Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{iso}/B_{eq}†
I	0.99379 (7)	0.86848 (2)	0.04163 (7)	4.76 (3)†
Sn	1.28070 (6)	0.866838 (16)	−0.03950 (5)	3.103 (18)†
C11	1.2325 (8)	0.8953 (3)	−0.2603 (8)	3.29 (12)
C12	1.3543 (10)	0.8940 (3)	−0.3436 (9)	4.03 (14)
C13	1.3363 (11)	0.9106 (3)	−0.4900 (11)	4.87 (18)
C14	1.1945 (12)	0.9300 (4)	−0.5521 (12)	5.3 (2)
C15	1.0734 (11)	0.9341 (3)	−0.4714 (11)	4.98 (18)
C16	1.0933 (10)	0.9159 (3)	−0.3244 (10)	4.13 (15)
O1	1.4905 (8)	0.8756 (2)	−0.2654 (8)	5.56 (14)
C17	1.6229 (15)	0.8708 (5)	−0.3404 (14)	7.1 (3)
C21	1.3477 (10)	0.7939 (3)	−0.0366 (9)	4.07 (15)
C22	1.3760 (11)	0.7708 (3)	0.0985 (11)	4.65 (17)
C23	1.4250 (14)	0.7228 (4)	0.1051 (14)	6.4 (2)
C24	1.4406 (17)	0.7027 (5)	−0.0270 (18)	8.7 (4)
C25	1.4085 (18)	0.7229 (6)	−0.1589 (18)	8.8 (4)
C26	1.3603 (14)	0.7716 (4)	−0.1689 (14)	6.5 (3)
O2	1.3537 (8)	0.7957 (2)	0.2180 (8)	5.37 (14)
C27	1.3786 (17)	0.7744 (5)	0.3632 (17)	8.5 (3)
C31	1.4403 (8)	0.9075 (2)	0.1119 (8)	3.04 (11)
C32	1.4084 (9)	0.9552 (3)	0.1326 (9)	3.68 (13)
C33	1.5150 (11)	0.9830 (3)	0.2253 (11)	4.79 (17)
C34	1.6521 (12)	0.9635 (4)	0.2987 (12)	5.3 (2)
C35	1.6859 (11)	0.9168 (3)	0.2797 (11)	4.72 (17)
C36	1.5786 (9)	0.8887 (3)	0.1860 (8)	3.46 (13)
O3	1.2697 (7)	0.9699 (2)	0.0535 (7)	4.63 (12)
C37	1.2268 (13)	1.0184 (4)	0.0664 (12)	5.7 (2)

Table 2. *Selected geometric parameters* (Å, °)

I—Sn	2.713 (1)	O1—C17	1.436 (14)
Sn—C11	2.124 (7)	C22—O2	1.329 (12)
Sn—C21	2.147 (9)	O2—C27	1.425 (16)
Sn—C31	2.115 (7)	C32—O3	1.356 (10)
C12—O1	1.373 (11)	O3—C37	1.435 (12)
I—Sn—C11	101.7 (2)	Sn—C21—C22	118.6 (6)
I—Sn—C21	105.8 (2)	Sn—C21—C26	119.7 (7)
I—Sn—C31	110.3 (2)	C21—C22—O2	116.1 (8)
C11—Sn—C21	112.8 (3)	C23—C22—O2	123.8 (9)
C11—Sn—C31	113.6 (3)	C22—O2—C27	120.1 (9)
C21—Sn—C31	111.8 (3)	Sn—C31—C32	119.4 (5)
Sn—C11—C12	116.6 (5)	Sn—C31—C36	121.5 (5)
Sn—C11—C16	125.0 (6)	C31—C32—O3	113.8 (7)
C11—C12—O1	113.4 (7)	C33—C32—O3	125.9 (8)
C13—C12—O1	124.5 (8)	C32—O3—C37	118.0 (7)
C12—O1—C17	118.8 (8)		

Compound (2), m.p. 428-430 K, was prepared from (2-$MeOC_6H_5)_4Sn$ and I_2 in $CHCl_3$ and recrystallized from ethyl acetate/petroleum ether (b.p. 333-353 K) mixture.

Data collection and cell refinement: Nicolet *P*3 software. Data collection used ω scan rates of 1.0 ($I_p < 150$) to 29.3° ($I_p > 2500$) min^{-1} with a constant scan width of 0.6° and background counts taken at ±1° in ω, where I_p is the prescan intensity. Data reduction: local program (Aberdeen). Structure solution, structure refinement and preparation of material for publication: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Isotropic displacement parameters were used for all but the Sn and I atoms.

Lists of structure factors, anisotropic displacement parameters for Sn and I, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71539 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1066]

References

Calogero, S., Ganis, P., Peruzzo, V., Taliavini, G. & Valle, G. (1981). *J. Organomet. Chem.* **220**, 11–20.

Cody, V. & Corey, E. R. (1969). *J. Organomet. Chem.* **19**, 359–366.

Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Nowell, I. W., Taylor, O. J. & Wardell, J. L. (1989). *J. Chem. Soc. Perkin Trans.* **1**, pp. 2017–2022.

Cox, P. J., Doidge-Harrison, S. M. S. V., Nowell, I. W., Howie, R. A., Randall, A. P. & Wardell, J. L. (1990). *Inorg. Chem. Acta*, **176**, 155–161.

Doidge-Harrison, S. M. S. V. (1992). PhD thesis, RGIT, Aberdeen.

Forrester, A. R., Garden, S. J., Howie, R. A. & Wardell, J. L. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2615–2621.

Forrester, A. R., Howie, R. A., Ross, J. N., Low, J. N. & Wardell, J. L. (1991). *Main Group Met. Chem.* **14**, 293–304.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Harston, P., Howie, R. A., McQuillan, G. P., Wardell, J. L., Zanetti, E., Doidge-Harrison, S. M. S. V., Stewart, N. S. & Cox, P. I (1991). *Polyhedron*, **10**, 1085–1090.

Kolb, U., Dräger, M. & Jousseaume, B. (1991). *Organometallics*, **10**, 2737–2742.

Ochiai, M., Iwaki, S., Ukita, T., Matsuura, Y., Shiro, M. & Nagao, Y. (1988). *J. Am. Chem. Soc.* **110**, 4606–4610.

Zakharov, L. N., Petrov, B. I., Lebedev, V. A., Kuz'min, E. A. & Belov, N. V. (1978). *Kristallografiya*, **23**, 1049–1051.

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$[(C_5H_5N)_2H]_3[PW_{12}O_{40}]$

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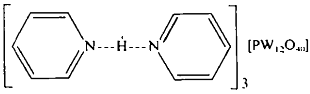
Abstract

The crystal structure of tris(dipyridinium) dodecatungstophosphate has been determined. The $[PW_{12}O_{40}]^{3-}$ heteropolyanion, having T_d symmetry, is disordered by the $\bar{3}$ symmetry. The pyridine molecules are paired around H^+ forming $(C_5H_5N)—H^+—(NC_5H_5)$ cations with their molecular planes almost parallel to the *ab* plane of the crystal.

Comment

The authors have reported previously that the anhydrous solid 12-tungsto- and molybdophosphates absorb polar organic solvents such as alcohols, ethers and amines, and that the very high catalytic activities of the aforementioned heteropolyacids, as solids, are explained by this phenomenon (pseudo-liquid phase) (Misono, Sakata, Yoneda & Lee, 1981; Misono, 1987). The metastable phases of $H_3PW_{12}O_{40}.n$(solvent) are observed with n = 3,6,(9) for various polar organic molecules (Misono *et al.*, 1982; Okuhara, Tatematsu, Lee & Misono, 1989) and their structures are closely related to the catalytic behaviour of heteropoly compounds (Lee *et al.*, 1992). Therefore, the elucidation of their structures is essential for the understanding of the catalysis and the catalyst. In the trial to detect the hexasolvated stage, the title compound (I) was obtained.



The crystal was prepared as follows: 2.0 g of almost anhydrous 12-tungstophosphoric acid (treated at 573 K for 3 h) was dissolved in 10 ml of pyridine (dehydrated with molecular sieve 3A); the precipitate formed was removed by decantation, and the solution was slowly evaporated at 353 K to obtain colourless hexagonal-plate crystals.

There are two possibilities for the space group of this crystal: $R3$ or $R\bar{3}$. When asymmetric $R3$ was assumed, (i) for the pyridine molecule, the molecular feature was largely distorted, interatomic distances and bond angles were unacceptable and anisotropic refinement was impossible for most of the atoms, and (ii) for the heteropoly anion, almost all O atoms could not be treated anisotropically. In assuming centrosymmetric $R\bar{3}$, these problems were overcome. For this reason, the centrosymmetric space group $R\bar{3}$ was selected though the orientation of the heteropolyanion shows disorder.

An *ORTEP*II (Johnson, 1976) view of the molecule is shown in Fig. 1. The Keggin anion, ideally having T_d symmetry (Keggin, 1933), lies on the crystallographic $\bar{3}$ symmetry element. The orientation of the heteropolyanion is disordered as a result of this symmetry. Each atom in the anion is located at its mean position, and O7 and O8 (O atoms in PO_4 site) are disordered with occupancies of 0.5 for their sites. The six pyridine molecules, surrounding the heteropolyanion, lie almost on one plane parallel to the *ab* plane of the unit cell. Each pyridine molecule is paired with another one facing its N atom at a distance of 2.68 (3) Å. This distance indicates that the N atoms are bound by hydrogen bonding; this pyridine pair can be regarded as a dipyridinium cation, $(C_5H_5N)—H^+—(NC_5H_5)$. Little interaction is present between the pyridine molecules and the heteropolyanion [with C—O distances 3.31 (5)-3.46 (3) Å]. Distances between unpaired pyridine molecules on the same plane [C—C 3.49 (6)-3.52 (6) Å] or between cation layers [3.43 (6) Å, $\frac{1}{3}$ of c axis] show that no interactions other than van der Waals contacts are formed between unpaired pyridine rings.

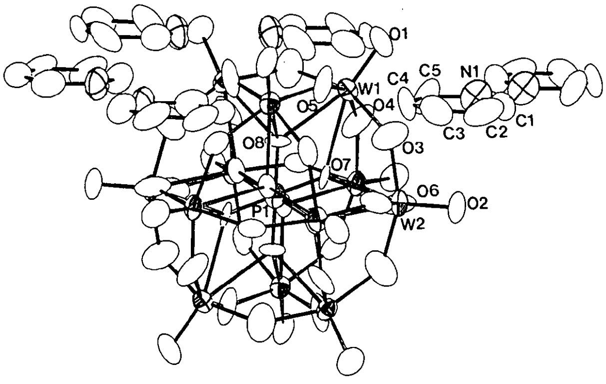


Fig. 1. An *ORTEP*II view of $[(C_5H_5N)_2H]_3[PW_{12}O_{40}]$.

Experimental

Crystal data

$[(C_5H_5N)_2H]_3[PW_{12}O_{40}]$
M_r = 3355.39
Rhombohedral (hexagonal setting)
$R\bar{3}$
a = 22.126 (2) Å
c = 10.290 (2) Å
V = 4377 (1) Å^3
Z = 3
D_x = 3.83 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.43-17.45°
μ = 24.264 mm^{-1}
T = 298 K
Hexagonal plate
0.15 × 0.15 × 0.10 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.43, $T_{\max}$ = 1.00
4630 measured reflections
3572 independent reflections

2447 observed reflections [$F \geq 3.0\sigma(F)$]
$\theta_{\max}$ = 35.1°
$h = -36 \rightarrow 36$
$k = 0 \rightarrow 36$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 200 reflections intensity variation: none

Refinement

Refinement on F
R = 0.057
wR = 0.056
S = 1.003
2447 reflections
141 parameters
$w = 1.2911/[\sigma^2(F) + 0.001152F^2]$
$(\Delta/\sigma)_{\max}$ = 0.002

$\Delta\rho_{\max}$ = 2.25 e Å^{-3}
$\Delta\rho_{\min}$ = −2.98 e Å^{-3}
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976) (C, H, N, O, P); *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) (W)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to solve structure: *UNICS*III (Sakurai & Kobayashi, 1979); *SHELXS*86 (Sheldrick, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
W1	0.09829 (3)	0.01295 (3)	0.28254 (6)	0.0266 (3)
W2	0.10631 (3)	−0.07850 (3)	0.00357 (6)	0.0294 (3)
P1	0	0	0	0.024 (3)
O1	0.1450 (7)	0.0184 (7)	0.411 (1)	0.057 (8)
O2	0.1563 (6)	−0.1153 (7)	0.006 (1)	0.062 (8)
O3	0.1077 (8)	−0.0537 (6)	0.176 (1)	0.062 (8)
O4	0.1664 (9)	0.0826 (6)	0.173 (1)	0.071 (9)
O5	0.0081 (6)	−0.0642 (6)	0.324 (2)	0.08 (1)
O6	0.1733 (9)	0.0172 (6)	−0.030 (1)	0.072 (10)
O7	0.0684 (9)	0.0080 (8)	0.051 (2)	0.023 (8)
O8	0	0	0.148 (3)	0.023 (10)
N1	0.2166 (8)	0.3159 (9)	0.336 (2)	0.062 (9)
C1	0.282 (1)	0.368 (1)	0.335 (2)	0.07 (1)
C2	0.338 (1)	0.356 (2)	0.334 (3)	0.08 (2)
C3	0.325 (1)	0.290 (2)	0.332 (3)	0.09 (2)
C4	0.261 (2)	0.239 (1)	0.333 (3)	0.09 (2)
C5	0.206 (1)	0.251 (1)	0.332 (2)	0.07 (1)

Table 2. *Contact distances* (Å)

N1···N1^{i}	2.68 (3)	C2···O2^{iv}	3.31 (5)
C2···C3^{ii}	3.49 (6)	C5···O1^{v}	3.39 (3)
C2···C2^{ii}	3.52 (6)	C5···O3^{vi}	3.34 (3)
C1···O1^{iii}	3.42 (3)	C5···O6^{vii}	3.45 (3)
C1···O3^{iii}	3.46 (3)		

Symmetry codes: (i) $\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$; (ii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iii) $\frac{1}{3} + y, \frac{2}{3} + y - x, \frac{2}{3} - z$; (iv) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (v) $x - y, x, 1 - z$; (vi) $-y, x - y, z$; (vii) $x - y, x, -z$.

All refinement calculations were carried out on a HITAC M680H computer at the Institute for Molecular Sciences, Myodaiji, Okazaki, Aichi 444, Japan

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71542 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1071]

References

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Keggin, J. F. (1933). *Nature* (*London*), **131**, 908-909.

Lee, K. Y., Arai, T., Nakata, S., Asaoka, S., Okuhara, T. & Misono, M. (1992). *J. Am. Chem. Soc.* **114**, 2836-2842.

Misono, M. (1987). *Catal. Rev. Sci. Eng.* **29**, 269-321.

Misono M., Mizuno, N., Katamura, K., Kasai, A., Konishi, Y., Sakata, K., Okuhara, T. & Yoneda, Y. (1982). *Bull. Chem. Soc. Jpn*, **55**, 400-406.

Misono, M., Sakata, K., Yoneda, Y. & Lee, W. Y. (1981). *Proceedings of the 7th International Congress on Catalysis*, pp. 1047-1059. Kodansha: Elsevier.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. T. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351-359.

Okuhara, T., Tatematsu, S., Lee, K. Y. & Misono, M. (1989). *Bull. Chem. Soc. Jpn*, **62**, 717-723.

Sakurai, T. & Kobayashi, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69-77.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

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C—H···I⁻ Interactions in Ferrocene Derivatives: Structures of (Ferrocenylmethyl)triphenylphosphonium Iodide and 1,1′-Ferrocenediylbis(methyltriphenylphosphonium Iodide) Dichloromethane Solvate (1/1)

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Abstract

The cations in (ferrocenylmethyl)triphenylphosphonium iodide, $[\{(C_5H_5)Fe(C_5H_4)\}CH_2P(C_6H_5)_3]^+.I^-$, (1), and in 1,1′-ferrocenediylbis(methyltriphenylphosphonium iodide) dichloromethane solvate, $[Fe\{(C_5H_4)CH_2P(C_6H_5)_3\}_2]^{2+}.2I^-.CH_2Cl_2$, (2), are involved in three-dimensional networks of C—H···I⁻ interactions between phenyl C—H groups and I⁻ anions. In (1), the cation resides in a general position while one I⁻ anion is on a twofold axis and a second I⁻ anion is at an inversion centre. The shortest C···I⁻ distances are 3.886 (2) and 3.989 (2) Å to the I⁻ ion which resides on an inversion centre. The cation in (2) has approximate mirror symmetry and lies in a general position in the unit cell along with its two I⁻ anions. The shortest C···I⁻ interactions are 3.810 (4) and 3.886 (5) Å.

Comment

Current interest in structural ferrocene chemistry focuses on a wide variety of derivatives which may have potential applications in (*a*) charge-transfer chemistry (Moore

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