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# Synthesis, Crystal Structure, and Thermal Behavior of Organically Templated Three-Dimensional Tunnel Structures Based on $\alpha$ -Keggin Phosphododecamolybdate and Diazines

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Three salts of diazonium cation ( $C_4H_5N_2^+$ ) encapsulated  $\alpha$ -Keggin phosphododecamolybdate, (pyridazinium) $_3[PMo_{12}O_{40}] \cdot 1/2 H_2O$  (**1**), (pyrimidinium) $_3[PMo_{12}O_{40}] \cdot 3H_2O$  (**2**), and (pyrazinium) $_3[PMo_{12}O_{40}] \cdot 3H_2O$  (**3**) have been synthesized at room temperature and atmospheric pressure in an organic–aqueous medium. Compounds **1–3** crystallize in the trigonal space group  $R\bar{3}$ . Crystal data for compound **1** is as follows:  $a = 17.704(6)$  Å,  $c = 22.918(3)$  Å,  $V = 6221(3)$  Å<sup>3</sup>,  $Z = 6$ ,  $R = 0.028$  for 3708 observed reflections with  $I > 3\sigma(I)$ ; for compound **2**,  $a = 19.022(1)$  Å,  $c = 21.524(1)$  Å,  $V = 6745(1)$  Å<sup>3</sup>,  $Z = 6$ , and  $R = 0.043$  for 2143 observed reflections with  $I > 2\sigma(I)$ ; for compound **3**,  $a = 17.820(2)$  Å,  $c = 24.369(2)$  Å,  $V = 6701(1)$  Å<sup>3</sup>,  $Z = 6$ , and  $R = 0.047$  for 3699 observed reflections with  $I > 3\sigma(I)$ . These compounds contain the Keggin clusters arranged in a three-dimensional tunnel structure where the organic templates are sandwiched by two polyanions. Although the three salts are isostructural, the arrangement of organic cations and water molecules relative to the polyanion framework shows some significant differences that have been analyzed by means of ab initio calculations. Differences in the thermal behavior of the three compounds have also been explained on the basis of the different crystal arrangements.

## Introduction

The early transition metals are able to form polynuclear oxometalate anions,<sup>1</sup> which can be viewed as discrete fragments of close-packed extended oxide structures with different degrees of complexity,<sup>2</sup> ranging from binuclear<sup>3</sup> to highly aggregated species such as the “molybdenum blue”,  $[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_7]^{(25\pm 5)-}$  [ref 4].

During the past two decades this class of compounds has aroused increasing interest due to their unique properties including size, electron and proton storage/transfer abilities, thermal stability, and lability of lattice oxygen.<sup>5</sup> In addition, some of these compounds have found applications in analytical and clinical chemistry,<sup>6</sup> as well as in the fields of catalysis,<sup>7</sup> photochemistry,<sup>8</sup> medicine and biology,<sup>9</sup> and materials science.<sup>10</sup>

The most active area of applications is catalysis, but this activity has involved only a small number of well-

known polyoxometalates. In particular, the bifunctional acidic and redox properties of heteropolyanions based upon Keggin unit structure<sup>11</sup> have been employed in many heterogeneous and homogeneous catalytic reactions<sup>12</sup> and have been used in new large-scale industrial processes such as oxidation of methacrolein,<sup>13</sup> hydration of olefins,<sup>14</sup> and polymerization of tetrahydrofuran.<sup>15</sup> On the other hand, the synthesis of microporous materials

(7) (a) Misono, M. *Catal. Rev.—Sci. Eng.* **1988**, *30*, 339. (b) Mizuno, M.; Misono, M. *J. Phys. Chem.* **1990**, *94*, 890. (c) Misono, M.; Nojiri, N. *Appl. Catal.* **1990**, *64*, 1. (d) Lee, K. Y.; Arai, T.; Nakata, S.; Asaoka, S.; Okuhara, T.; Misono, M. *J. Am. Chem. Soc.* **1992**, *114*, 2836. (e) Kozhevnikov, I. V.; Matveev, K. I. *Appl. Catal.* **1983**, *5*, 135. (f) Newmann, R.; Lissel, M. *J. Org. Chem.* **1989**, *54*, 4607. (g) Ilkenhaus, T.; Herzog, B.; Braun, T.; Schlögl, R. *J. Catal.* **1995**, *153*, 275. (h) Belanger, R.; Moffat, J. B. *J. Catal.* **1995**, *152*, 171. (i) Corma, A. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 559. (j) Hill, C. L.; Prosser-Mccartha, M. *Coord. Chem. Rev.* **1995**, *143*, 407. (k) Kozhevnikov, I. V. *Catal. Rev.—Sci. Eng.* **1995**, *37*, 311.

(8) (a) Naruke, H.; Yamase, T. *J. Lumin.* **1991**, *50*, 50. (b) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1. (c) Hill, C. L.; Prosser-Mccartha, M. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Complexes*; Kalyanasundaran, K., Grätzel, M., Eds.; Kluwer Academic Publishers: Dordrecht, 1993; p 307.

(9) (a) Hill, C. L.; Weeks, M. S.; Schinazu, R. F. *J. Med. Chem.* **1990**, *33*, 2767. (b) Inouye, Y.; Tale, Y.; Tokutake, Y.; Yoshida, T.; Yamamoto, A.; Yamase, T.; Nakamura, S. *Chem. Pharm. Bull.* **1990**, *38*, 285. (c) Yamase, T.; Fujita, M.; Fukushima, K. *Inorg. Chim. Acta* **1988**, *151*, 15. (d) Chottard, G.; Michelon, M.; Hervé, M.; Hervé, G. *Biochim. Biophys. Acta* **1987**, *916*, 402.

(10) (a) Baker, C. W.; Simmons, V.; Wasfi, S. H.; Candela, G.; Kahn, A. H. *J. Am. Chem. Soc.* **1972**, *94*, 5499. (b) Gómez-García, C. J.; Coronado, E.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 240. (c) Coronado, E.; Gómez-García, C. J. *Comments Inorg. Chem.* **1995**, *17*, 255.

(11) Keggin, J. F. *Proc. R. Soc.* **1934**, *A144*, 75.

(12) (a) Stobbe-Kreemers, A. W.; Dielis, R. B.; Makkee, M.; Scholten, J. J. F. *J. Catal.* **1995**, *154*, 175. (b) Hamamoto, M.; Nakayama, K.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1993**, *58*, 6421.

(13) (a) Ai, M. *J. Catal.* **1989**, *116*, 23. (b) Ueshima, M.; Tsuneki, H.; Shimizu, N. *Hyoumen* **1986**, *24*, 582.

\* To whom all correspondence should be addressed.

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1997.

(1) (a) Pope, M. T.; Müller, A., Eds. *Polyoxometalates: from Platonic Solids to Antiretroviral Activity*, Kluwer: Dordrecht, The Netherlands, 1994. (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(2) Pope, M. T. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley and Sons: New York, 1991; p 181.

(3) Baker, L. C. W. *Advances in the Chemistry of Coordination Compounds*; MacMillan: New York, 1961; p 604.

(4) Müller, A.; Meyer, J.; Krickemeyer, E.; Diemann, E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1206.

(5) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(6) (a) Osmond, F. *Bull. Soc. Chim. Fr.* **1887**, *47*, 745. (b) Keana, J. F. W.; Wu, Y.; Wu, G. *J. Org. Chem.* **1987**, *52*, 2571. (c) Parker, G. A. *Analytical Chemistry of Molybdenum*; Springer-Verlag: New York, 1983.

that are exploited as catalysts in shape-selective processes is facilitated by the use of structure-directing agents.<sup>16</sup> These species, which are generally organic bases, can template inorganic groups to form materials with tailorable pore shapes and sizes.<sup>17</sup> Recently, progress has been made toward preparing microporous materials (under hydrothermal conditions) containing the Mo–P–O, W–P–O, and V–P–O systems.<sup>18–20</sup>

We have explored the general applicability of the use of organic bases for the synthesis of microporous materials. In the present paper, we report the room temperature and atmospheric pressure synthesis, chemical and structural characterization, and thermal behavior of three diazonium ( $C_4H_5N^+$ ) sandwiched phosphododecamolybdates: (pyridazinium)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] $\cdot\frac{1}{2}H_2O$  (**1**), (pyrimidinium)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] $\cdot 3H_2O$  (**2**), and (pyrazinium)<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] $\cdot 3H_2O$  (**3**), which contain the Keggin clusters arranged in a three-dimensional tunnel structure. These compounds could follow the Haushalter's conditions for a "solid state inorganic enzyme".<sup>18</sup> In addition, weak interactions between the organic template and the inorganic counterpart are possible in many of these salts. Therefore, these compounds could be very interesting for modeling the interaction between organic substrates and catalytic oxide surfaces in order to develop improved oxidation catalysts.

### Experimental Section

**Materials.** Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, Fluka), sodium pyrophosphate decahydrate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O, Aldrich), pyridazine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>, Aldrich), pyrimidine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>, Fluka), pyrazine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>, Fluka), 32% hydrochloric acid (HCl, Merck), and acetonitrile (CH<sub>3</sub>CN, Aldrich) were used as purchased without further purification.

**Instrumentation.** Infrared spectra were obtained (KBr pellets) on a Mattson 1000 FT-IR spectrometer. Thermogravimetric studies were performed using 8–15 mg samples in a Setaram Tag 24 S16 instrument under a 50 mL/min flow of synthetic air; the temperature was ramped from 20 to 600 °C at a rate of 5 °C/min for the decomposition processes and 1 °C/min for the dehydration processes.

**Synthesis.** A general method was followed in the preparation of the three compounds. HCl (6.5 mL) and acetonitrile (75 mL) were added to an aqueous solution (45 mL) of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (1.50 g, 6.2 mmol) and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (0.28 g 0.63 mmol). The resulting yellow solution was stirred for 1 h at room temperature. Addition of the corresponding diazine (1.5 mmol) pro-

duced a fine yellow precipitate, which was removed by filtration on a Grade 3 glass sinter. The solids were then washed with water and diethyl ether. Single crystals of the compounds **1–3** were obtained by recrystallization from acetonitrile. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>Mo<sub>12</sub>N<sub>6</sub>PO<sub>40</sub>· $\frac{1}{2}H_2O$  (**1**): C, 6.95; H, 0.78; N, 4.05%. Found: C, 7.02; H, 0.87; N, 4.04%. Anal. Calcd for C<sub>12</sub>H<sub>15</sub>Mo<sub>12</sub>N<sub>6</sub>PO<sub>40</sub>·3H<sub>2</sub>O **2** and **3**: C, 6.80; H, 1.00; N, 3.96%. Found for **2**: C, 7.03; H, 0.98; N, 4.13%. Found for **3**: C, 6.75; H, 0.90; N, 4.09%.

**X-ray Crystallography.** Single-crystals suitable for X-ray analysis were obtained as described in the synthesis section. Structural measurements for compounds **1–3** were performed on an Enraf-nonius CAD-4 diffractometer (graphite-monochromated Mo K $\alpha$  radiation,  $\lambda$  = 0.710 69 Å). The data were collected at 22 ± 1 °C using  $\omega/2\theta$  scan technique up to 60° in  $2\theta$ . A significant decay in intensity was observed in compounds **2** (54%) and **3** (15%); compound **1** decays less than 1%. The intensity data were corrected for Lorentz polarization and decay effects. An empirical absorption correction was applied to data following the procedure DIFABS,<sup>21</sup> resulting in transmission factors ranging from 0.913 to 1.086 for **1**, from 0.805 to 1.127 for **2**, and from 0.774 to 1.202 for **3**. Neutral atom scattering factors and anomalous dispersion factors were taken from the literature.<sup>22</sup> Experimental details and crystal data for both compounds are given in Table 1.

The structure was solved using direct methods.<sup>23</sup> Non-hydrogen atoms were refined anisotropically by full-matrix least-squares analysis using the X-RAY76 System.<sup>24</sup> Hydrogen atoms were placed in calculated positions except for H1 in compound **1** and H1, H2, and H6 in compound **2**, which were clearly visible in a difference Fourier synthesis. Atomic position parameters and equivalent isotropic temperature factors for compounds **1–3** are listed in Tables 2–4, respectively.

**Computational Details.** The ab initio MO calculations of the three diazonium cations were performed at the MP2 (frozen-core) level of theory employing the 6-31G(d,p) basis set, with bond lengths and angles fixed at the experimental geometry. Atomic charges were fitted to the electrostatic potential at points selected according to the Merz–Singh–Kollman scheme.<sup>25</sup> The computations were carried out using the Gaussian 94 suite of programs.<sup>26</sup> The superposition of the Keggin anions in the three crystal structures was done with the

(21) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(23) Beurkens, P. T.; Admiraal, G.; Beurkens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(24) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. The X-RAY76 System. Technical Report TR-446; Computer Science Center, University of Maryland, College Park, Maryland, 1976.

(25) (a) Besler, B. H.; Merz, K. M.; Kollman, P. A. *J. Comput. Chem.* **1990**, 11, 431. (b) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, 5, 129.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. I.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.: Gaussian 94, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1996.

(14) (a) Aoshima, A. *Shokubai* **1987**, 29, 378. (b) Yamade T.; Muto, T.; Yamaguchi, K. *Kagaku Kogaku* **1986**, 50, 565.

(15) Aoshima, A. *Petrotech* **1988**, 11, 1016.

(16) *Selectivity in Catalysis*; Davis, M. E., Suib, S. L., Eds.; ACS Symposium Series 517; American Chemical Society: Washington, DC, 1993.

(17) (a) Schöllhorn, R. *Chem. Mater.* **1996**, 8, 1747. (b) Suib, S. L. *Chem. Rev.* **1993**, 93, 803. (c) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2328.

(18) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, 4, 31.

(19) (a) Stein, A.; Fendorf, M.; Jarvie, T. P.; Mueller, K. T.; Benesi, A. J.; Mallouk, T. E. *Chem. Mater.* **1995**, 7, 304. (b) Hölscher, M.; Englert, U.; Zibrowius, B.; Hölderich, W. F. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 2491.

(20) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J.; Lee, Y.-S. *Chem. Mater.* **1993**, 5, 1690. (b) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 610. (c) Zhang, Y.; Clearfield, A.; Haushalter, R. C. *Chem. Mater.* **1995**, 7, 1221.

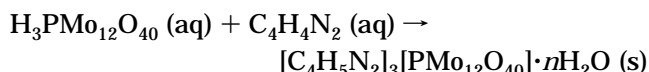
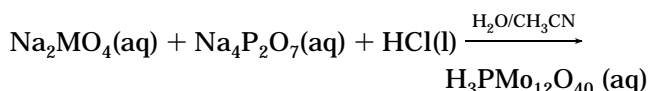
**Table 1. Crystal Data and Data Collection Parameters for Compounds 1–3**

	compound		
	1	2	3
formula	C <sub>12</sub> H <sub>15</sub> Mo <sub>12</sub> N <sub>6</sub> PO <sub>40</sub> ·1/2H <sub>2</sub> O	C <sub>12</sub> H <sub>15</sub> Mo <sub>12</sub> N <sub>6</sub> PO <sub>40</sub> ·3H <sub>2</sub> O	C <sub>12</sub> H <sub>15</sub> Mo <sub>12</sub> N <sub>6</sub> PO <sub>40</sub> ·3H <sub>2</sub> O
molecular weight	2074.60	2119.57	2119.57
system	trigonal	trigonal	trigonal
space group	<i>R</i> 3̄ (No. 148)	<i>R</i> 3̄ (No. 148)	<i>R</i> 3̄ (No. 148)
<i>a</i> (Å)	17.704(6)	19.022(1)	17.820(2)
<i>c</i>	22.918(3)	21.524(1)	24.369(2)
<i>V</i> (Å <sup>3</sup> )	6221(3)	6745(1)	6701(1)
<i>Z</i>	6	6	6
<i>F</i> (0 0 0)	5838	5988	5988
<i>D<sub>x</sub></i>	3.32	3.13	3.15
<i>μ</i> (cm <sup>-1</sup> )	35.829	33.102	33.315
shape	prism	plaque	cube
color	yellow	yellow	yellow
size (mm <sup>3</sup> )	0.58 × 0.50 × 0.40	0.24 × 0.20 × 0.06	0.50 × 0.50 × 0.50
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
temperature (K)	295(1)	295(1)	295(1)
radiation (Å)	0.71069	0.71069	0.71069
monochromator	Graphite	Graphite	Graphite
scan mode	w/2θ	w/2θ	w/2θ
θ range (deg)	1–30	1–30	1–30
<i>h k l</i>	0, 24; ±24; ±32	0, 26; -22, 26; ±30	0, 25; -21, 25; ±34
independent reflctns	4010	4385	4331
observed reflctns	3708 [ <i>I</i> ≥ 3σ( <i>I</i> )]	2143 [ <i>I</i> ≥ 2σ( <i>I</i> )]	3699 [ <i>I</i> ≥ 3σ( <i>I</i> )]
no. of variables	219	232	223
average (Δ/ <i>σ</i> )	0.033	0.018	0.009
<i>R</i>	0.028	0.043	0.047
<i>R<sub>w</sub></i>	0.032	0.038	0.057

TINKER molecular modeling package.<sup>27</sup> All programs were running on a DEC AlphaServer 2100 workstation.

## Results and Discussion

**Synthesis and Spectroscopic Studies.** The preparation of framework solids with micropores must be carried out at as low a temperature as possible, because lower temperatures and pressures favor more open structures.<sup>18</sup> Most of the microporous materials containing the Mo–P–O system have been synthesized via cooperative assembly of inorganic and organic species under hydrothermal conditions at *T* ≤ 400 °C. We have prepared compounds **1–3** at room temperature in an organic–aqueous medium according to the reaction:



The IR spectra of the compounds were compared with the IR spectrum of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]. This compound was taken as reference because (a) the tetra *n*-butylamonium cation presents a very low polarizing power, (b) it cannot form hydrogen bonds, and (c) it is bulky enough to separate the polyanions so as to remove the possibility of anion–anion interactions occurring.<sup>28</sup> The vibrational bands of Mo–O<sub>b</sub>–Mo and Mo–O<sub>c</sub>–Mo have red shifts of 5–15 cm<sup>-1</sup> with respect to the TBA salt, due to the presence of partial charge transfer between the organic donor and polyoxometalate acceptor (Table 5).

(27) Ponder, J. W.: TINKER 3.1: Software Tools for Molecular Design; School of Medicine, Washington University: Saint Louis, MO, 1996.

(28) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, M.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

**Table 2. Atomic Coordinates for the Compound 1**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
Mo1	0.122 65 (2)	0.029 00 (2)	0.095 15 (1)	162(1)
Mo2	0.214 69 (2)	0.181 03 (2)	0.219 74 (1)	154(1)
Mo3	0.174 68 (2)	-0.043 69 (2)	0.233 73 (1)	148(1)
Mo4	0.101 50 (2)	0.134 58 (2)	0.347 49 (1)	143(1)
P1	0.000 00	0.000 00	0.225 03 (5)	69
O1	0.199 32 (19)	0.053 03 (21)	0.044 41 (12)	279(8)
O2	0.321 36 (17)	0.252 20 (19)	0.212 27 (14)	268(7)
O3	0.267 11 (18)	-0.047 35 (20)	0.226 84 (14)	266(7)
O4	0.127 63 (19)	0.177 61 (19)	0.415 31 (11)	248(7)
O5	0.028 17 (17)	-0.068 92 (17)	0.065 59 (10)	199(6)
O6	0.181 88 (16)	0.133 28 (16)	0.147 64 (11)	198(6)
O7	0.150 01 (16)	-0.026 21 (16)	0.152 20 (10)	177(6)
O8	0.166 92 (15)	0.254 05 (15)	0.215 29 (11)	178(6)
O9	0.214 40 (16)	0.073 56 (16)	0.242 54 (11)	182(6)
O10	0.146 93 (16)	-0.071 96 (17)	0.311 28 (11)	187(6)
O11	0.204 45 (15)	0.189 93 (16)	0.307 64 (11)	184(6)
O12	0.095 51 (16)	0.029 55 (16)	0.356 10 (11)	178(6)
O13	0.000 00	0.000 00	0.158 15 (16)	108
O14	0.062 47 (14)	0.092 28 (14)	0.247 30 (9)	128(5)
O01	0.000 00	0.000 00	0.500 00	162
N1	0.248 08 (29)	0.106 85 (34)	0.469 66 (18)	39(1)
N2	0.230 17 (31)	0.029 09 (30)	0.453 99 (20)	43(1)
C3	0.267 57 (41)	0.023 89 (40)	0.406 04 (28)	48(2)
C4	0.322 58 (37)	0.097 51 (63)	0.372 85 (24)	59(2)
C5	0.339 39 (36)	0.176 82 (50)	0.392 02 (28)	54(2)
C6	0.298 85 (33)	0.179 93 (32)	0.442 72 (24)	37(1)

<sup>a</sup> *U<sub>eq</sub>* = 1/3Σ *U<sub>ij</sub>* *a<sub>i</sub>*<sup>\*</sup> *a<sub>j</sub>*<sup>\*</sup> *a<sub>i</sub>* *a<sub>j</sub>* cos(*a<sub>i</sub>*, *a<sub>j</sub>*) [(Å<sup>2</sup> × 10<sup>4</sup>) for Mo, P, and O and (Å<sup>2</sup> × 10<sup>3</sup>) for C and N].

**Crystal Structures.** The three compounds crystallize in the same trigonal space group *R*3̄ and could be consider almost isostructural. However, they show significant differences in their cell dimensions owing to different degrees of hydration and the arrangement of the corresponding organic cation with respect to the polyoxoanion.

The Keggin structure of the [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion consists of a central PO<sub>4</sub> tetrahedron surrounded by four Mo<sub>3</sub>O<sub>13</sub> groups which result from the association of three edge-sharing MoO<sub>6</sub> octahedra in such a way that the ideal polyanion has *T<sub>d</sub>* symmetry, (Figure 1). In compounds **1–3** the Keggin anion presents a *C*<sub>3</sub> crystal-

**Table 3. Atomic Coordinates for the Compound 2**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
Mo1	0.113 67 (5)	0.025 60 (6)	0.101 34 (4)	222(3)
Mo2	0.213 41 (6)	0.133 63 (6)	0.246 42 (4)	253(3)
Mo3	0.125 50 (6)	-0.087 38 (6)	0.236 54 (4)	257(3)
Mo4	0.097 13 (6)	0.122 43 (6)	0.371 12 (4)	292(3)
P1	0.000 00	0.000 00	0.238 89 (21)	16(1)
O1	0.180 75 (42)	0.035 64 (43)	0.046 62 (30)	30(3)
O2	0.313 92 (42)	0.183 06 (46)	0.239 26 (34)	38(4)
O3	0.196 31 (44)	-0.113 73 (45)	0.229 56 (33)	33(4)
O4	0.130 32 (50)	0.161 67 (45)	0.441 36 (31)	40(4)
O5	0.015 61 (39)	-0.071 10 (40)	0.069 43 (28)	25(3)
O6	0.176 92 (41)	0.100 73 (42)	0.160 62 (30)	29(3)
O7	0.117 47 (41)	-0.054 84 (42)	0.157 76 (29)	27(3)
O8	0.189 08 (42)	0.217 89 (42)	0.227 62 (31)	31(3)
O9	0.187 93 (41)	0.026 05 (41)	0.257 67 (29)	29(3)
O10	0.105 18 (42)	-0.104 83 (42)	0.326 96 (30)	29(3)
O11	0.200 35 (41)	0.148 11 (44)	0.330 13 (31)	30(3)
O12	0.085 30 (43)	0.013 84 (43)	0.379 66 (30)	32(3)
O13	0.000 00	0.000 00	0.167 31 (45)	18(2)
O14	0.068 81 (38)	0.081 41 (36)	0.262 36 (28)	20(3)
O01	0.245 11 (65)	0.298 31 (71)	0.107 27 (39)	74(7)
N1	0.327 56 (63)	0.131 39 (64)	0.405 87 (50)	45(5)
C2	0.362 14 (73)	0.123 35 (83)	0.354 64 (56)	44(6)
N3	0.344 39 (62)	0.052 88 (74)	0.331 09 (43)	48(6)
C4	0.289 63 (79)	-0.014 30 (74)	0.361 74 (54)	43(6)
C5	0.254 40 (75)	-0.008 48 (73)	0.415 03 (53)	42(6)
C6	0.272 61 (80)	0.065 60 (86)	0.437 55 (55)	43(6)

<sup>a</sup>  $U_{eq} = 1/3 \sum U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j) [(\text{\AA}^2 \times 10^4) \text{ for Mo, P and } (\text{\AA}^2 \times 10^3) \text{ for C, N, and O}].$

**Table 4. Atomic Coordinates for the Compound 3**

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub></i>
Mo1	0.119 69 (3)	0.022 55 (3)	0.090 89 (2)	285(1)
Mo2	0.218 44 (3)	0.170 34 (3)	0.209 80 (2)	295(1)
Mo3	0.163 27 (3)	-0.058 82 (3)	0.219 78 (2)	329(1)
Mo4	0.104 38 (3)	0.131 33 (3)	0.328 53 (2)	364(1)
P1	0.000 00	0.000 00	0.212 37 (7)	20(1)
O1	0.195 74 (28)	0.043 84 (34)	0.042 95 (18)	43(1)
O2	0.325 00 (26)	0.237 39 (31)	0.202 50 (23)	46(1)
O3	0.252 14 (30)	-0.068 20 (34)	0.212 56 (24)	48(2)
O4	0.134 80 (40)	0.175 51 (39)	0.390 93 (22)	54(2)
O5	0.022 99 (25)	-0.071 85 (25)	0.062 42 (15)	31(1)
O6	0.182 53 (23)	0.124 50 (24)	0.140 72 (16)	31(1)
O7	0.142 12 (25)	-0.037 59 (26)	0.143 45 (16)	33(1)
O8	0.178 13 (25)	0.249 20 (24)	0.203 17 (18)	34(1)
O9	0.210 56 (24)	0.059 51 (25)	0.229 10 (17)	33(1)
O10	0.135 99 (29)	-0.084 13 (31)	0.293 49 (19)	40(1)
O11	0.207 83 (27)	0.179 63 (27)	0.290 42 (18)	38(1)
O12	0.093 24 (29)	0.023 34 (28)	0.336 60 (17)	38(1)
O13	0.000 00	0.000 00	0.149 81 (22)	22(1)
O14	0.065 60 (22)	0.090 07 (22)	0.233 36 (14)	26(1)
O01	0.393 43 (58)	0.070 14 (65)	0.274 05 (40)	86(3)
N1	0.227 95 (88)	0.076 58 (123)	0.455 97 (47)	98(5)
C2	0.220 59 (96)	0.004 67 (120)	0.437 75 (66)	93(5)
C3	0.261 86 (72)	-0.003 74 (97)	0.392 70 (66)	91(5)
N4	0.313 70 (74)	0.069 68 (90)	0.367 07 (45)	84(4)
C5	0.322 86 (75)	0.146 21 (90)	0.381 66 (56)	78(4)
C6	0.283 10 (97)	0.153 62 (121)	0.428 40 (60)	89(5)

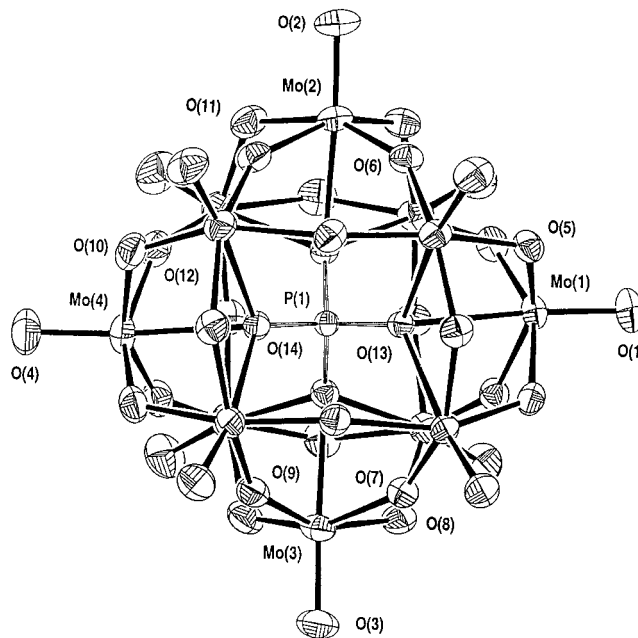
<sup>a</sup>  $U_{eq} = 1/3 \sum U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j) [(\text{\AA}^2 \times 10^4) \text{ for Mo and P and } (\text{\AA}^2 \times 10^3) \text{ for C, N, and O}].$

lographic symmetry and contains four types of oxygen atoms: O<sub>a</sub> (the oxygen atoms linked to phosphorus atom), O<sub>b</sub> (the bridging oxygen atoms between two corner sharing octahedra), O<sub>c</sub> (the bridging oxygen atoms between two edge-sharing octahedra), and O<sub>t</sub> (the terminal oxygen atoms). The Mo–O bond distances of the polyoxometalate are in the range of 1.663–1.690 Å for terminal oxygens, 1.814–2.030 Å for bridging oxygens, and 2.407–2.440 Å for oxygens of the PO<sub>4</sub> group. Selected Mo–O bond distances are listed in Table 6. The bond lengths and angles relating to the organic cations are normal and are not discussed further.

**Table 5. Assignments (cm<sup>-1</sup>) in the Vibration Spectra of [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> Anions for the Compounds 1–3 ( $\Delta\nu \pm 2$  cm<sup>-1</sup>)**

	compounds			
	1	2	3	TBA <sup>a</sup>
$\nu_{as}(\text{P}-\text{O}_a)$	1057 s	1062 s	1059 s	1063
$\nu_{as}(\text{Mo}-\text{O}_t)$	972 vs	970 vs	970 vs	965
	951 s	958 vs	955 vs	955
$\nu_{as}(\text{Mo}-\text{O}_b-\text{Mo})$	865 s	869 s	867 s	880
$\nu_{as}(\text{Mo}-\text{O}_c-\text{Mo})$	793 vs	791 vs	801 sh	805
	751 vs		782 vs	
			762 sh	

<sup>a</sup> Tetra-*n*-butylammonium salt. O<sub>a</sub> (oxygen atoms linked to phosphorus atom), O<sub>b</sub> (bridging oxygen atoms between two corner sharing octahedra), O<sub>c</sub> (bridging oxygen atoms between two edge-sharing octahedra), and O<sub>t</sub> (terminal oxygen atoms).

**Figure 1.** ORTEP view of [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion with atom labeling.

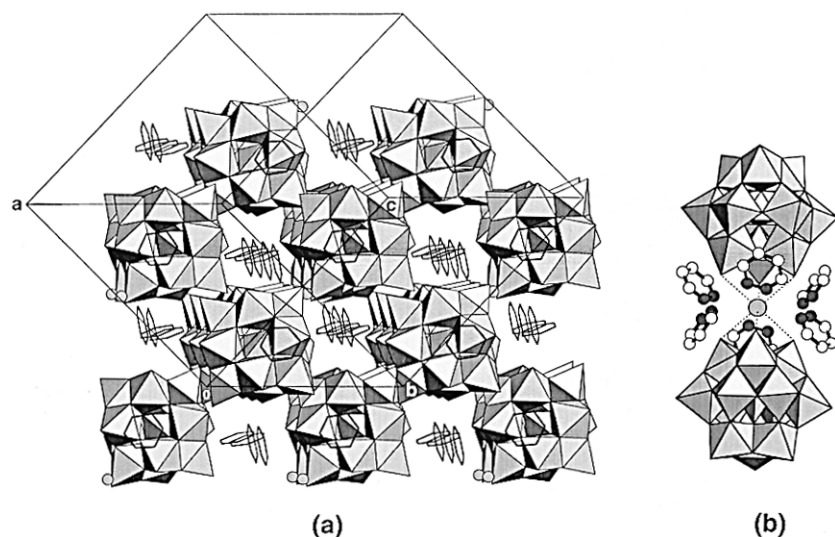
The properties of organic–inorganic compounds are strongly affected by the packing pattern of the components in the solid. Compounds containing organic planar cations and bulky Keggin anions adopt two different packing arrangements: (a) based on alternating layers of organic donors and Keggin polyoxoanions and (b) based on alternating arrangements of cations and anions.<sup>29</sup> Packing type a is present in salts which contain  $\pi$ -donor organic radicals, e.g., tetrathiafulvalene, and reduced Keggin anions<sup>30</sup> or Keggin type anion derivatives which contain paramagnetic centers.<sup>31</sup> As far as we are aware, the benzene-solvated heteropolyacid [H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>] $\cdot$ 3C<sub>6</sub>H<sub>6</sub><sup>32</sup> and the three com-

(29) Coronado, E.; Gómez-García, C. J. in ref 1a, p 233.

(30) (a) Attanasio, D.; Bonamico, M.; Fares, V.; Imperatori, P.; Suber, L. *J. Chem. Soc., Dalton Trans.* **1990**, 3221. (b) Gómez-García, C. J.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Le Magueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaès, P. *Inorg. Chem.* **1995**, *34*, 4139. (c) Bellitto, C.; Bonamico, M.; Fares, V.; Federici, F.; Righini, G.; Kurmoo, M.; Day, P. *Chem. Mater.* **1995**, *7*, 1475. (d) Ouahab, L.; Grandjean, D.; Bencharif, M. *Acta Crystallogr.* **1991**, *C47*, 2670.

(31) (a) Gómez-García, C. J.; Ouahab, L.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Delhaès, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 223. (b) Galán-Mascarós, J. R.; Giménez-García, C.; Triki, S.; Gómez-García, C. J.; Coronado, E.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1460.

(32) Lyxell, D. G.; Boström, D.; Hashimoto, M.; Petersson, L. *Acta Chem. Scand.* **1996**, *50*, 985.



**Figure 2.** Compound 1: (a) crystal packing, (b) detail of water molecule environment.

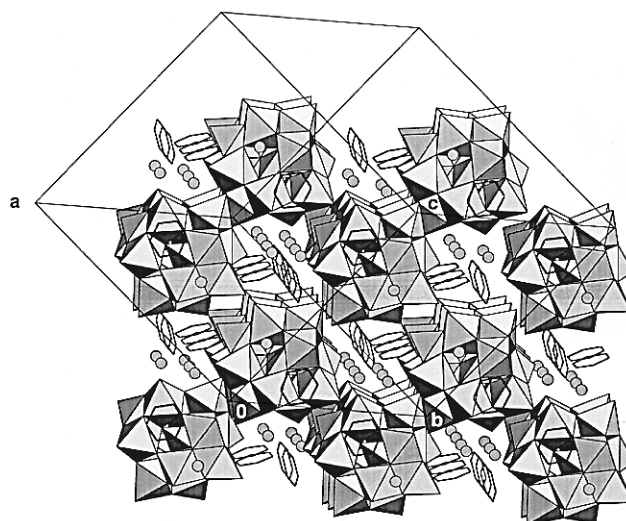
**Table 6. Selected Bond Distances for Compounds 1–3**

	1	2	3
Mo1–O1	1.673 (3)	1.676 (8)	1.682 (5)
Mo1–O5	1.834 (3)	1.976 (6)	1.839 (5)
Mo1–O7 <sup>b</sup>	1.836 (4)	1.983 (8)	1.838 (5)
Mo1–O5 <sup>a</sup>	1.991 (3)	1.849 (9)	1.990 (6)
Mo1–O6	2.005 (2)	1.844 (6)	1.999 (3)
Mo1–O13	2.439 (2)	2.424 (6)	2.432 (3)
Mo2–O2	1.674 (3)	1.663 (7)	1.672 (6)
Mo2–O6	1.814 (3)	1.962 (6)	1.841 (4)
Mo2–O8	1.868 (3)	1.921 (9)	1.878 (5)
Mo2–O9 <sup>b</sup>	1.971 (3)	1.868 (8)	1.966 (5)
Mo2–O11	2.036 (3)	1.858 (7)	1.989 (4)
Mo2–O14	2.428 (3)	2.437 (7)	2.429 (4)
Mo3–O3	1.678 (5)	1.662 (10)	1.682 (8)
Mo3–O9	1.840 (3)	1.926 (7)	1.852 (6)
Mo3–O10	1.845 (3)	1.980 (6)	1.857 (5)
Mo3–O7	1.978 (2)	1.838 (7)	1.972 (4)
Mo3–O8	1.990 (3)	1.898 (6)	1.972 (6)
Mo3–O14	2.436 (3)	2.409 (8)	2.437 (3)
Mo4–O4	1.690 (3)	1.664 (7)	1.672 (5)
Mo4–O12	1.819 (3)	1.971 (9)	1.844 (5)
Mo4–O11	1.825 (3)	1.978 (8)	1.848 (5)
Mo4–O10	1.993 (3)	1.859 (8)	1.983 (6)
Mo4–O12 <sup>a</sup>	2.020 (3)	1.839 (7)	1.981 (6)
Mo4–O14	2.407 (2)	2.441 (6)	2.427 (3)
P1–O13	1.533 (4)	1.541 (11)	1.525 (5)
P1–O14	1.532 (2)	1.530 (5)	1.526 (3)

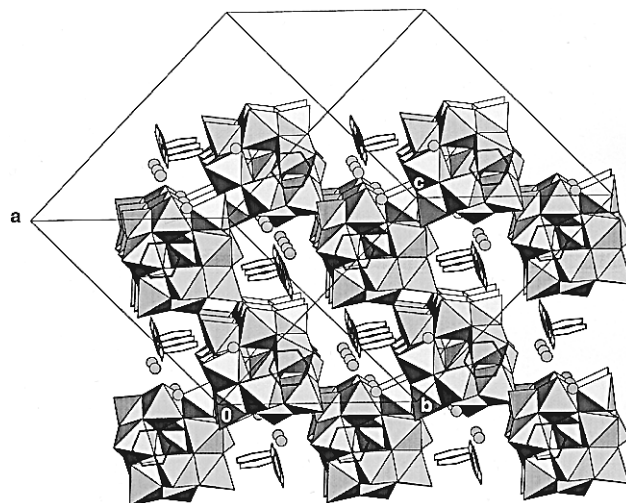
<sup>a</sup>  $-y, x - y, z$ . <sup>b</sup>  $-x + y, -x, z$ .

pounds described in this work are the only examples that show a type b packing. Therefore, the crystal packing in the compounds 1–3 consists of sequences ...anion–cation... arranged along three orthogonal directions which are parallel to the  $S_4$  axes of the idealized  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anion, (Figures 2–4). This ordering of polyanions forms tunnels where the organic templates are encapsulated in such a way that each polyanion is surrounded by six diazonium cations disposed parallel to the tetrameric  $\text{Mo}_4\text{O}_{18}$  units. Therefore, the planar organic cations are sandwiched by two polyanions as can be seen in Figure 5, where the distances from cation's centroid to the mean plane defined by the eight surface oxygen atoms of the tetrameric unit range from 2.81 to 3.11 Å, (Table 7).

One interesting conclusion of the data presented in this work is the ability of Keggin clusters to interact with rings having extended  $\pi$  systems in a surprisingly strong manner.

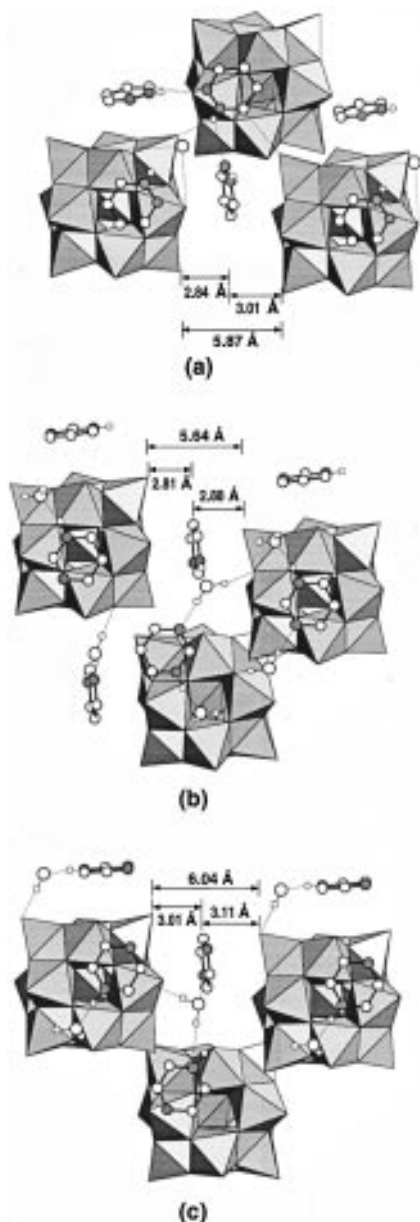


**Figure 3.** Crystal packing for compound 2.



**Figure 4.** Crystal packing for compound 3.

The position of the cations relative to the two neighboring anions is shown in Figure 6. While pyridazinium and pyrazinium locations are very similar, the location of pyrimidinium deviates markedly. It is safe to assume that the cation–anion interaction is dominated by electrostatic forces, although some degree of orbital



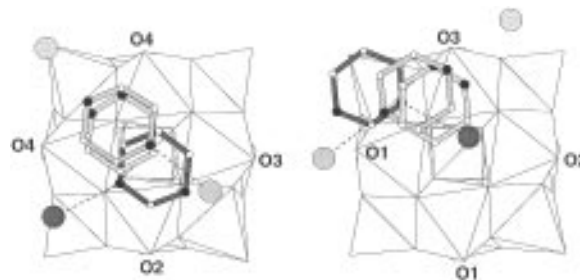
**Figure 5.** Detail of crystal packing showing the cations sandwiched by two polyanions in (a) compound **1**, (b) compound **2**, and (c) compound **3**.

**Table 7. Long Range Distances**

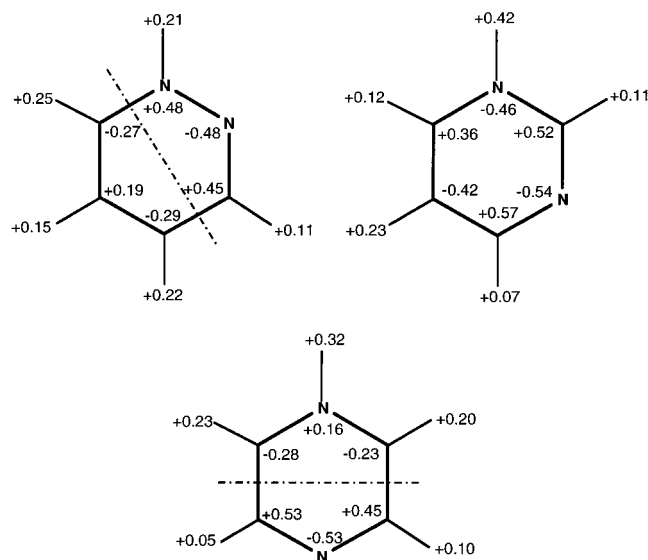
	compounds					
	<b>1</b>		<b>2</b>		<b>3</b>	
	distance <sup>a</sup>	angle <sup>b</sup>	distance <sup>a</sup>	angle <sup>b</sup>	distance <sup>a</sup>	angle <sup>b</sup>
plane 1 <sup>c</sup> –plane 2 <sup>d</sup>	5.86	0.19	5.64	1.23	6.04	0.91
plane 1–plane 3 <sup>e</sup>	2.84	10.6	2.81	5.8	3.01	4.6
plane 2–plane 3	3.01	10.7	2.88	6.3	3.11	4.1
P1–P1 <sup>f</sup>	12.603		11.240		14.018	
P1–P1 <sup>g</sup>	12.761		13.118		13.109	
P1–P1 <sup>h</sup>	10.566		11.414		10.527	

<sup>a</sup> All distances in angstroms. <sup>b</sup> All angles in degrees. <sup>c</sup> Plane 1 defined by O4 (*x*, *y*, 1 – *z*), O10, O3, O9, O2, O11, O4, and O12. <sup>d</sup> Plane 2 defined by O3 ( $\frac{1}{3}$  + *x*,  $\frac{2}{3}$  + *y*,  $\frac{1}{3}$  – *z*), O8 ( $\frac{2}{3}$  – *x*,  $\frac{1}{3}$  – *y*,  $\frac{1}{3}$  – *z*), O2 ( $\frac{2}{3}$  – *x*,  $\frac{1}{3}$  – *y*,  $\frac{1}{3}$  – *z*), O6 ( $\frac{2}{3}$  – *x*,  $\frac{1}{3}$  – *y*,  $\frac{1}{3}$  – *z*), O10 ( $\frac{2}{3}$  – *x*,  $\frac{1}{3}$  – *y*,  $\frac{1}{3}$  – *z*), O5 ( $\frac{1}{3}$  + *x*,  $\frac{2}{3}$  + *y*,  $\frac{1}{3}$  – *z*), O10 ( $\frac{1}{3}$  + *x*,  $\frac{2}{3}$  + *y*,  $\frac{1}{3}$  – *z*), and O7 ( $\frac{1}{3}$  + *x*,  $\frac{2}{3}$  + *y*,  $\frac{1}{3}$  – *z*). <sup>e</sup> Plane 3 defined by non-hydrogen atoms of the diazonium rings. <sup>f</sup> *x*, *y*, 1 – *z*. <sup>g</sup>  $\frac{1}{3}$  + *x*,  $\frac{2}{3}$  + *y*,  $\frac{1}{3}$  – *z*. <sup>h</sup>  $\frac{2}{3}$  – *x*,  $\frac{1}{3}$  – *y*,  $\frac{1}{3}$  – *z*.

interaction cannot be neglected as shown by the short distances between the cation and the oxygens of the tetrameric unit they face. Theoretical calculations on



**Figure 6.** Position of the cations relative to the two adjacent anions they are sandwiched by. Dotted filling for compound **1**, black filling for compound **2**, and gray filling for compound **3**. Nitrogen atoms are black circles and water molecules large filled circles.

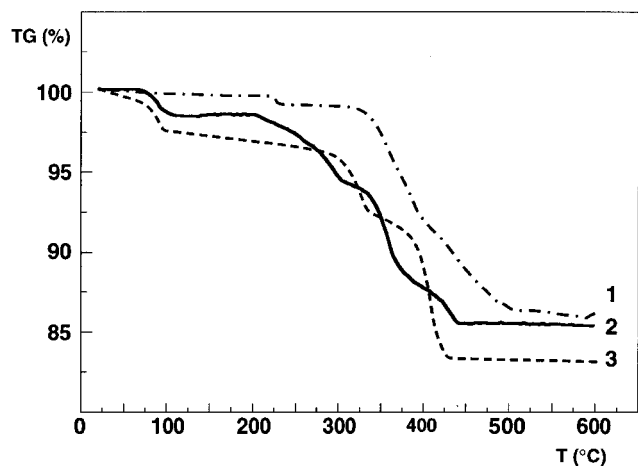


**Figure 7.** Charge distribution of cations for compounds **1–3**, calculated by fitting to the electrostatic potential.

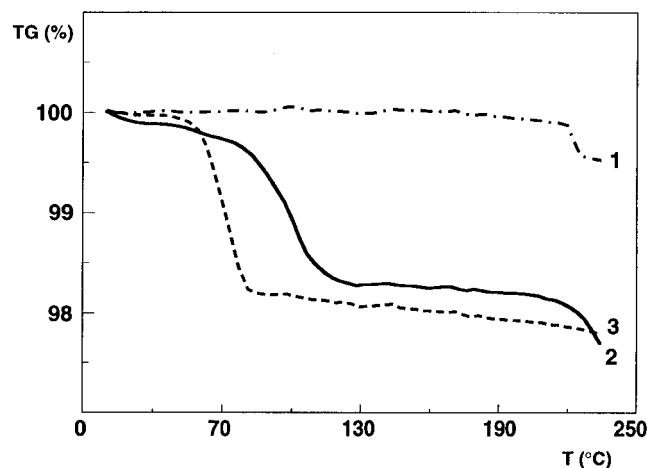
the diazonium cations' charge distribution have been carried out. The charges computed by fitting to the ab initio derived electrostatic potential are displayed in Figure 7. The ring atoms show an alternating positive-negative charge distribution with the largest negative charge always on the nonprotonated nitrogen atom, but some differences can be found.

The absolute values of the charges on the non-hydrogen atoms of the pyrimidinium cation span a small range (0.36–0.57), giving rise to a quite uniform distribution of charge on the aromatic ring. On the other hand, the pyridinium and pyrazinium cations show a high charge concentration on one-half side of the aromatic ring, due to the wider range spanned by the charges (0.19–0.48 for pyridinium, 0.16–0.55 for pyrazinium). These different charge distributions correlate nicely with the different disposition of the cations relative to the anions displayed in Figure 6.

Water molecules in compound **2** and **3** are located in the tunnels and connect the corresponding organic cations with the surrounding Keggin anions via hydrogen bonding. On the other hand, the water molecule of compound **1** sits on a  $\bar{3}$  crystallographic axis and is confined in the octahedral site delimited by six  $\bar{3}$  axis related terminal oxygen atoms of two adjacent polyanions, [Figure 2b]. This water molecule does not hydrogen bond to the pyridinium cations, although the 12 nitrogen atoms (from six organic cations) are



(a)



(b)

**Figure 8.** TG curves for the thermal decomposition (a) and dehydration (b) of compounds **1–3** in synthetic air atmosphere.

situated less than 4.0 Å from it. Hydrogen contacts are summarized in Table 8.

**Thermal Behavior.** Thermal decomposition of compounds **1–3** starts at room temperature with the release of water molecules. These dehydration processes are followed by steps corresponding to the oxidation of cations, which take place in the temperature range 300–500 °C for **1**, 270–420 °C for **2**, and 200–450 °C for **3**, giving in all cases a mixture of  $P_2O_5$  and  $MoO_3$  as the final residue [Figure 8(a)].

It is interesting to analyze the dehydration processes. The decomposition of compound **1** starts at room temperature with the gradual emission of external surface sorbed water, while the water of crystallization is

**Table 8.** Hydrogen Contacts for Compounds **1–3**

bond type	X–H <sup>a</sup>	X···O <sup>a</sup>	H···O <sup>a</sup>	∠X–H···O <sup>b</sup>
compound <b>1</b>				
N1–H1···O4 <sup>c</sup>	0.71 (13)	2.875 (5)	2.27 (12)	143 (13)
N1–H1···N2 <sup>d</sup>	0.71 (13)	3.215 (9)	2.65 (16)	138 (12)
C5–H5···O1 <sup>e</sup>	0.99	3.150 (6)	2.299	143
C6–H6···O3 <sup>f</sup>	1.00	3.171 (8)	2.297	145
O01···O4 <sup>h</sup>		3.414 (3)		
compound <b>2</b>				
N1–H1···O01 <sup>g</sup>	0.96 (18)	2.640 (18)	1.70 (16)	165 (15)
C2–H2···O1 <sup>e</sup>	1.18 (9)	3.297 (14)	2.12 (9)	179 (8)
C6–H6···O4 <sup>c</sup>	0.96 (17)	3.209 (15)	2.36 (13)	148 (12)
O01–H01···O8	1.07	2.925 (11)	1.875	165
O01–H02···N3 <sup>e</sup>	0.99	2.807 (16)	1.82	180
compound <b>3</b>				
N4–H4···O01	1.00	2.673 (16)	1.68	172
C5–H5···O1 <sup>e</sup>	0.98	3.419 (13)	2.50	157
C6–H1···O01 <sup>f</sup>	0.98	3.071 (18)	2.42	124
O01–H01···O6 <sup>e</sup>	1.04	2.944 (10)	1.91	178
O01–H02···O3	0.98	2.908 (9)	1.93	177

<sup>a</sup> Distances in angstroms. <sup>b</sup> Angles in degrees. <sup>c</sup> Symmetry code:  $y, -x + y, -z + 1$ . <sup>d</sup> Symmetry code:  $x - y, x, -z + 1$ . <sup>e</sup> Symmetry code:  $-x + 2/3, -y + 1/3, -z + 1/3$ . <sup>f</sup> Symmetry code:  $y + 1/3, -x + y + 2/3, -z + 2/3$ . <sup>g</sup> Symmetry code:  $-y + 2/3, x - y + 1/3, z + 1/3$ . <sup>h</sup> Six contacts with O4 at  $x, y, z, -x, -y, -z + 1; -y, x - y, z, y, -x + y, -z + 1; -x + y, -x, z, x - y, x, -z + 1$ .

released in the temperature range 200–245 °C. On the other hand, the water molecules in compounds **2** and **3** are released at temperatures below 130 °C, [Figure 8b]. According to Petit and Coquerel,<sup>33</sup> the mechanism of dehydration is dependent on topological and energetic considerations, so that it is favored by the accessibility of water molecules to the tunnels existing in the crystal structure and by the low liberation energy. The evacuation of water in compound **1** requires higher temperatures because it is buried in an octahedral site with no easy access to the tunnel in the lattice. On the other hand, water molecules in compounds **2** and **3**, despite forming stronger hydrogen bonds, are released at lower temperatures due to their location in the tunnels.

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**Supporting Information Available:** Tables giving crystal data and details of structure determination, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom locations, and a full list of bond length and angles; a listing of the observed and calculated structure factors of compounds **1–3** (31 pages). Ordering information is given on any current masthead page.

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(33) Petit, S.; Coquerel, G. *Chem. Mater.* **1996**, *8*, 2247.