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Key indicators

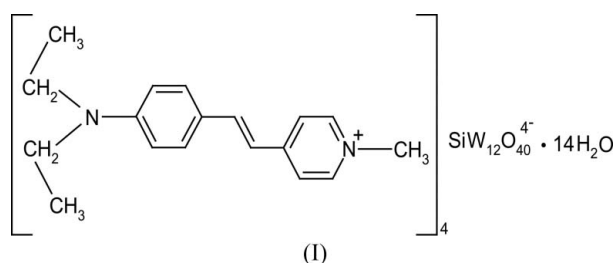
Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.037$ Å
H-atom completeness 77%
Disorder in main residue
 R factor = 0.061
 wR factor = 0.160
Data-to-parameter ratio = 17.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis{*trans*-4-[(*N,N*-diethylamino)styryl]-1-methylpyridinium} dodecatungstosilicate tetradecahydrate

In the title compound, $(\text{C}_{18}\text{H}_{23}\text{N}_2)_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O}$, the asymmetric unit contains two *trans*-4-[(*N,N*-diethylamino)styryl]-*N*-methylpyridinium (DEASP) cations, one half dodecatungstosilicate ($\text{SiW}_{12}\text{O}_{40}$) anion and seven water molecules. The two DEASP cations form a periodically layered arrangement perpendicular to their molecular planes and the $\text{SiW}_{12}\text{O}_{40}$ anions have a disordered 'pseudo-Keggin' structure around an inversion centre. They are linked into an infinite three-dimensional assembly *via* electrostatic forces and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds.

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Comment

trans-4-[*p*-(*N,N*-Diethylamino)styryl]-*N*-methylpyridinium iodide (DEASPI) has been claimed to have two-photon absorption properties, and its two-photon up-conversion efficiency is as high as 10.7% at 2.14 mJ input energy, which is the largest among the few laser dyes with such a high up-conversion efficiency (Wang *et al.*, 2000). Meanwhile, Marder *et al.* (1990) have claimed that finding the correct counter-ions of ionic chromophores in the crystal structure may be a promising approach for the synthesis of new materials with large bulk optical nonlinearities. This paper deals with the preparation and crystal structure of the title compound, (I), in which the I^- in DEASPI is replaced by the Keggin-type $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion.



The asymmetric unit of (I) contains one half dodecatungstosilicate ($\text{SiW}_{12}\text{O}_{40}$) anion, two *trans*-4-[*p*-(*N,N*-diethylamino)styryl]-*N*-methylpyridinium cations (denoted DEASP-I and DEASP-II) and seven water molecules (Figs. 1 and 2). The $\text{SiW}_{12}\text{O}_{40}$ anion shows a disordered 'pseudo-Keggin' structure, but with local site symmetry $m\bar{3}m (O_h)$, instead of the tetrahedral symmetry of the α -Keggin ion (Evans & Pope, 1984). This fact can be interpreted as an orientational disorder of normal α -Keggin ions over two positions related by an inversion centre (Attanasio *et al.*, 1990). The Si atom lies on an inversion centre and is surrounded by a distorted cube of disordered O atoms at

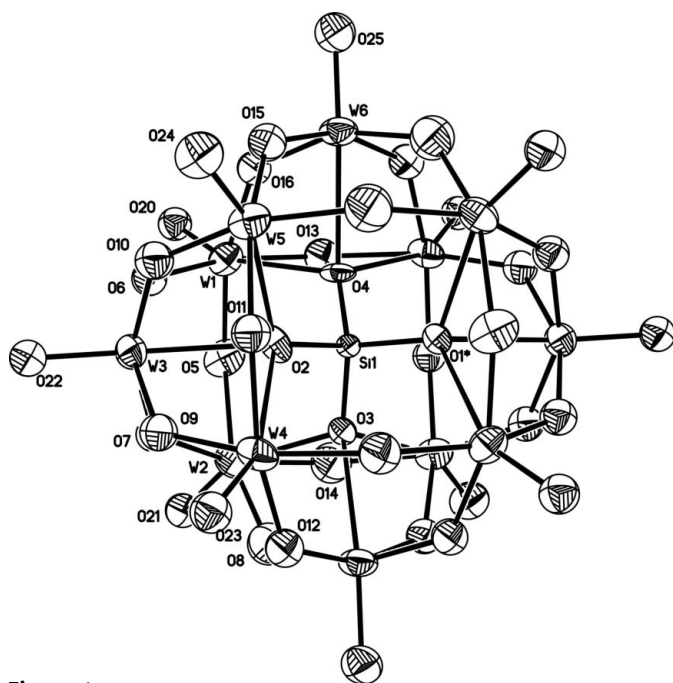


Figure 1
A view of the $\text{SiW}_{12}\text{O}_{40}$ anion, showing 30% probability displacement ellipsoids. One of two possible orientations of the central SiO_4 group (O1/O2*/O3*/O4*) has been omitted for clarity. The atom labelled with an asterisk (*) and unlabelled atoms are at the symmetry-related position $(1-x, 2-y, 1-z)$.

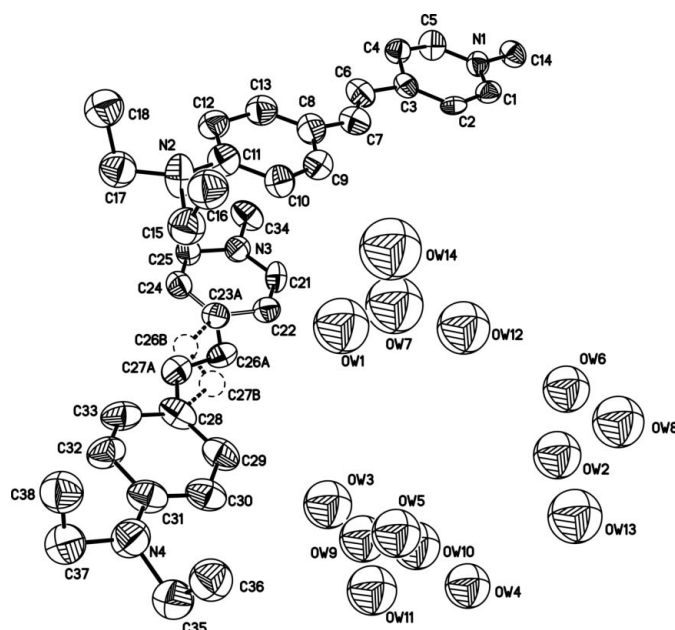


Figure 2
The two DEASP cations and the water molecules in the asymmetric unit. The occupancy factors of the atoms C23A/C26A/C27A and C23B/C26B/C27B are 0.57 (3) and 0.43 (3), respectively, while OW1–OW14 are half occupied. The disordered C26B and C27B are shown as dotted circles and lines, and all H atoms have been omitted for clarity.

1.566 (17)–1.687 (18) Å (Table 1), with each O site half-occupied. There are two possible combinations, O1/O2¹/O3¹/O4¹ and O1¹/O2/O3/O4 [symmetry code: (i) $1-x, 2-y, 1-z$].

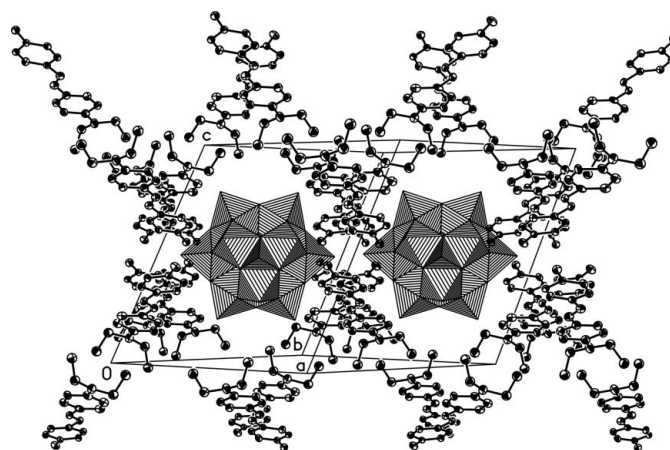


Figure 3
A partial packing diagram of (I). All of the disordered units, water molecules and H atoms have been omitted.

In the DEASP cations, DEASP-I (containing N1/N2/C1–C18) shows no obvious disorder, but DEASP-II (N3/N4/C21–C38) has conformational disorder. The framework of DEASP-I and DEASP-II both show near-planarity, approximately parallel to $(\bar{4} 4 17)$ (plane-I) and $(\bar{3} 4 15)$ (plane-II), respectively. Plane-I and plane-II are nearly parallel and the dihedral angle is only $1.1 (1)^\circ$. In the crystal structure, they both form a periodically layered arrangement perpendicular to their molecular planes. If we view the crystal structure along $[1\bar{1}0]$, all of the DEASP cations will be found to form a huge fishing net, and $\text{SiW}_{12}\text{O}_{40}$ anions are like inset gems (Fig. 3). There are C–H \cdots O interactions (Table 2) between DEASP and $\text{SiW}_{12}\text{O}_{40}$. Thus, besides electrostatic forces, hydrogen bonds help link the anions, cations and water molecules into an infinite three-dimensional network.

Experimental

trans-4-[*p*-(*N,N*-Diethylamino)styryl]-*N*-methylpyridinium iodide (DEASPI) was prepared following Wang *et al.* (2000). Compound (I) was prepared by reacting a 0.01 mol l^{-1} DEASPI/ethanol solution and a 0.01 mol l^{-1} $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ /ethanol solution in the molar ratio 4:1. The precipitate was filtered off, dried and recrystallized from DMF (yield 78%). After 40 days of slow diffusion of water into the DMF solution at room temperature, red crystals of (I) were obtained. Elemental analysis calculated: C 20.61, H 2.88, N 2.67%; found: C 20.97, H 2.95, N 2.13%.

Crystal data

$(\text{C}_{18}\text{H}_{23}\text{N}_2)_4[\text{SiW}_{12}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$
 $M_r = 4195.91$
 Triclinic, $P\bar{1}$
 $a = 15.019 (4) \text{ \AA}$
 $b = 15.056 (4) \text{ \AA}$
 $c = 16.080 (4) \text{ \AA}$
 $\alpha = 64.393 (3)^\circ$
 $\beta = 79.436 (4)^\circ$
 $\gamma = 65.578 (3)^\circ$

$V = 2985.5 (14) \text{ \AA}^3$
 $Z = 1$
 $D_x = 2.318 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 11.60 \text{ mm}^{-1}$
 $T = 298 (2) \text{ K}$
 Block, red
 $0.45 \times 0.21 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer	16302 measured reflections
φ and ω scans	10904 independent reflections
Absorption correction: part of the refinement model (ΔF) (Parkin <i>et al.</i> , 1995)	5387 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.065$, $T_{\max} = 0.311$	$R_{\text{int}} = 0.049$
	$\theta_{\text{max}} = 25.5^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.061$	$w = 1/[\sigma^2(F_o^2) + (0.0704P)^2]$
$wR(F^2) = 0.160$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{\text{max}} < 0.001$
10904 reflections	$\Delta\rho_{\text{max}} = 2.18 \text{ e } \text{\AA}^{-3}$
627 parameters	$\Delta\rho_{\text{min}} = -1.51 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Si1—O1 ⁱ	1.619 (17)	Si1—O3	1.687 (18)
Si1—O2	1.566 (17)	Si1—O4	1.618 (18)
O2—Si1—O1 ⁱ	108.9 (9)	O2—Si1—O3	108.9 (9)
O3—Si1—O1 ⁱ	111.3 (9)	O2—Si1—O4	109.3 (10)
O4—Si1—O1 ⁱ	110.7 (9)	O3—Si1—O4	107.8 (9)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots O8	0.93	2.53	3.27 (2)	137
C2—H2A \cdots O9	0.93	2.52	3.34 (2)	148
C4—H4A \cdots O25 ⁱⁱ	0.93	2.48	3.30 (2)	147
C14—H14A \cdots O23 ⁱⁱⁱ	0.96	2.44	3.39 (2)	169
C22—H22A \cdots O24	0.92	2.48	3.33 (2)	153
C25—H25A \cdots O14 ^{iv}	0.93	2.47	3.20 (2)	136

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

One of the DEASP cations shows conformational disorder, and atoms C23, C26 and C27 have two possible sets of positions *A* and *B* with occupation factors 0.57 (3) and 0.43 (3), respectively. For the DEASP cations, restraints were applied to maintain reasonable geometry. Solvent water molecules show positional disorder. Atoms OW1–OW14 were treated as half occupied and refined isotropically in order to avoid abnormal displacement parameters, their H atoms being not positioned. All other H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H distances 0.93–0.97 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl groups. The highest peak is 1.05 \AA from W6 and the deepest hole is 0.10 \AA from O16.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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*.

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