Photochemical Synthesis, Properties and X-Ray Crystal Structure of Tetrabutylammonium Dodecamolybdophosphate Heteropoly Blue

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The title heteropoly blue, $(Bu_4N)_6H_{10}[PMo^{VI}_{11}Mo^{V}O_{40}]_4\cdot H_2O$ has been photochemically synthesized and characterized with elemental analysis, solid diffusion reflectance electronic spectra, CV, ESR, XPS, IR spectra, conductivity measurement and X-ray single crystal analysis. The crystallographic data for $C_{96}H_{218}Mo_{48}N_6O_{169}P_4$ are as follows: $M_r = 8889.76$, triclinic, $P\bar{1}$, $a = 1.4142(3)$ nm, $b = 2.6027(5)$ nm, $c = 2.6403(5)$ nm, $\alpha = 113.96(3)°$, $\beta = 90.05(3)°$, $\gamma = 105.71(3)°$, $V = 8.481(3)$ nm^3, $Z = 1$, $D_c = 1.741$ g/cm^3, $F(000) = 4264$, $\mu = 1.798$ mm^{-1}. The X-ray crystal structure analysis reveals that there is one independent molecule in the unit cell of the title heteropoly blue which contains four mixed-valence heteropoly anions, six tetrabutylammonium cations and one water molecule. Its molecular structure possesses a centrosymmetrical arrangement in the unit cell. The phosphorus atom is in the crystallographic inversion center of the heteropoly anion and the eight oxygen atoms surrounding central phosphorus atom comprise of a distorted hexahedron. Heteropoly anion has two equal sets of PO_4 tetrahedron. The PO_4 tetrahedron and the MoO_6 octahedron in the polyanion are greatly distorted.

Keywords tetrabutylammonium dodecamolybdophosphate heteropoly blue, photosensitive agent, photochemical reduction, crystal structure characterization

Heteropoly blue is the reduced product of the polyoxometalates. It has attracted much attention because of its novel structure, unique properties and potential applications in the fields of catalysis, pharmaceutical chemistry and functional materials.[1-3] At early stage, heteropoly blue was prepared by chemical reduction method.[4] This method has some disadvantages, *e.g.*, impurities are difficult to be separated from products. In 1990s, electrolytic reduction method was developed.[5] But this method still has disadvantages, such as long preparation period, harsh condition and difficulty in controlling. Compared to the methods mentioned above, photochemical synthesis has more advantages, such as moderate reaction condition, high selectivity and high conversion.[6] This paper reports the photochemical synthesis, the spectral properties and X-ray crystal structure of dodecamolybdophosphate heteropoly blue.

Experimental

Materials and measurements

All chemicals were of analytical grade. The contents of P and Mo were determined by a Leeman-8410 ICP. The C, H and N analyses were determined with a PE-240 instrument. The water content was determined by thermogravimetric analysis (TGA) on a P-E TG 7

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thermal analysis system, with a heating rate of 10° min^{-1}. The IR spectrum was recorded on a PerKin-Elmer spectrum type I FT-IR spectrophotometer with KBr pellet. The solid reflectance spectrum measurement was made on a UV2501 PC spectrophotometer. ESR spectra were taken on a JES-FE-3AX spectrometer, and the X wave band was selected. The cyclic voltammetry was carried out on a BAS-100A electochemical analyzer. The XPS was performed on a KRATOS XSAM800 X-ray photoelectron spectroscopy, with Mg K_α 1253.6 eV as excitation source and $C(1s) = 285.0$ eV as energy reference. The conductivity was measured on a SZ-82 digital four-probe instrument. The crystal data were collected by a Siemens P4 four-circle diffractometer and the structure of the crystal was solved using the SHELXTL-PLUS program system.

Preparation of the heteropoly blue

$H_3PMo_{12}O_{40} \cdot 5H_2O$ (1.00 g, 0.1566 mmol) was dissolved in 50 mL of *N*,*N*-dimethyl formamide (DMF) and then $(n\text{-Bu})_4NBr$ (0.3 g, 0.9306 mmol) was added. The mixture was stirred at room temperature for 24 h under the radiation of 450-W Hg lamp ($\lambda < 400$ nm) and further distilled under reduced pressure at room temperature. The gray-green solid obtained was washed by warm water, alcohol and ether for three times, respectively. After recrystallization from DMF and drying over for 24 h, the gray-green crystals of the title compound $(Bu_4N)_6H_{10}[PMo^{VI}_{11}Mo^{V}O_{40}]_4 \cdot H_2O$ were obtained in 72% yield. Anal. calcd for $C_{96}H_{218}Mo_{48}N_6O_{169}P_4$: C 12.96, H 2.45, N 0.94, P 1.3, Mo 51.84; found C 12.72, H 2.42, N 0.98, P 1.21, Mo 50.03.

X-ray crystal structure analysis

A crystal (0.50 nm × 0.44 nm × 0.40 nm) was mounted on the Siemens P4 four-circle diffractometer with graphite monochromated Mo K_α radiation (λ = 0.071073 nm) using $\omega - 2\theta$ scan mode at 18 ℃. From a total of 20,727 independent reflections measured for $1.51 \leqslant \theta \leqslant 21.00°$, 17,374 $[I \geqslant 2\sigma(I)]$ were used for the determination and the refinement of the structure. All intensity data are corrected by empirical absorption. The structure was solved by direct methods using the SHELXTL-PLUS procedure. The refinement was completed by full-matrix least-squares methods for 17,374 parameters which weighted and converged to the final $R = 0.0627$, $wR = 0.1629$, $w = 1/[\sigma^2(F_0^2) + (0.1001P)^2]$, $P = \max(F_0^2 + 2F_c^2)/3$, $S = 1.036$, $(\triangle/\sigma)_{\max} = 0.014$. The maximum and minimum peaks in the final difference Fourier map are 1265 e/nm^3 and − 826 e/nm^3, respectively. All calculations were performed on a PC-486 computer, using SHELXL PC program system.

Results and discussion

IR spectrum

The IR data of the title compound and the mother heteropoly acid are listed in Table 1, respectively.

Comparing the IR spectrum of the title compound with that of the heteropoly acid, we find that the characteristic vibrational bands of the four metal oxygen bonds have red shifts or blue shifts, showing weakening or strengthening of the corresponding bonds, respectively. The vibrational bands of $P—O_a$ and $Mo = O_d$ have red shifts of 2.11 cm^{-1} and 4.61 cm^{-1}, respectively, and those of $Mo—O_{b(c)}—Mo$ bands have blue shifts of 10.43 cm^{-1} and 16.52 cm^{-1}. As mentioned above, we conclude that the heteropolyanions maintain the Keggin structure of the mother heteropolyacid in spite of some structural distortions.

Electronic spectra

The solid diffusion reflectance electronic spectra of

Table 1 IR data of the title compound and the mother heteropoly acid (cm^{-1})

Compound	$\nu_{C=O}$	ν_{C-N}	δ_{C-N}	$\nu_{as}(P-O_a)$	$\nu_{as}(Mo=O_d)$	$\nu_{as}(Mo-O_{b(c)}-Mo)$
$H_3PMo_{12}O_{40}$				1065	960	870, 790
$(Bu_4N)_6H_{10}[PMo_{12}O_{40}]_4 \cdot H_2O$	1676	1471	1381	1063	955	880, 807

Table 2 XPS data of the title complex and the mother heteropoly acid (eV)

Compound	O_{1s}	P_{2p}	Mo_{3d}	N_{1s}
$H_3PMo_{12}O_{40}$	531.86	134.80	233.49	
$(Bu_4N)_6H_{10}[PMo_{12}O_{40}]_4 \cdot H_2O$	531.82	134.52	233.40	402.12

the complex were measured at room temperature. A new characteristic broad peak at 793 nm is assigned to the intervalence absorption of Mo(V) → Mo(VI) of $PMo_{12}O_{40}^{4-}$, which indicates that electron transfer occurs in the DMF and heteropoly anion, converting $PMo_{12}O_{40}^{3-}$ to the mixed valence heteropoly blue $PMo_{12}O_{40}^{4-}$.[7]

ESR

Based on the ESR data of the title complex at 77 K, we calculated the $g_{\parallel}$ to be 1.939 and $g_{\perp}$ 1.958, which are in accordance with those of the reduced α-$PMo_{12}O_{40}^{4-}$ *i.e.*, $g_{\parallel} = 1.938$ and $g_{\perp} = 1.949$.[8,9] The ESR results verified the formation of the mixed valence heteropoly blue.

XPS

The XPS data of the title complex and the mother heteropoly acid are shown in Table 2. It can be seen that the binding energy of the inner electrons of O_{1s}, P_{2p} and Mo_{3d} atoms underwent a little bit change. Therefore, we can deduce that there is only slight structural difference between $H_3PMo_{12}O_{40}$ and $(Bu_4N)_6H_{10}[PMo_{12}O_{40}]_4 \cdot H_2O$. Compared with the mother heteropoly acid, the binding energies of O_{1s}, P_{2p} and Mo_{3d} decreased 0.04 eV, 0.28 eV and 0.09 eV respectively, due to the increase of the charge density of the reduced heteropoly anions.

CV

The cyclic voltammetry of the title compound was measured in DMF using 0.1 mol/L of $KClO_4$ as supporting electrolyte. The sample concentration is 1.0×10^{-4} mol/L. The scanning speed is 100 mV/s. Only one oxidation peak appeared at 869 mV, while no reduction peak existed, indicating that the compound underwent an irreversible single electron oxidation process. In other words, there exists the mixed valence state in the compound.

Reaction mechanism

The heteropoly compound possesses photosensitivity, since photoelectron transfer reaction occurred in 12-molybdenum phosphoric acid and dimethyl formamide. When the sample was irradiated by a 450-W Hg lamp or sunlight, organic solvent molecule was oxidized and heteropoly anion was reduced to be heteropoly blue. In the reflectance electronic spectra of the title compound, a new adsorption band appeared at *ca*. 793 nm, which corresponds to a characteristic band of $PMo_{12}O_{40}^{4-}$ polyanion. The ESR spectra of the gray-green crystal of the title compound at 77 k was determined to be $g = 1.95$ which is ascribed paramagnetic signal of the Mo(V). The α-Keqgin structure anion is known to exist in three valence states, *i.e.*, III, IV and V. A cyclic voltammetry of the title compound in DMF has only one oxidation peak at 869 mV and has no corresponding reduction peak. This indicates that the compound corresponds to a one-electron oxidation. According to the results, the reaction mechanism is proposed as follows, namely, pseudo-first-order "photochemical reduction and electrochemical oxidation" electron transfer mechanism between $PMo_{12}O_{40}^{3-}$ and DMF (Eqs. C and E).[10]

$$C:\ PMo_{12}O_{40}^{3-} + DMF \xrightarrow{h\nu} PMo_{12}O_{40}^{4-} + DMF^{+}$$
$$E:\ PMo_{12}O_{40}^{4-} \rightleftharpoons PMo_{12}O_{40}^{3-} + e$$

Conductivity

The powder of the title compound was tabletted to 0.1 mm thickness under 600 kg pressure. The conductivity was measured by four-probe method, using 0.5 mm diameter tungsten carbide probe, 1 mm probe spacing, and 100 mA measurement current. The conductivity of the title compound is 4.14×10^{-1} S/cm at room temperature, which indicates that it is a semiconductor.

Crystal structure of the title compound

The coordinates and thermal parameters of selected non-hydrogen atoms, bond lengths and bond angles are listed in Tables 3, 4 and 5, respectively. The crystal structure of the title compound and its molecular packing are shown in Figs. 1 and 2, respectively. Fig. 1 shows that the compound consists of six tetrabutylammonium cations, four 12-molybdophosphate anions and one H_2O molecule. The central phosphorus atom is connected with eight disordered oxygen atoms shown in four full lines and four dotted lines. The coordination number of phosphorus atom is four and the occupancy of each oxygen atom is 1/2. The P—0_a bond length of the PO_4 unit range from 0.140 nm to 0.161 nm. The average lengths of P—0_a of the four PO_4 units are 0.156 nm, 0.155 nm, 0.155 nm and 0.154 nm, respectively. The phosphorus atom is in the crystallographic inversion center of the heteropoly anion. The distortion of the hexahedron consists of the eight oxygen atoms, which surround the central phosphorus atom.

PO_4 tetrahedron unit distorted the tetrahedron structure. Tables 4 and 5 presented the selected bond distances and selected bond angles. The bond lengths of Mo = 0_d range from 0.1630(13) nm to 0.1698(13) nm with an average value of 0.1656 nm. The longest bond value of Mo—0_a is an average value of 0.2428 nm range from 0.230(2) nm to 0.250(2) nm. The bond length of Mo—$0_{b(c)}$—Mo range from 0.178(2) nm to 0.200(2) nm, which are shorter than those of common bonds (0.242 nm), demonstrating the increase of the bond energy of the bridging oxygen and the change of the bond angles. The bond angle of Mo-0_b-Mo range from 137.9(7)° to 141.0(8)° which are 12.1—9.0° smaller than that of unreduced Mo-0_6-Mo (150°). The Mo-0_c-Mo bond angles range from 91.2(7)° to 96.5(8)°, which are 28.8°—23.5° smaller than that of unreduced Mo-0_c-Mo (120°). It can be concluded from the above data that there are significant distortions in MoO_6 octahedron and in the overall skeleton of the heteropoly anions. The MoO_6 octahedral unit is also greatly distorted.

Table 3 Coordinates (× 10^4) and thermal parameters (× 10 nm^2) of some non-hydrogen atoms

Atom	*x*	*y*	*z*	*U*(eq)
Mo(1)	5642(1)	1543(1)	405(1)	40(1)
Mo(2)	7213(1)	942(1)	907(1)	47(1)
Mo(3)	3399(1)	800(1)	747(1)	40(1)
Mo(10)	7599(1)	9201(1)	4253(1)	40(1)
Mo(11)	9098(1)	8457(1)	4595(1)	40(1)
Mo(12)	11271(1)	9058(1)	4092(1)	47(1)
Mo(13)	11337(1)	9304(1)	5524(1)	45(1)
Mo(14)	8077(1)	9433(1)	5667(1)	40(1)
Mo(15)	9626(1)	9579(1)	3536(1)	47(1)
Mo(16)	12655(1)	4344(1)	4165(1)	50(1)
Mo(18)	14743(1)	5064(1)	3690(1)	60(1)
Mo(20)	16965(1)	5901(1)	4628(1)	67(1)
P(1)	5000	0	0	33(2)
P(4)	15000	5000	5000	50(2)
O(3)	8204(8)	1407(5)	1350(5)	63(4)
O(6)	2722(9)	1206(6)	1131(5)	62(4)
O(7)	5946(10)	2249(5)	551(5)	71(4)
O(13)	7595(11)	867(8)	233(5)	89(5)
O(16)	4597(9)	1434(5)	791(5)	60(4)
O(17)	12006(8)	8987(6)	5746(5)	59(4)
O(18)	7136(10)	9182(6)	5963(6)	75(4)
O(19)	13554(9)	4554(5)	3665(5)	62(4)
O(20)	8439(9)	8791(6)	5272(5)	58(4)
O(21)	10320(11)	9098(5)	3572(7)	93(6)
O(24)	3063(8)	691(5)	38(5)	59(4)
O(26)	14197(8)	5702(5)	4192(5)	53(3)
O(27)	6508(8)	8795(5)	3879(5)	59(4)
O(28)	10033(9)	8511(8)	4138(5)	96(6)
O(30)	7666(11)	9936(6)	4352(6)	86(5)
O(32)	6529(11)	1500(7)	870(6)	87(5)
O(33)	12035(11)	9777(6)	4166(6)	79(4)
O(38)	10886(11)	10205(7)	3765(6)	91(5)
O(42)	16823(13)	4180(7)	4487(7)	104(5)
O(43)	15443(13)	4561(8)	3528(7)	112(6)
O(48)	16567(11)	6463(7)	5181(6)	89(5)
O(49)	15181(12)	3688(7)	3792(7)	102(5)
O(52)	16708(13)	6464(7)	278(7)	105(5)
O(55)	16747(12)	6312(7)	6087(7)	99(5)
O(63)	14062(15)	4473(9)	4732(8)	40(6)
O(65)	16021(14)	5708(8)	4069(8)	118(6)
O(68)	16928(10)	4022(6)	3405(6)	72(4)
O(69)	17899(10)	6292(6)	4456(6)	71(4)
O(75)	11738(11)	9131(6)	4764(6)	80(4)
O(81)	10547(15)	9875(9)	4455(8)	38(6)
O(83)	15397(14)	4916(8)	521(8)	32(5)
O(84)	15492(15)	5078(9)	4478(8)	38(6)
O(87)	14303(15)	4974(9)	361(8)	39(6)
O(88)	14312(16)	5025(9)	4634(9)	43(6)
N(1)	11307(12)	6813(7)	265(7)	72(5)
N(3)	4133(14)	3018(8)	1878(8)	85(6)
N(5)	20512(12)	6815(7)	5272(7)	72(5)
OW	18086(14)	5010(8)	− 2502(8)	127(6)

Table 4 Selected bond lengths (nm)

Mo(1)—O(7)	0.1643(12)	Mo(4)—O(25)	0.167(11)
Mo(1)—O(32)	0.180(2)	Mo(4)—O(15)	0.182(13)
Mo(1)—O(16)	0.1824(12)	Mo(4)—O(34) #1	0.198 (14)
Mo(1)—O(12)	0.200(12)	Mo(4)—O(53)	0.249(2)
Mo(1)—O(22)	0.1998(12)	Mo(4)—O(12)	0.179(14)
Mo(1)—O(53)	0.240(2)	Mo(4)—O(13)	0.200(12)
Mo(2)—O(3)	0.1651(13)	Mo(4)—O(78) #1	0.250(2)
Mo(2)—O(31)	0.1798(14)	Mo(5)—O(2)	0.1682(13)
Mo(2)—O(13)	0.1780(13)	Mo(5)—O(35)	0.181(2)
Mo(2)—O(23) #1	0.197 (12)	Mo(5)—O(31) #1	0.1987(14)
Mo(2)—O(32)	0.199(2)	Mo(5)—O(22)	0.1788(12)
Mo(2)—O(86)	0.247(2)	Mo(5)—O(24)	0.1981(12)
Mo(2)—O(53)	0.247(2)	Mo(5)—O(86) #1	0.238(2)
Mo(3)—O(34)	0.1817(14)	Mo(6)—O(23)	0.182(12)
Mo(3)—O(16)	0.1980(14)	Mo(6)—O(35)	0.198(2)
Mo(3)—O(85)	0.249(2)	Mo(6)—O(86) #1	0.249(2)
Mo(3)—O(6)	0.165(14)	Mo(6)—O(1)	0.1641(13)
P(1)—O(78)	0.157(2)	Mo(6)—O(39)	0.182(2)
P(1)—O(53)	0.155(2)	Mo(6)—O(15)	0.197(13)
P(1)—O(86)	0.158(2)	Mo(6)—O(86) #1	0.249(2)
P(1)—O(85) #1	0.147(2)	P(1)—O(78) #1	0.158(2)
Mo(3)—O(24)	0.1819(11)	P(1)—O(53) #1	0.157(2)
Mo(3)—O(39) #1	0.200(2)	P(1)—O(86) #1	0.158(2)
Mo(3)—O(78)	0.237(2)	P(1)—O(85)	0.149(2)

Table 5 Selected bond angles (°)

O(78) #1-P(1)-O(53) #1	106.4(10)	Mo(9)-O(11)-Mo(7)	140.2(8)
O(78) #1-P(1)-O(53)	73.6(11)	Mo(4)-O(15)-Mo(6)	140.6(10)
O(53) #1-P(1)-O(53)	180.000(4)	Mo(9)-O(40)-Mo(22)	136.3(7)
O(78)-P(1)-O(86) #1	106.8(11)	Mo(23) #2-O(44)-Mo(24)	138.8(1)
O(53)-P(1)-O(86) #1	107.2(11)	Mo(1)-O(53)-Mo(4)	93.8(7)
O(78)-P(1)-O(86)	73.2(11)	Mo(4)-O(53)-Mo(2)	91.9(7)
O(53) #1-P(1)-O(86)	107.2(11)	Mo(7) #2-O(66)-Mo(24) #2	95.1(8)
O(78) #1-P(1)-O(85)	112.2(11)	Mo(8)-O(59)-Mo(24) #2	96.5(8)
O(53) #1-P(1)-O(85)	112.2(11)	Mo(16)-O(61)-Mo(17)	138.8(8)
O(86) #1-P(1)-O(85)	68.3(12)	Mo(17) #4-O(64)-Mo(19) #4	96.3(8)
O(78) #1-P(1)-O(85) #1	67.8(11)	O(7)-Mo(1)-O(32)	103.3(8)
O(53) #1-P(1)-O(85) #1	67.8(11)	O(32)-Mo(1)-O(16)	96.8(7)
O(86) #1-P(1)-O(85) #1	111.7(12)	O(32)-Mo(1)-O(12)	86.7(6)
O(78) #1-P(1)-O(86)	106.8(11)	O(16)-Mo(1)-O(22)	86.1(6)
O(78)-P(1)-O(85) #1	113.0(10)	O(7)-Mo(1)-O(53)	158.9(7)
O(86)-P(1)-O(85)	112.2(11)	O(7)-Mo(1)-O(12)	101.2(7)
O(78)-P(1)-O(53)	106.4(11)	O(16)-Mo(1)-O(12)	154.3(6)
O(53)-P(1)-O(85) #1	112.2(11)	O(32)-Mo(1)-O(22)	154.0(7)
O(85)-P(1)-O(85) #1	180.000(3)	O(12)-Mo(1)-O(22)	80.0(6)
Mo(4)-O(12)-Mo(1)	140.6(9)	O(32)-Mo(1)-O(53)	64.6(7)
Mo(1)-O(53)-Mo(4)	93.8(7)	O(12)-Mo(1)-O(53)	62.4(7)
Mo(16)-O(63)-Mo(19) #4	94.3(8)	O(3)-Mo(2)-O(31)	103.5(7)
Mo(3)-O(78)-Mo(4) #1	94.0(7)	O(31)-Mo(2)-O(23) #1	86.2(6)
Mo(10)-O(76)-Mo(14)	139.5(8)	O(86)-Mo(2)-O(53)	44.6(7)

#1: $-x+1$, $-y$, $-z$; #2: $-x+3$, $-y+1$, $-z$; #3: $-x+2$, $-y+2$, $-z+1$; #4: $-x+3$, $-y+1$, $-z+1$.

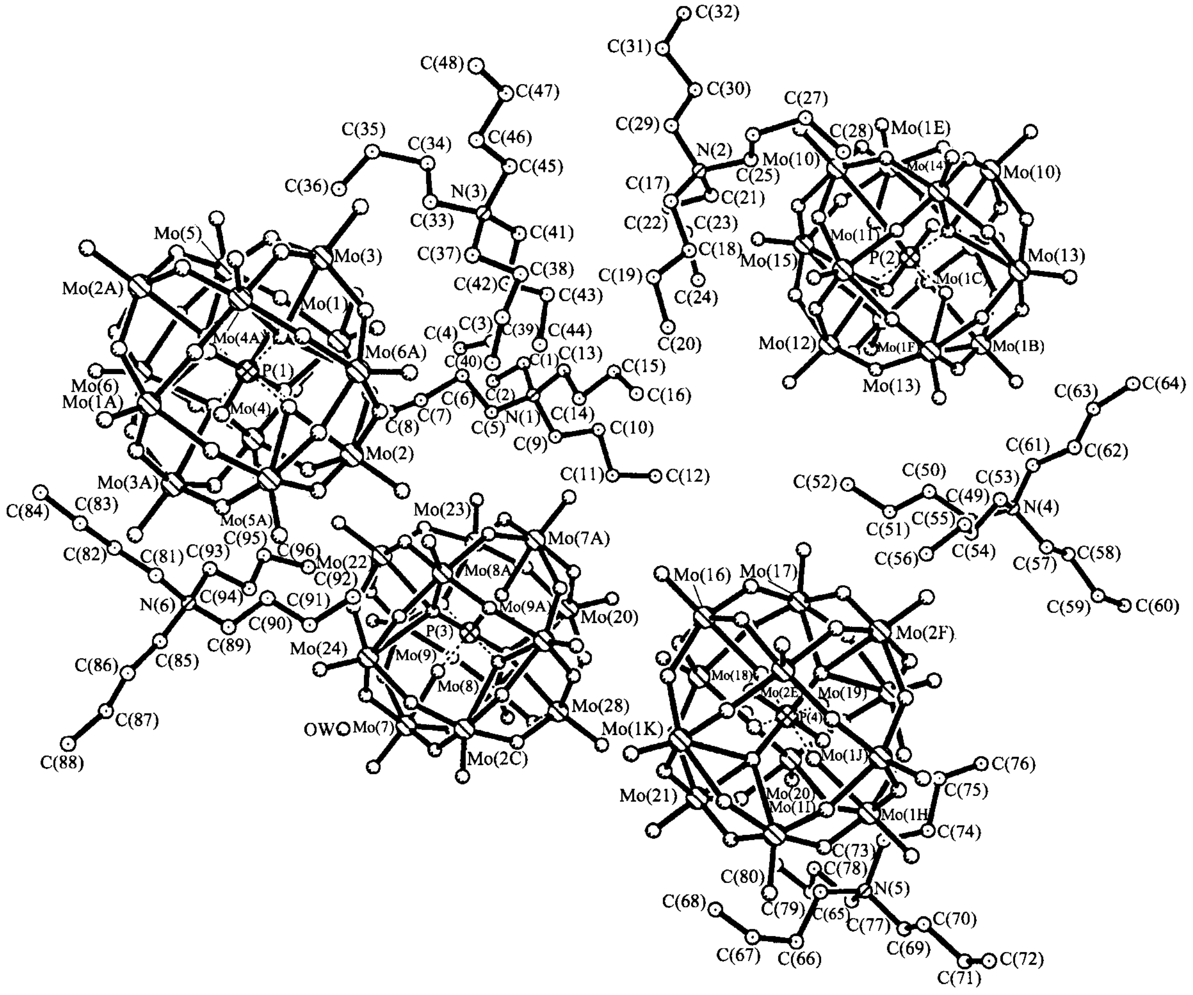

Fig. 1 Molecular structure of the title compound.

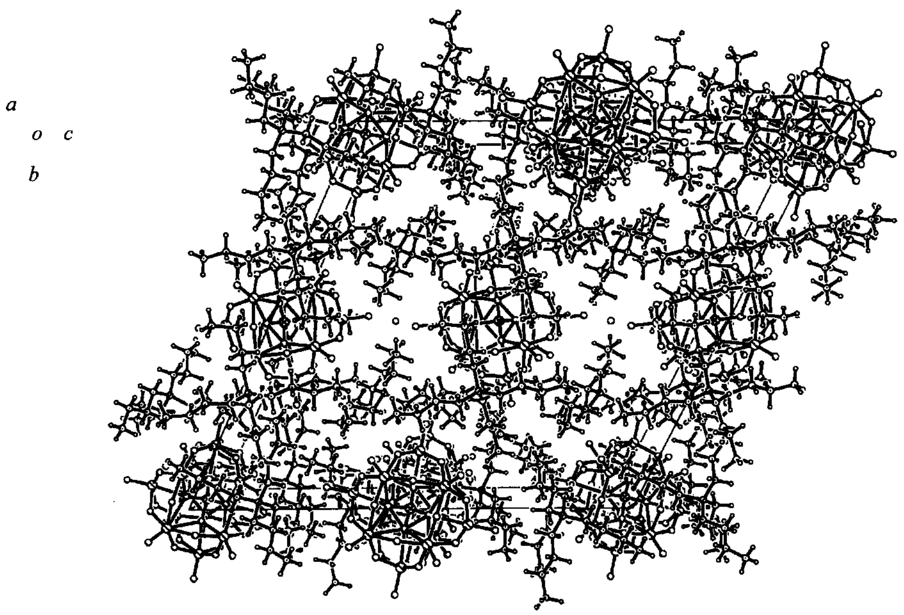

Fig. 2 Molecular packing of the title compound in the unit cell.

References

1 Pope, M. T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlay, New York, **1983**, p. 101.

2 Muller, A.; Peters, F.; Pope, M. T. *Chem. Rev*. **1998**, *98*, 239.

3 Pope, M. T. *Mixed-Valence Compounds*, NATO-ASI Ser. Ed.; Brown C. D. B., Reidel Dordrecht, **1980**, p. 365.

4 Wang, E.-B.; Hu, C.-W.; Xu, L. *Introduction of Polyoxometalates Chemistry*, Chemical Industry, Beijing, **1998**, p. 83 (in Chinese).

5 Wang, E.-B.; zhang, L.-C.; Shen, E.-H.; Wang, Z.-P. *Sci. in China* (*B*) **1992**, *7*, 673 (in Chinese).

6 Kang, X.-H.; Liu, M.-Q. *Principle and Application of Photochemistry*, Yianjin University press, Tianjin, **1995**, p. 258 (in Chinese).

7 Zhang, X.-M.; Shen, B.-Z.; You, X.-Z. *Polyhedron* **1997**, *16*, p. 95.

8 Sanchez, C.; Livage, J.; Launag, P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc*. **1982**, *104*, 3194.

9 So, H.; Pope, M. T. *Electron Hopping and Delocalization in Mixed-Valence Matal-Oxygen Clusters*, Elsevier Science, Germany, **1992**, p. 71.

10 Bond, A. M.; Way, D. M.; Wedd, A. G.; Compton, A. G.; Booth, J.; Eklund, J. C. *Inorg. Chem*. **1999**, *34*, 3378.

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