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Tris{*trans*-4-[*p*-(*N*,*N*-diethylamino)styryl]-*N*-methylpyridinium} dodecatungstophosphate

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Key indicators

Single-crystal X-ray study
T = 288 K
Mean σ(C–C) = 0.046 Å
R factor = 0.078
wR factor = 0.214
Data-to-parameter ratio = 18.2

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

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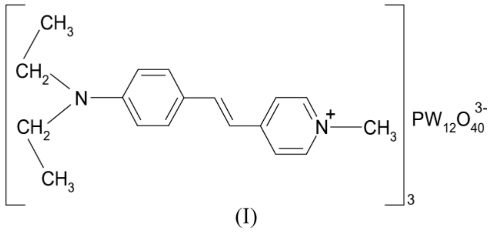
In the title compound, $(C_{18}H_{23}N_2)_3[PW_{12}O_{40}]$, three *trans*-4-[*p*-(*N*,*N*-diethylamino)styryl]-*N*-methylpyridinium cations lie around one dodecatungstophosphate anion and they form an infinite three-dimensional assembly *via* electrostatic forces. The three similar cations are distorted to different extents because of different packing environments, *e.g.* the dihedral angles between the benzene rings and the pyridine rings are 3.4 (1)–29.0 (3)°. The Keggin structure polyanion is also severely distorted.

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). X. M. Wang and co-workers have synthesized a series of analogous π-conjugated chromophores and studied systematically the relationships between the structure and two-photon properties (Wang, Zhou, Wang *et al.*, 2001; Wang, Zhou, Yu *et al.*, 2001; Wang *et al.*, 2002). However, they have not examined the effects of counter-anions. On the other hand, 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.



(I)

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 (Desiraju 1995; Niu *et al.*, 2003). Ideally, one would like to identify substructural units in a target supramolecule that can be assembled from logically chosen precursor molecules. We attempt here to use normal methods to realize such molecular assemblies. This paper deals with the preparation and crystal structure of the title compound, (I), which is a new intermolecular compound obtained from the reaction of DEASPI and Keggin-type $H_3PW_{12}O_{40}$.

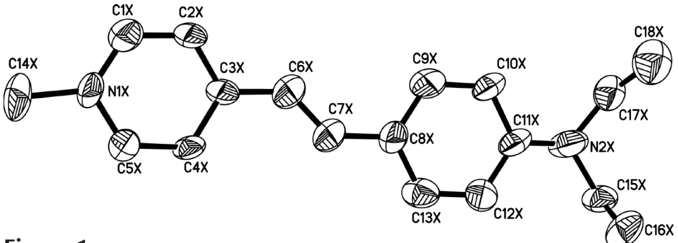


Figure 1
The structure of one of the DEASP cations, with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

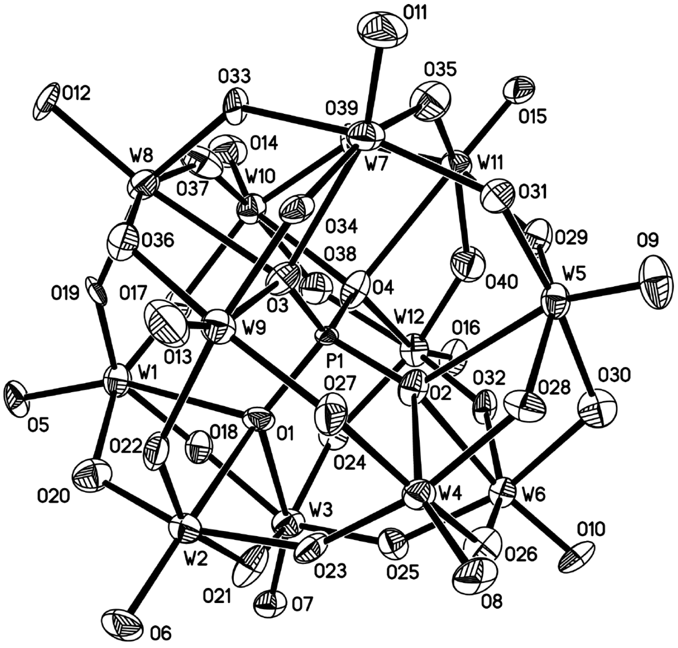


Figure 2
A 30% probability displacement ellipsoid plot of the PW12 anion. H atoms have been omitted for clarity.

Compound (I) is built from three *trans*-4-[*p*-(*N*,*N*-diethylamino)styryl]-*N*-methylpyridinium cations (denoted DEASP-*A*, DEASP-*B* and DEASP-*C*; Fig. 1) and one dodecatungstophosphate anion, $PW_{12}O_{40}^{3-}$ (denoted PW12), *via* electrostatic forces (Fig. 2). The three DEASP cations lie around PW12, one to the left (DEASP-*B*), one to the right (DEASP-*C*) and one above (DEASP-*A*) (Fig. 3); this configuration maximizes the attractive electrostatic interactions. The three DEASP cations are distorted to different extents. In DEASP-*A*, the dihedral angle between the planes of the benzene and pyridine rings is 3.4 (1)°, while in DEASP-*B* and DEASP-*C*, the dihedral angles are 29.0 (3)° and 10.5 (2)°, respectively.

The Keggin structure PW12 consists of one PO_4 tetrahedron (containing atom O*a*) surrounded by four corner-sharing W_3O_{13} sets formed by three edge-sharing WO_6 octahedra (the corner-sharing atom between W_3O_{13} groups is denoted O*b*, the edge-sharing atom inside W_3O_{13} is denoted O*c* and the unshared terminal O atom is denoted O*t*). The P—O*a* bond distances range from 1.45 (2) (P1—O4) to 1.657 (18) Å (P1—O2), and the angles from 101.2 (11) (O1—P1—O2) to 118.9 (12)° (O3—P1—O4), indicating that the PO_4 tetrahedron is severely distorted. In the WO_6 octahedra, the W—O*t*, W—O*a* and W—O*b*/*c* bond distances fall in the ranges 1.55 (3) (W12—O16)–1.81 (2) (W9—O13), 2.397 (19) (W2—O1)–2.524 (16) (W7—O3) and 1.64 (2) (W4—O28)–2.11 (3) Å (W7—O31), and the mean values are 1.68, 2.447 and 1.91 Å, respectively. These results show that the WO_6 octahedra of the polyanions in (I) are also severely distorted because of the influence of the surrounding cations (Attanasio *et al.*, 1990; Niu *et al.*, 2002, 2003; Pope, 1983; Zhang *et al.*, 1997).

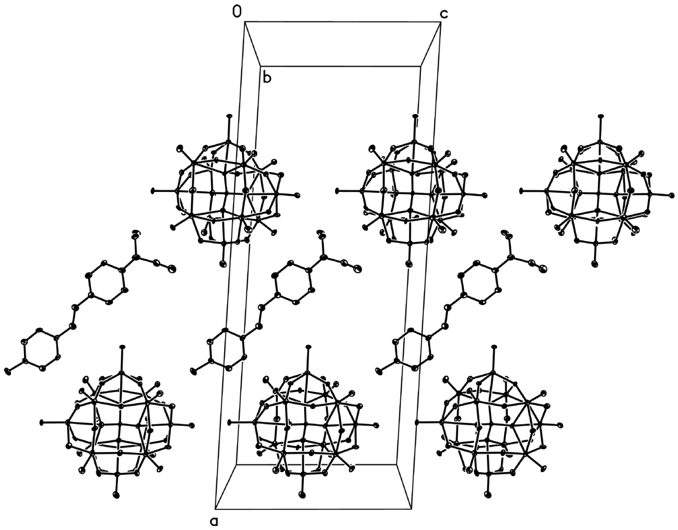


Figure 3
A partial packing diagram for (I), viewed along the *b* axis, showing the packing mode of PW12 anions and DEASP-A cations. Displacement ellipsoids are shown at the 10% probability level and all H atoms have been omitted.

In the crystal structure, the three DEASP cations are nearly parallel to the *ac* plane (Fig. 3), and DEASP-*B* and DEASP-*C* have a head-to-head arrangement (approximately parallel). The packing comprises layers parallel to the *bc* plane, in which PW12, DEASP-*B* and DEASP-*C* form zigzag chains in two dimensions. The layers are further linked by DEASP-*A* into a three-dimensional network. The dark red (almost black) color of (I) implies that there should be other non-covalent intermolecular interactions (*e.g.* hydrogen bonds, C—H$\cdots\pi$ interactions, *etc*) besides electrostatic forces, which help to link them together.

Experimental

All organic solvents and common materials used for the synthesis were of reagent grade and used without further purification. *trans*-4-[*p*-(*N*,*N*-Diethylamino)styryl]-*N*-methylpyridinium iodide (DEASPI) was prepared according to the method of Wang *et al.* (2000). Compound (I) was prepared by reacting a DEASPI/ethanol solution (0.01 mol l^{-1}) and an $H_3PW_{12}O_{40}\cdot24H_2O$/ethanol solution (0.01 mol l^{-1}) in the molar ratio of 3:1. The precipitate was filtered off, dried and recrystallized from DMF. After 30 days of slow evaporation of DMF at room temperature, dark red crystals of (I) were obtained. Elemental analysis calculated: C 17.62, H 1.89, N 2.28%; found: C 18.75, H 2.15, N 2.87%. IR (KBr, cm^{-1}): 1078, 976, 894, 809 ($PW_{12}O_{40}^{3-}$), 3018 (=C—H), 2968 (–C—H), 1665, 1578, 1522, 1174, 1154 (pyridine ring and benzene ring).

Crystal data

$(C_{18}H_{23}N_2)_3[PW_{12}O_{40}]$
M_r = 3679.32
Monoclinic, *Cc*
a = 32.394 (4) Å
b = 21.167 (3) Å
c = 13.0130 (15) Å
β = 93.467 (2)°
V = 8907 (2) Å^3
Z = 4
D_x = 2.744 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 380 reflections
θ = 7.5–27.0°
μ = 15.53 mm^{-1}
T = 288 (2) K
Block, dark red
0.48 × 0.27 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min}$ = 0.010, $T_{\max}$ = 0.158
26 688 measured reflections
16 779 independent reflections
12 364 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.041
$\theta_{\max}$ = 27.0°
$h = -41 \rightarrow 36$
$k = -26 \rightarrow 21$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.214
S = 1.07
16 777 reflections
923 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1095P)^2 + 138.0939P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 3.79 e Å^{-3}
$\Delta\rho_{\min}$ = −1.67 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 7126 Friedel pairs
Flack parameter: 0.48 (3)

Table 1
Selected interatomic distances (Å).

C1*A*—C2*A*	1.33 (2)	C11*B*—N2*B*	1.441 (18)
C1*A*—N1*A*	1.37 (3)	N2*B*—C17*B*	1.47 (3)
C2*A*—C3*A*	1.31 (3)	N2*B*—C15*B*	1.48 (3)
C3*A*—C6*A*	1.40 (3)	C15*B*—C16*B*	1.50 (3)
C3*A*—C4*A*	1.47 (3)	C17*B*—C18*B*	1.44 (4)
C4*A*—C5*A*	1.33 (3)	C1*C*—C2*C*	1.32 (3)
C5*A*—N1*A*	1.30 (3)	C1*C*—N1*C*	1.37 (3)
N1*A*—C14*A*	1.51 (3)	C2*C*—C3*C*	1.31 (3)
C6*A*—C7*A*	1.27 (3)	C3*C*—C6*C*	1.40 (2)
C7*A*—C8*A*	1.43 (3)	C3*C*—C4*C*	1.48 (3)
C11*A*—N2*A*	1.45 (2)	C4*C*—C5*C*	1.33 (3)
N2*A*—C15*A*	1.46 (3)	C5*C*—N1*C*	1.31 (3)
N2*A*—C17*A*	1.49 (3)	N1*C*—C14*C*	1.50 (3)
C15*A*—C16*A*	1.54 (3)	C6*C*—C7*C*	1.26 (2)
C17*A*—C18*A*	1.55 (3)	C7*C*—C8*C*	1.42 (2)
C1*B*—C2*B*	1.33 (3)	C11*C*—N2*C*	1.446 (18)
C1*B*—N1*B*	1.37 (3)	N2*C*—C17*C*	1.46 (3)
C2*B*—C3*B*	1.31 (3)	N2*C*—C15*C*	1.47 (3)
C3*B*—C6*B*	1.44 (3)	C15*C*—C16*C*	1.47 (3)
C3*B*—C4*B*	1.47 (3)	C17*C*—C18*C*	1.54 (5)
C4*B*—C5*B*	1.33 (3)	P1—O4	1.45 (2)
C5*B*—N1*B*	1.31 (3)	P1—O3	1.530 (19)
N1*B*—C14*B*	1.464 (19)	P1—O1	1.63 (2)
C6*B*—C7*B*	1.30 (3)	P1—O2	1.657 (18)
C7*B*—C8*B*	1.454 (18)		

Because a regularly shaped crystal could not be obtained, and the faces could not be indexed adequately, our attempts to apply a numerical absorption correction were unsuccessful. Multi-scan absorption corrections were therefore used, contributing to the high *R* value (0.078) and the high standard uncertainties of bond lengths and angles (bonds: 0.016–0.04 Å; angles: 0.5–4.0°). For the same reasons, restraints and constraints were used in the refinement to control the geometry and displacement parameters of the atoms in the DEASP cations. Two reflections were partially obscured by the beam stop and were omitted from the refinement.

The systematic extinctions and the diffraction symmetry yielded two possible space groups, *viz.* *C*2/*c* and *Cc*. However, a reasonable structure model could only be established with space group *Cc*. In space group *C*2/*c*, only the PW12 anion and two fragmentary DEASP cations could be found, and no reasonable structural model could be established. The refinement of (I) was carried out on an inversion-twinned crystal, with refined volume fractions of 48.05 (15) and 51.95 (15)% for the two twin components, leading to a Flack parameter of 0.48 (3) (Irmer & Sheldrick, 1998; Britton & Brennessel, 2004; Glidewell *et al.*, 2004). All the H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$ for methyl H atoms and 1.2 $U_{\rm eq}$(C) for the other H atoms.

The highest peak in the difference map is 0.93 Å from W5 and the deepest hole is 1.18 Å from O3. Solvent-accessible voids of 1517.9 Å^3 (Spek, 2003), which could be occupied by approximately 14 molecules of DMF [approximate volume 103 Å^{-3} at 288 K (Hofmann, 2002)], from which the crystals were grown, seem to be empty. No DMF molecules could be confirmed in the difference map, which might be because the spaces are too constricted (*i.e.* dumb-bell-shaped) to accommodate DMF (Bajue *et al.*, 2003).

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

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