

Xue-Jie Tan,^{a,b} Si-Xiu Sun,^{a*}
Lian-Dong Liu,^c Jian-Ping Ma^c
and Dian-Xiang Xing^b

^aKey Laboratory of Colloid and Interface Chemistry of the State Education Ministry, Shandong University, Jinan 250100, People's Republic of China, ^bDepartment of Chemical Industry, Shandong Institute of Light Industry, Jinan 250100, People's Republic of China, and ^cSchool of Chemistry, Shandong Normal University, Jinan 250100, People's Republic of China

Correspondence e-mail: sxx@sdu.edu.cn

Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.042 \text{ \AA}$
Disorder in main residue
R factor = 0.100
wR factor = 0.226
Data-to-parameter ratio = 9.3

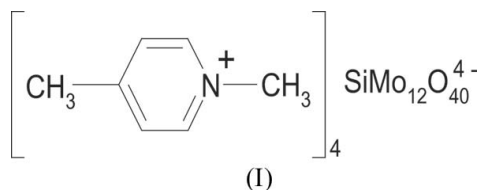
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Tetrakis(1,4-dimethylpyridinium) dodecamolybdsilicate

The anion of the title compound, $(\text{C}_7\text{H}_{10}\text{N})_4[\text{SiMo}_{12}\text{O}_{40}]$, has a disordered centrosymmetric 'pseudo-Keggin' structure and neighboring anions are linked into a layered structure *via* weak C—H...O hydrogen bonding involving the DMP cations.

Comment

In crystal engineering and polyoxometalate (POM) chemistry, one of the major challenges is to establish reliable connections between new molecular and supramolecular structures on the basis of intermolecular interactions, because these materials may exhibit cooperative properties typically associated with the POM network solids (Desiraju, 1995; Coronado & Gómez-García, 1998). Ideally one would like to identify substructural units in a target supermolecule that can be assembled from logically chosen precursor molecules. Here, we attempt to use normal methods to realize such molecular assemblies. This paper deals with the preparation and crystal structure of the title compound, (I), obtained from the reaction of 1,4-dimethylpyridinium iodide (DMPI) and Keggin-type $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$.



The crystal structure of (I) consists of 1,4-dimethylpyridinium (DMP) cations and dodecamolybdsilicate anions (SiMo_{12}). The SiMo_{12} anion lies across an inversion center and shows a disordered 'pseudo-Keggin' structure (Fig. 1), but with site symmetry $m\bar{3}m (O_h)$ instead of the tetrahedral symmetry observed for the α -Keggin molecule (Evans & Pope, 1984). This can be interpreted as an orientational disorder of normal α -Keggin molecules over two positions related by an inversion center (Attanasio *et al.*, 1990). The SiO_4 group is disordered over two sites, the Si atom at $(\frac{1}{2}, \frac{1}{2}, 1)$ being surrounded by a cube of disordered O atoms (each with 0.5 site occupancy), with the Si—O distances in the range 1.60 (2)–1.68 (2) Å (Table 1). All of the bridging O atoms of the SiMo_{12} anion are disordered over two sites, with site-occupancy factors of 0.5, similar to that found in a similar compound (Tan *et al.*, 2005). The asymmetric unit includes two DMP cations (DMP-A and DMP-B) (Fig. 1). DMP-A and DMP-B display different orientations, the dihedral angle between the mean planes being 33.2 (6)°.

Received 16 May 2005
Accepted 19 July 2005
Online 27 July 2005

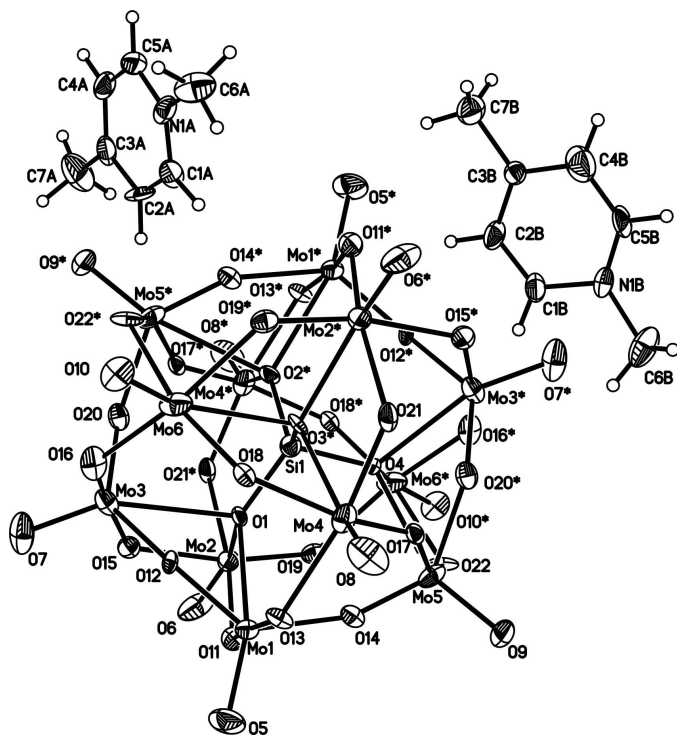


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. One disordered component has been omitted for clarity [symmetry code: (*) $1 - x, 1 - y, 2 - z$].

In the crystal structure, the cations and anions are connected mainly by electrostatic forces. *PLATON* analysis (Spek, 2003) suggests the existence of weak C—H...O hydrogen bonding (Krishnamohan Sharma & Desiraju, 1994) between the cations and anions in (I) (Table 2). The DMP-A and DMP-B cations link SiMo₁₂ anions *via* hydrogen bonding into a layered supramolecular structure (Fig. 2).

Experimental

All organic solvents and common materials used were of reagent grade and were used without further purification. H₄SiMo₁₂O₄₀ was prepared according to the literature method of Claude *et al.* (1983). 1,4-Dimethylpyridinium iodide (DMPI) was prepared according to Zhao *et al.* (1995). The title compound, (I), was prepared by mixing a 0.01 mol l⁻¹ DMPI/DMF solution and a 0.01 mol l⁻¹ H₄SiMo₁₂O₄₀/DMF solution in a 4:1 molar ratio. The precipitate was filtered off and dried. Recrystallization was performed from DMF. Yellow single crystals of (I) were obtained after 40 d. Elemental analysis calculated: C 14.93, H 1.79, N 2.49%; found: C 15.19, H 1.91, N 2.43%.

Crystal data

| | |
|---|---|
| (C ₇ H ₁₀ N) ₄ [SiMo ₁₂ O ₄₀] | Z = 1 |
| <i>M_r</i> = 2252.01 | <i>D_x</i> = 2.760 Mg m ⁻³ |
| Triclinic, <i>P</i> $\bar{1}$ | Mo <i>K</i> α radiation |
| <i>a</i> = 11.033 (5) Å | Cell parameters from 378 reflections |
| <i>b</i> = 11.951 (5) Å | θ = 1.8–25.0° |
| <i>c</i> = 12.034 (5) Å | μ = 2.81 mm ⁻¹ |
| α = 69.081 (5)° | <i>T</i> = 298 (2) K |
| β = 77.369 (4)° | Block, yellow |
| γ = 66.626 (5)° | 0.4 × 0.2 × 0.05 mm |
| <i>V</i> = 1355.1 (10) Å ³ | |

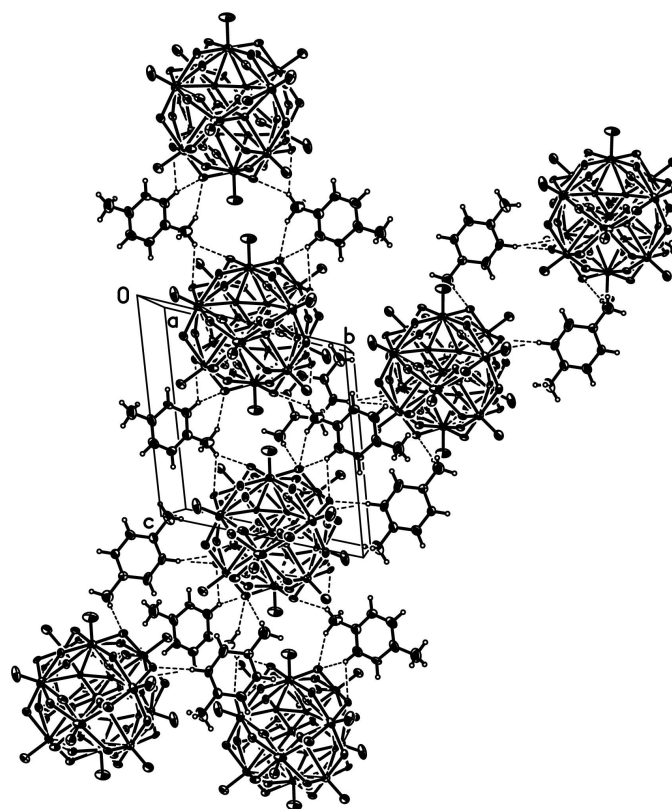


Figure 2
A packing diagram for (I), showing DMP-A and DMP-B linking the SiMo₁₂ anions *via* hydrogen bonding (dashed lines).

Data collection

| | |
|--|--|
| Bruker SMART CCD area-detector diffractometer | 4474 independent reflections |
| φ and ω scans | 4355 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $R_{\text{int}} = 0.026$ |
| $T_{\text{min}} = 0.513, T_{\text{max}} = 0.872$ | $\theta_{\text{max}} = 25.0^\circ$ |
| 8908 measured reflections | $h = -12 \rightarrow 13$ |
| | $k = -12 \rightarrow 14$ |
| | $l = 0 \rightarrow 14$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.100$ | $w = 1/[\sigma^2(F_o^2) + 102.4837P]$ |
| $wR(F^2) = 0.226$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.15$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 4474 reflections | $\Delta\rho_{\text{max}} = 2.49 \text{ e \AA}^{-3}$ |
| 483 parameters | $\Delta\rho_{\text{min}} = -1.23 \text{ e \AA}^{-3}$ |

Table 1

Selected interatomic distances (Å).

| | | | |
|---------|----------|---------|----------|
| C1A—N1A | 1.31 (4) | C2B—C3B | 1.33 (3) |
| C1A—C2A | 1.34 (4) | C3B—C4B | 1.36 (4) |
| C2A—C3A | 1.40 (4) | C3B—C7B | 1.52 (3) |
| C3A—C4A | 1.38 (4) | N1B—C5B | 1.30 (3) |
| C3A—C7A | 1.49 (4) | N1B—C6B | 1.49 (3) |
| N1A—C5A | 1.32 (3) | C4B—C5B | 1.38 (5) |
| N1A—C6A | 1.44 (4) | O1—Si1 | 1.64 (2) |
| C4A—C5A | 1.39 (4) | O2—Si1 | 1.60 (2) |
| C1B—C2B | 1.32 (3) | O3—Si1 | 1.68 (2) |
| C1B—N1B | 1.39 (3) | O4—Si1 | 1.68 (2) |

Table 2
Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C1A—H1A...O14A ⁱ | 0.93 | 2.42 | 3.21 (4) | 143 |
| C1A—H1A...O17A ⁱ | 0.93 | 2.58 | 3.23 (4) | 127 |
| C2B—H2B...O10 ⁱⁱ | 0.93 | 2.51 | 3.15 (3) | 126 |
| C5B—H5B...O17 ⁱⁱⁱ | 0.93 | 2.58 | 3.47 (4) | 160 |
| C5B—H5B...O17A ⁱⁱⁱ | 0.93 | 2.26 | 3.17 (3) | 167 |
| C6A—H6A...O14A ⁱ | 0.96 | 2.32 | 3.22 (4) | 156 |
| C6A—H6C...O11 ^{iv} | 0.96 | 2.41 | 3.27 (5) | 150 |
| C6A—H6C...O15 ^{iv} | 0.96 | 2.49 | 3.31 (5) | 144 |
| C6B—H6D...O15A ^v | 0.96 | 2.58 | 3.47 (4) | 155 |
| C7B—H7F...O14A ^{iv} | 0.96 | 2.49 | 3.43 (4) | 168 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $x - 1, y, z$; (iii) $-x + 1, -y, -z + 2$; (iv) $x, y, z - 1$; (v) $x, y - 1, z$.

The assignment of Me—C (C3*X*) and Me—N (N1*X*) in the pyridine ring of the DMP cations was made on the basis of the displacement parameters. The disorder of O atoms in the SiMo₁₂ cluster contributes to the high $U_{eq}(\text{max})/U_{eq}(\text{min})$ values of some of the O atoms. Eight approximate isotropic restraints (for O11, O12, O14, O15, O16, O17, O18A and O19) were used in the refinement to lower these values. The relatively high R1 value is the result of disorder and the poor quality of the crystal. All H atoms were located geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.96 Å, and with $U_{iso}(\text{H}) = 1.5U_{eq}(\text{C})$ for methyl H atoms and $1.2U_{eq}(\text{C})$ for the other H atoms. The highest peak in the difference map is 1.34 Å from atom O20A and the deepest hole is 1.46 Å from atom C1A.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE-Plus* (Bruker, 2000); program(s) used to solve

structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

The authors thank Professors Yu Wen-Tao (State Key Laboratory of Crystal Materials, Shandong University) and Dong Yu-Bin (School of Chemistry, Shandong Normal University) for their encouragement and helpful discussion.

References

- Attanasio, D., Bonamico, M., Fares, V., Imperatori, P. & Suber, L. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3221–3228.
- Bruker (2000). *SMART* (Version 5.625), *SAINTE-Plus* (Version 6.22), *SADABS* (Version 2.03) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Claude, R. D., Michel, F., Raymonde, F. & Rene, T. (1983). *Inorg. Chem.* **22**, 207–216.
- Coronado, E. & Gómez-García, C. J. (1998). *Chem. Rev.* **98**, 273–296.
- Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
- Evans, H. T. & Pope, M. T. (1984). *Inorg. Chem.* **23**, 501–504.
- Krishnamohan Sharma, C. V. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2345–2352.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Tan, X.-J., Sun, S.-X., Ma, J.-P., Liu, S.-L. & Xing, D.-X. (2005). *Acta Cryst.* **E61**, m711–m713.
- Zhao, C. F., He, G. S., Bhawalkar, J. D., Park, C. K. & Prasad, P. N. (1995). *Chem. Mater.* **7**, 1979–1983.