compounds **2**−**4**. Only blue-colored solutions, containing Mo^{5+}, are obtained, when stoichiometric mixtures of reactants are employed for the synthesis of compounds **1** and **5**. These two compounds could be synthesized under only the optimized conditions described above. Compounds **2**−**4** are obtained in lower yield, when different ratios of reactants are used. Our efforts to synthesize $K_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ by ion-exchange reactions of compound **5** with aqueous solution of K_2CO_3, both at room temperature and under refluxing conditions, were not successful. The other four compounds also have been found to be inert toward ion-exchange reactions.

Contrary to the expectations for compounds of hexavalent molybdenum, compounds **1**−**3** and **5** are colored, and all five compounds are paramagnetic, indicating the presence of Mo^{5+} content. The values of molar susceptibilities of compounds **1**−**5** vary from 2.25×10^{-4} emu/mol at room temperature to 8.97×10^{-4} emu/mol at 20 K and are extremely small, when compared to the values calculated for compositions with molybdenum exclusively in +5 oxidation state. From the values of magnetic susceptibility at 20 K, the maximum amount of Mo^{5+} in these compounds is calculated to be 1% of total molybdenum and corroborated by conventional chemical analysis, by redox-titrations using ceric ammonium sulfate.

These five compounds were analyzed for carbon and nitrogen content using Carlo Erba Model EA1112 elemental analyzer. For **1**: Found C, 3.99%; N, 4.97%, requires C, 4.86%; N, 5.67%. For **2**: Found C, 2.78% requires C, 2.77%. For **3**: Found C, 3.18% requires C, 3.32%. For **4**: Found C, 3.76% requires C, 3.82%. For **5**: Found C, 4.41% requires C, 4.65%.

X-ray Diffraction and Crystal Structure. The powder X-ray diffraction (XRD) patterns of the five, new compounds **1**−**5** were recorded on XD-D1 X-ray Diffractometer, Shimadzu, using CuKα

---

(16) Serre, C.; Ferey, G. *Inorg. Chem.* **2001**, *40*, 5350.

(17) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 223. (b) Soghomonian, V.; Diaz, R.; Haushalter, R. C.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1995**, *34*, 4460.

(18) Arnold, D. I.; Ouyang, X.; Clearfield, A. *Chem. Mater*. **2002**, *14*, 2020.

(19) (a) Poojary, D. M.; Clearfield, A. *J. Am. Chem. Soc.* **1995**, *117*, 11278. (b) Zhang, Y.; Clearfield, A. *Inorg. Chem.* **1992**, *31*, 2821.

(20) Vermeulen, L. A.; Thompson, M. E. *Nature* **1992**, *358*, 656.

(21) Segawa, K.; Ozawa, T. *J. Mol. Catal. A* **1999**, *141*, 249.

(22) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264.

(23) Seip, C. T.; Byrd, H.; Talham, D. R. *Inorg. Chem.* **1996**, *35*, 3479.

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

(25) Harrison, W. T. A.; Dussack, L. L.; Jacobson, A. J. *Inorg. Chem.* **1995**, *34*, 4774.

(26) Kobayashi, A.; Yagasaki, A. *Inorg. Chem.* **1997**, *36*, 126.

(27) Minimol, M. P.; Prabhakara Rao, K.; Ram Sai, Y.; Vidyasagar, K. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **2003**, *115*, 419.

($\lambda = 1.5406$ Å) radiation. The powder XRD patterns of these five compounds are all similar and compare well with those simulated, using the LAZY-PULVERIX program,[28] on the basis of single-crystal X-ray structures of compounds **1** and **5**, confirming their compositions and isostructural nature. For each one of the three compounds **2**−**4**, the XRD patterns were simulated for both $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ and $A(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ compositions, based on the crystal structures of **1** and **5**, respectively. Those simulated patterns differ significantly in the relative intensities of some of the reflections, due to difference in the A^+ ion content of the two compositions. The observed powder XRD patterns agree with those simulated for the $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ compositions, corroborating the results of spectroscopic and CHN elemental analysis. The orthorhombic unit cell parameters of compounds **2**−**4** are the following: for **2**, $a = 25.746(9)$, $b = 10.25(1)$, $c = 9.58(1)$; for **3**, $a = 26.171(9)$, $b = 10.158(9)$, $c = 9.95(1)$; for **4**, $a = 25.669(9)$, $b = 10.027(8)$, $c = 9.61(1)$ Å. The values of *a*-axis and the unit cell volumes of these five compounds seem to vary in accordance with the relative size of A^+ ion.

Single crystals of compounds **1** and **5**, suitable for X-ray diffraction, were selected and mounted on thin glass fibers with glue. The data sets were gathered from the crystals at 25 °C, using Mo-Kα radiation ($\lambda = 0.71073$ Å), on an ENRAF-NONIUS CAD4 automated four-circle diffractometer, by the standard procedures involving ω-2θ scan techniques. These data sets were reduced by routine computational procedures. The structure solution and refinements were carried out by the program[29] SHELXL-97, and the graphic programs[30,31] ATOMS and ORTEP were used to draw the structures.

For both compounds **1** and **5**, the systematic absences of the measured data indicated two possible space groups, noncentrosymmetric *Cc2a* and centrosymmetric *Ccmb*. Both the space groups turned out to be equally good for successful structure solution and refinement. However, the centrosymmetric one was preferred and transformed to the standard setting, *Cmca*. For compound **1**, the positions of molybdenum and phosphorus atoms were located by direct methods. These positions were refined, and a subsequent Fourier difference map led to the location of the remaining non-hydrogen atoms of the asymmetric unit. The positional parameters of compound **1** were initially used as the structural model for compound **5**. It became evident, during the refinement, that the potassium content per formula unit is one. The chemical composition of compound **5**, deduced from single-crystal X-ray structure determination, in conjunction with infrared spectroscopic study, is $K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$. For both **1** and **5**, the ethylene protons, H(1) and H(2), were located and included in the refinement, and all non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms could not be located in the final Fourier difference maps. Pertinent crystallographic data of compounds **1** and **5** are given in Table 1.

Spectroscopic Data. The infrared and Raman spectra, in the range 400−4000 cm^{-1}, were measured on a Bruker IFS 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent disks for infrared spectroscopic study. Solid-state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 121.5 and 75.5 MHz for ^{31}P and ^{13}C, respectively. Chemical shifts were referenced to an external standard of 85% H_3PO_4 for ^{31}P and glycine for ^{13}C. The recycle delay times were 5 and 2 s, and the pulse lengths were 4.75 and 3.0 μs for ^{31}P and ^{13}C, respectively, whereas the spinning frequency was 7.0 kHz for both.

Table 1. Pertinent Crystallographic Data for $(NH_4)_2[(Mo_2O_5)(O_3PCH_2CH_2PO_3)]$ (**1**) and $K(H_3O)[(Mo_2O_5)(O_3PCH_2CH_2PO_3)]$ (**5**) Compounds

compound	**1**	**5**
formula	$N_2Mo_2P_2O_{11}C_2H_{12}$	$KMo_2P_2O_{12}C_2H_7$
formula weight	493.96	516.0
cryst syst	orthorhombic	orthorhombic
a (Å)	25.60(1)	25.63(1)
b (Å)	10.016(4)	10.007(2)
c (Å)	9.635(3)	9.512(1)
V (Å^3)	2471(2)	2439(1)
space group (No.)	*Cmca* (64)	*Cmca* (64)
Z	8	8
ρ_{calcd} (g/cm^3)	2.656	2.810
μ(Mo Kα) (mm^{-1})	2.347	2.718
total reflections	1241	1102
independent reflections	1034	920
R^a	0.0342	0.0347
$R_w{}^b$	0.0822	0.0811

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

Thermal Analysis. Thermogravimetric analytical data were collected on a Perkin-Elmer Delta series TG instrument. The samples were heated to 800 °C at a rate of 20 °C per minute under flowing nitrogen gas.

Magnetic Susceptibility. Magnetic susceptibility measurements were carried out on Standard Faraday force magnetometer (George Associates, U.S.A.) over a temperature range of 20−300 K.

Results and Discussion

Single-Crystal X-ray Structure. $(NH_4)_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**1**) is a two-dimensional compound consisting of $[Mo_2O_5(O_3PCH_2CH_2PO_3)]^{2-}$ anionic layers and ammonium ions. As shown in Figure 1, these anionic layers, stacked along *a*-axis, are related to one another by crystallographic mirror plane and built from diphosphonate $P_2C_2H_4O_6$ and bioctahedral Mo_2O_{11} units. Each Mo_2O_{11} unit is corner-connected, through six of its oxygen atoms, to four diphosphonate units, and each diphosphonate unit, in turn, is connected to four Mo_2O_{11} units. The anionic layer could be described as consisting of two sublayers (Figure 1), each one having only one phosphonate moiety of a diphosphonate unit. These sublayers are staggered and connected through C−C bonds. The perpendicular view of one sublayer projects only the triangular base of oxygen atoms of phosphonate moiety, whereas that of the other shows carbon atom of phosphonate moiety as well (Figure 2). It is evident that each Mo_2O_{11} unit is connected to four phosphonate moieties and each phosphonate moiety to two Mo_2O_{11} units. The anionic layer has cavities made by the edges of four MoO_6 octahedra and four phosphonate tetrahedra, in an alternating fashion.

The asymmetric unit contains only half of one formula unit, $Mo_2P_2O_{11}N_2C_2H_{12}$. Molybdenum and crystallographically distinct oxygen atoms, O(1)−O(6), constitute the bioctahedral Mo_2O_{11} unit, in which the two MoO_6 octahedra are connected through O(1), with Mo−O(1) bonds of about

---

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

(29) Sheldrick, G. M. SHELXL-97 Program for the Solution of Crystal Structures, University of Gottingen Germany, 1985.

(30) Dowty, E. ATOMS A Computer Program for Displaying Atomic Structures, Kingsport, Tennessee, 1985.

(31) (a) Johnson, C. K. ORTEP; Oak Ridge National Laboratory, Oak Ridge, TN, 1976. (b) Farrugia, L. J. (ORTEP). *J. Appl. Crystallogr.* **1997**, *30*, 565.

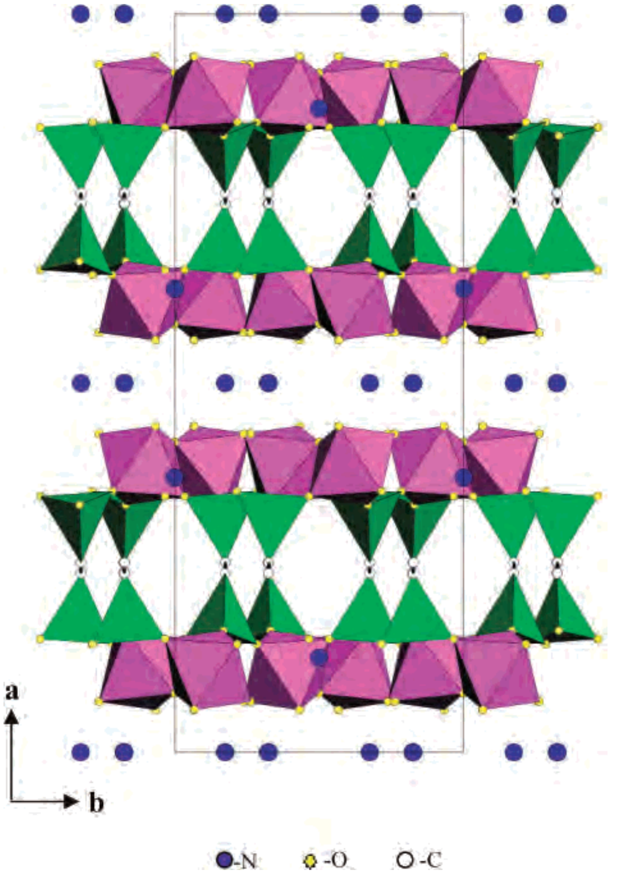

Figure 1. Polyhedral representation of unit cell of $(NH_4)_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**1**), viewed along *c*-axis.

1.93 Å length. O(2) and O(3) are the terminal oxygen atoms that are exclusively bonded to molybdenum, with short molybdyl bonds of about 1.71 Å length. The oxygen atoms, O(4)−O(6), form longer bonds with molybdenum and trans to other three oxygen atoms. They also represent the oxygen atoms of the diphosphonate unit. The values of O−Mo−O bond angles deviate from the ideal value of 90°, by as much as 13.22°. The molybdenum atom is displaced, from the best geometric center of the MoO_6 octahedron, by about 0.30 Å, toward the O(2)- - -O(3) edge.

The diphosphonate unit is a pillaring agent, with each phosphonate moiety connected to two Mo_2O_{11} units of a sublayer, through the oxygen atoms, O(4)−O(6), in both monodentate and bidentate fashion. The value of ∼148° for Mo−O(1)−Mo bond angle is probably due to the bidentate mode of connectivity of the diphosphonate unit. The values of bond lengths and angles of the diphosphonate unit are comparable with those reported.[13−17]

Each of the crystallographically distinct nitrogen atoms, N(1) and N(2), represent half of the charge-compensating ammonium ions. N(1) atoms encapsulated in the eight-membered cavity of the anionic layer, whereas N(2) atoms lie on crystallographic mirror plane between the anionic layers. With the cutoff value of 3.2 Å for the N−O bonding through hydrogen, N(1) and N(2) atoms are found to be coordinated to 8 and 10 oxygen atoms, respectively.

The potassium and ammonium compounds, **1** and **5**, are structurally similar in the sense that both possess the identical layered anion, $[Mo_2O_5(O_3PCH_2CH_2PO_3)]^{2-}$. The positions of N(1) and N(2) in compound **1** are occupied respectively by K^+ and O(7) of H_3O^+ in compound **5**. Thus, K^+ is eight coordinated and O(7) is hydrogen-bonded to 10 oxygen atoms.

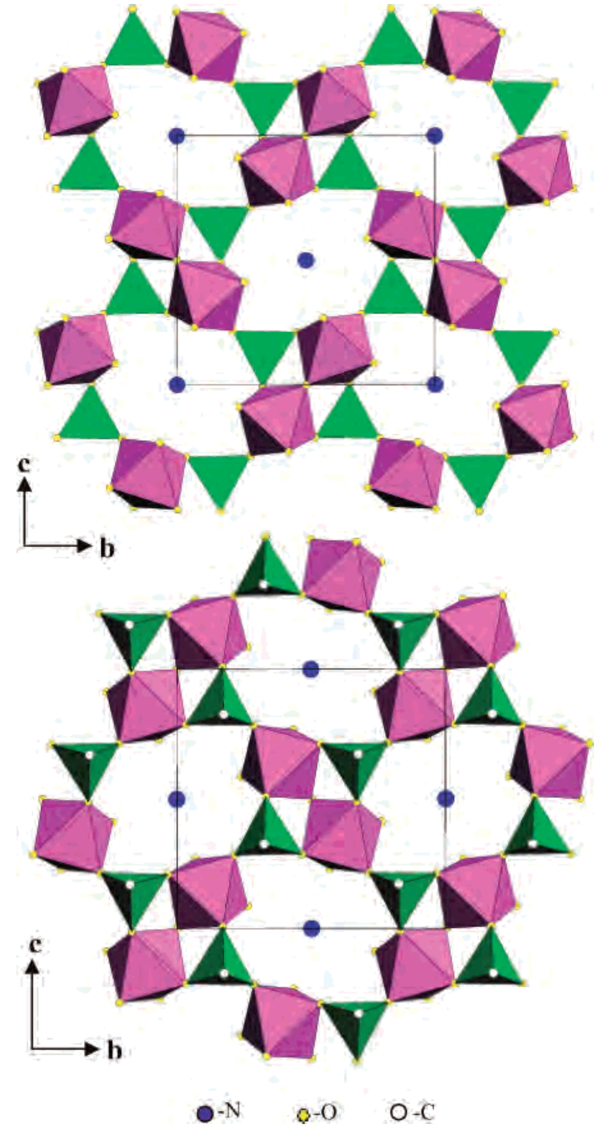

Figure 2. Polyhedral representations of sublayers, viewed along the *a*-axis, of $[Mo_2O_5(O_3PCH_2CH_2PO_3)]^{2-}$ anionic layer in $(NH_4)_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ (**1**).

Among many diphosphonates reported,[11−18] only the following two compounds[13a,b] have structural similarity with **1**−**5**. $Cs[(VO)(OH)(O_3PCH_2CH_2PO_3)]$ is the only two-dimensional, pillared ethylenediphosphonate, whereas $K[(V_2O_3)(H_2O)(O_3P(CH_2)_3PO_3)]$ is a three-dimensional, pillared diphosphonate having similar eight-membered windows with K^+ ions inside them.

Spectroscopic and Thermal Studies. The infrared spectrum of ammonium compound **1** shows two peaks at 3262 and 1406 cm^{-1} corresponding to the stretching and bending vibrations of the ammonium ion.[32] In the case of the potassium compound, two peaks observed at 3169 and 1405

---

[32] Frink, K. J.; Wang, R. C.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438.

cm^{-1} correspond to the stretching and bending vibrations of the hydronium ion, H_3O^+. The C−H stretching vibrations around 2960 and 2904 cm^{-1} and their bending vibrations[14b] in the region 1384−1410 cm^{-1}, the P−O stretching vibrations[14b] in the region 1200−1000 cm^{-1}, the O−P−O bending vibrations in the region 540−410 cm^{-1}, and the peaks at 950−730 cm^{-1}, probably due to one or more of the vibrations of Mo−O or P−O bonds, are the common features observed in the infrared spectra of all the five compounds **1**−**5**. The stretching frequencies of C−H, Mo−O, and P−O bonds are observed in their Raman spectra. All these five compounds show one ^{13}C signal between 25.44 and 26.87 ppm and one ^{31}P signal between 22.44 and 25.90 ppm in their solid-state ^{13}C and ^{31}P NMR spectra respectively, indicating that the two carbon atoms, and similarly the two phosphorus atoms, of the diphosphonate unit are chemically equivalent.

Thermogravimetric analysis of these five compounds revealed that compounds **2**−**4** are stable up to about 550 °C, after which they undergo one-step weight loss of 3.2%, 4.1%, and 7.8%, respectively, whereas compounds **1** and **5** show, in two steps, total weight losses of 16% and 15%, respectively, in the temperature range of 250−800 °C. These observed values of weight losses do not correspond to those calculated for MoO_3 or A-Mo−P−O oxides as the final products of decomposition.

Concluding Remarks

New compounds, $A_2[Mo_2O_5(O_3PCH_2CH_2PO_3)]$ ($A = NH_4$, Tl, Rb, Cs) and $K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$, have been synthesized under hydrothermal conditions and characterized by X-ray diffraction and spectroscopic studies. They possess pillared layered structure and represent the first examples of ethylene diphosphonates of molybdenum.

Acknowledgment. We gratefully acknowledge the financial support (Project No: 98/37/29/BRNS) received from the Board of Research in Nuclear Sciences, Government of India. We thank the Regional Sophisticated Instrumentation Center of our institute for single crystal X-ray data and Sophisticated Instrumentation Facility of Indian Institute of Science, Bangalore for solid-state NMR spectroscopic data. We thank Dr. N. Y. Vasanthacharya of Indian Institute of Science, Bangalore for magnetic susceptibility measurements.

Supporting Information Available: The X-ray crystallographic files, in CIF format, for $(NH_4)_2[(Mo_2O_5)(O_3PCH_2CH_2PO_3)]$ and $K(H_3O)[(Mo_2O_5)(O_3PCH_2CH_2PO_3)]$ compounds. This material is available free of charge via the Internet at http//:pubs.acs.org.

IC035081P