Hydrothermal Synthesis and Structure of a Mixed Valent Heteropoly-oxometallate Keggin Salt: $[PMo_{4.27}W_{7.73}O_{40}^{6-}]\,[H_3N(CH_2)_6NH_3^{2+}]_3$

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The polyoxometallate Keggin (α type) $[PMo_{4.27}W_{7.73}O_{40}^{6-}]$ $[H_3N(CH_2)_6NH_3^{2+}]_3$, involving molybdenum and tungsten present in both V and VI oxidation states, has been synthesized under hydrothermal conditions and its structure determined by single crystal X-ray analysis. Black platelet crystals are formed in the monoclinic system, space group $C2/m$ (No. 12), $a = 10.336(9)$, $b = 20.097(5)$, $c = 13.276(6)$ Å, $\beta = 106.41(7)°$, $V_{cell} = 2645(3)$ Å^3, $Z = 8$, $d_{calc} = 3.555$ Mg m^{-3} (Cu$K\alpha$ radiation, $2\theta_{max} = 144°$, $R(F) = 6.56$ for 1729 reflections). Due to its location at the origin (2/m site), the anion is found to be disordered, its four independent metal sites occupied with molybdenum and tungsten atoms; a significant preferred localization of the molybdenum on two sites is also reported. The structure has a lamellar organization formed from alternating organic–inorganic planes with their normal parallel to *c*. A study by ESR has proven the presence of paramagnetic Mo/W(V) in the compound with the observation of a strong signal ($g = 1.983$). © 1997 Academic Press

INTRODUCTION

Heteropoly-oxometallates of the molybdenum and tungsten (1, 2), such as the Keggin ion $M_{12}XO_{40}^{n-}$ and the Dawson ion $M_{18}X_2O_{62}^{m-}$ ($X = P$; $M = Mo, W$; $n = 3, 4$; $m = 6$), have been thoroughly studied (3), are being used as catalysts (4), and in the case of mixed Mo/W polyoxometallates were used as intermediates in the low temperature synthesis of Mo/W alloys (5). The heteropolyanions of the Dawson-type structure are formed spontaneously in molybdophosphate solutions of the appropriate stoichiometry and acidity, but the tungstate only form slowly in solutions with a large excess of phosphate. Molybdenum, being well known for its ability to assume many different oxidation states, has been shown to form numerous molybdenum phosphates involving Mo(III), Mo(IV), Mo(V), and Mo(VI)

species (6, 7). In addition, the introduction of hydrothermal conditions has recently lead to the synthesis of new condensed phases, such as WO$_3$ pyrochlores (8), sodium tungstates (9), layered molybdate (10), and Keggin species (11–13), and has allowed Hölscher *et al.* (14) to obtain a mixed organic–inorganic open framework material containing a reduced Dawson-type anion, viz. $[H_3N(CH_2)_6NH_3]_4[W_{18}P_2O_{62}] \cdot 3H_2O$. Since we were unable to prepare the analogous Mo compound of the latter, we examined whether such Dawson ion compounds containing both Mo and W could be prepared. We carried out the hydrothermal synthesis with 1,6-hexanediamine, but produced instead a dense Keggin anion compound containing both metals as well as the amine. In this article, we describe the structure of this novel material and compare it to results reported by Leclaire *et al.* (12) concerning an hydrothermal synthesis, under similar conditions, of the mixed valent Keggin polyoxometallate involving molybdenum and tungsten, $K_6Mo_3W_9PO_{40}$.

EXPERIMENTAL

Hydrothermal Preparation

MoO$_3$/WO$_3$ (Fluka, ratio 4:4), Mo metal/W metal (Kochlight, ratio 0.5:0.5), 1,6-hexanediamine (Aldrich), H$_3$PO$_4$ (Ranbaxy), and double distilled water were mixed together for 1 h in a 150 ml Teflon beaker in molar ratios of 8:1:27:42:4400. The resulting pale blue colored solution (pH 2) was then placed in an autoclave (150 ml, Parr bomb) and maintained for 4 days at 200 °C. The resulting products were washed with distilled water, filtered from the mother liquor (ending pH 3, black color) and air dried. The sample was multiphasic, containing a minor proportion of yellow microcrystalline bronze (13) and highly cleavable shiny black platelets. The latter were isolated for structural and compositional characterization.

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Characterization and Analysis

FT-IR spectra were recorded with 4 cm^{-1} resolution on a Nicolet Magna 850 spectrometer. The transmission infrared spectra were obtained from KBr pellets using a DTGS-KBr detector by co-addition of 9000 spectra. The spectrum showed four bands between 1200 and 600 cm^{-1}, at 1059 (strong), 964 (very strong), 844 (strong), and 787 cm^{-1} (very strong).

Quantitative microprobe analysis were performed on polished crystals inserted into an epoxy matrix using a Cameca SX-50 electron microprobe wavelength dispersive system. Instrument conditions were 15 kV, 15 nA. WO_3 was used as a tungsten standard, MoO_4H_2 as a molybdenum standard, and synthetic Cl-apatite as a phosphorous standard. Five measurements on different crystals gave the following average values (wt%): Mo = 15.5(3), W = 51.3(9), P = 1.17(4), O = 22.7(3), in very good agreement with the formula obtained from the X-ray structure determination (wt%) (Mo = 15.3, W = 48.5, P = 1.09, O = 22.6).

Single Crystal X-Ray Diffraction

A black platelet-like crystal (dimensions $0.1 \times 0.05 \times 0.01$ mm) was carefully chosen from the batch sample. It is to be noted that most crystals were twinned, probably favored by the lamellar structure of the compound. The intensity data were collected on an Enraf-Nonius CAD4-MACH diffractometer equipped with a Rigaku rotating anode source (graphite-monochromated Cu$K\alpha$ radiation $\lambda = 1.541788$ Å. The unit cell dimensions and crystal-orientation matrix were obtained by least-squares refinement of the setting angles of 25 reflections with $13.19° \leq \theta \leq 36.55°$, $a = 10.336(9)$, $b = 20.097(5)$, $c = 13.276(6)$ Å, $\beta = 106.41(7)°$, $V_{cell} = 2645(3)$ Å^3, and $Z = 8$. Intensity data were recorded in the range $3.47° \leq \theta \leq 71.99°$ for the quadrant $-12 \leq h \leq 12$, $-24 \leq k \leq 24$, $-1 \leq l \leq 16$. The $\omega - \theta/2$ scan method was used; scan width $\Delta\omega = (1.30 + 0.15 \tan\theta)°$ extended 25% on each side for background measurement, and horizontal counter aperture $\Delta l = (2.20 + 0.20 \ \tan\theta)$ mm; prescan speed, $1.83°$/min; $\sigma(I)/I = 0.05$; maximum time for final scan, 180 s. Three orientation and three intensity control reflections checked every 250 reflections (maintained within $0.2°$) and every half hour, respectively, showed a maximum decay of 20.9% over a period of 168 h of X-ray exposure time. The data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on the Ψ-scans method was applied (maximum correction 1.91, minimum correction 0.99). The 4299 reflections were measured of which 2484 were unique [$R_{int} = 0.046$]; 1729 reflections with $I > 3\sigma(I)$ were considered to be observed and used in the calculations.

The observed systematic absences (hkl: $h + k = 2n$; h0l: $h = 2n$; 0kl: $k = 2n$; hk0: $h + k = 2n$; 0k0: $k = 2n$; h00: $h = 2n$) are compatible with the space groups $C2$, Cm, or $C2/m$. The structure was first solved using the direct methods program SHELXS-86 (16) in the noncentrosymmetric space group $C2$ (No. 5), revealing all the tungsten atom positions. Most of the remaining nonhydrogen atoms were located after the application of alternating full-matrix least-squares refinement and difference Fourier synthesis. However, the solution obtained was very unstable and did not converge, even with strong constraints. This first solution was then used to build a model in the centrosymmetric space group $C2/m$ (No. 12). This choice of space group was confirmed by the subsequent structure refinements. All nonhydrogen atoms were finally refined with anisotropic thermal parameters (except for the five atoms with a small occupancy, where the neighborhood of heavy metals atoms precluded such refinement). The relative occupancies of W and Mo were refined independently for each site with the constraint of the sum to remain equal to one per site. Once converged, these occupancies were fixed. Hydrogen atoms were placed geometrically and allowed to ride on the atoms to which they were bonded. An extinction coefficient (refined value 5.6(7)) was also included in the last cycle of least squares. Expression minimized $\sum[(\omega \cdot \Delta F)^2]$ for 196 parameters. The final reliability factors were $R = 6.56$ and $R_\omega = 7.80$, for a goodness of fit $S = 1.00$, where the calculated weights are based on the Tukey–Prince (17) algorithm (using a four-term Chebyshev polynomial). The maximum shift/e.s.d. was $(\Delta/\sigma)_{max} = 0.00$; the highest and smallest peaks in the final Fourier syntheses were 1.97 (ghost of the phosphorous atom) and -3.25 e/Å^3, respectively. All calculations were carried out using the Oxford CRYSTALS (18) program running on a Silicon Graphics Personal IRIS 4D workstation. Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from the International Tables for Crystallography (19). The resulting atomic coordinates, including isotropic (equivalent) temperature parameters, anisotropic temperature factors, and a selection of bond distance and angles are shown in Tables 1, 2, and 3, respectively.

DISCUSSION

The asymmetric unit consists of a quarter of an anion and two half-amine molecules (see Fig. 1 for their numeration and representation with 50% thermal motion ellipsoids). The Keggin anion is centered with P(1) at the origin ($2/m$ site). $M(1)$ (where $M = $ Mo, W) and O(1) are situated on the twofold axis, $M(4)$, O(4), O(6), O(7), O(22), and O(33) are on the mirror, and $M(2)$, $M(3)$, and the remaining oxygen atoms are in general positions. Finally, the central PO_4^{2-} tetrahedron is disordered between two positions; the phosphorous atom is thus situated at the center of a cube of oxygen atoms, each of the latter having an occupancy of 0.5.

TABLE 1
Atomic Parameters for $[PMo_{4.27}W_{7.73}O_{40}^{6-}]\,[H_3N(CH_2)_6NH_3^{2+}]_3$

Atom	x/a	y/b	z/c	$U_{eq}{}^a$	Occ
Mo(1)	0.0000	−0.17577(7)	0.0000	0.0415	0.233(6)
Mo(2)	−0.1014(1)	−0.08794(5)	−0.24268(8)	0.0412	0.415(6)
Mo(3)	0.2438(1)	−0.08897(5)	−0.09243(8)	0.0383	0.430(6)
Mo(4)	0.3440(1)	0.0000	0.1492(1)	0.0445	0.346(6)
W(1)	0.0000	−0.17577(7)	0.0000	0.0415	0.767(6)
W(2)	−0.1014(1)	−0.08794(5)	−0.24268(8)	0.0412	0.585(6)
W(3)	0.2438(1)	−0.08897(5)	−0.09243(8)	0.0383	0.570(6)
W(4)	0.3440(1)	0.0000	0.1492(1)	0.0445	0.654(6)
P(1)	0.0000	0.0000	0.0000	0.0346	
O(1)	0.0000	−0.2566(9)	0.0000	0.0511	
O(2)	−0.147(2)	−0.1296(9)	−0.357(1)	0.0593	
O(3)	0.357(2)	−0.129(1)	−0.135(2)	0.0670	
O(4)	0.499(2)	0.0000	0.217(2)	0.0645	
O(5)	−0.027(2)	−0.063(1)	0.057(1)	0.022(4)	0.5000
O(6)	0.142(3)	0.0000	−0.007(2)	0.030(7)	0.5000
O(7)	0.102(3)	0.0000	0.112(2)	0.022(6)	0.5000
O(12)	−0.094(2)	−0.157(1)	−0.140(2)	0.0814	
O(13)	0.164(2)	−0.160(1)	−0.032(1)	0.0798	
O(22)	−0.089(4)	0.0000	−0.287(3)	0.0934	
O(23)	0.083(2)	−0.0934(9)	−0.212(1)	0.0613	
O(24)	0.270(2)	0.0654(8)	0.220(2)	0.0641	
O(33)	0.273(3)	0.0000	−0.131(2)	0.0676	
O(34)	0.344(2)	−0.0667(8)	0.046(1)	0.0629	
N(1)	0.388(3)	0.194(1)	0.168(2)	0.0681	
N(2)	0.813(5)	0.0000	0.358(3)	0.1008	
C(1)	0.476(4)	0.206(2)	0.261(3)	0.1109	
C(2)	0.420(4)	0.229(2)	0.351(2)	0.0917	
C(3)	0.524(4)	0.227(2)	0.456(2)	0.0930	
C(4)	0.743(7)	0.042(3)	0.414(5)	0.09(2)	0.5000
C(5)	0.658(6)	0.0000	0.455(4)	0.1109	
C(6)	0.546(6)	−0.029(3)	0.499(6)	0.10(2)	0.5000

^{a} $U_{eq} = (U_1 U_2 U_3)^{1/3}$, where U_i are the principle axes of the displacement ellipsoid.

TABLE 2
Anisotropic Thermal Parameters for $[PMo_{4.27}W_{7.73}O_{40}^{6-}]\,[H_3N(CH_2)_6NH_3^{2+}]_3$

Atom^a	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
M(1)	0.0560(9)	0.0304(7)	0.0427(7)	0.0000	0.0151(6)	0.0000
M(2)	0.0585(7)	0.0414(7)	0.0344(6)	−0.0084(4)	0.0182(5)	−0.0113(5)
M(3)	0.0442(6)	0.0385(6)	0.0392(6)	0.0006(5)	0.0188(5)	0.0058(5)
M(4)	0.0378(8)	0.0460(9)	0.0499(9)	0.0000	0.0114(6)	0.0000
P(1)	0.047(5)	0.031(5)	0.031(4)	0.0000	0.016(4)	0.0000
O(1)	0.09(2)	0.020(9)	0.08(1)	0.0000	0.03(1)	0.0000
O(2)	0.09(1)	0.06(1)	0.045(8)	−0.010(7)	0.028(8)	−0.020(9)
O(3)	0.11(1)	0.08(1)	0.08(1)	0.03(1)	0.07(1)	0.05(1)
O(4)	0.04(1)	0.08(2)	0.08(2)	0.0000	−0.01(1)	0.0000
O(12)	0.08(1)	0.13(2)	0.08(1)	0.04(1)	0.02(1)	−0.03(1)
O(13)	0.06(1)	0.14(2)	0.06(1)	0.03(1)	0.004(8)	−0.01(1)
O(22)	0.14(3)	0.05(1)	0.18(4)	0.0000	0.10(3)	0.0000
O(23)	0.07(1)	0.07(1)	0.08(1)	0.034(9)	−0.000(9)	−0.034(9)
O(24)	0.13(2)	0.034(9)	0.16(2)	0.01(1)	0.11(2)	−0.011(9)
O(33)	0.12(2)	0.06(1)	0.04(1)	0.0000	−0.00(1)	0.0000
O(34)	0.14(2)	0.045(9)	0.044(8)	0.003(7)	0.022(9)	−0.02(1)
N(1)	0.11(2)	0.09(2)	0.06(1)	−0.04(1)	0.04(1)	−0.06(2)
N(2)	0.16(4)	0.12(3)	0.09(3)	0.0000	0.08(3)	0.0000
C(1)	0.11(3)	0.13(3)	0.11(3)	−0.00(2)	0.03(2)	−0.03(2)
C(2)	0.12(3)	0.12(3)	0.07(2)	−0.01(2)	0.04(2)	−0.04(2)
C(3)	0.13(3)	0.11(2)	0.06(2)	−0.03(2)	0.03(2)	−0.01(2)
C(5)	0.19(7)	0.20(7)	0.04(2)	0.0000	−0.02(3)	0.0000

^{a} M can be either Mo or W.

1.90(3) Å] (because of the pseudo-octahedral symmetry of the disordered molecule, these two groups cannot be distinguished here), and O_i coordinated to three M atoms and forming vertices of the tetrahedral cavity $[d(M–O_i)_{aver} = 2.46(4)$ Å]. All four metal sites are occupied with molybdenum and tungsten atoms (see Table 1), but there is a significant preference for a localization of the molybdenum on the sites $M(2)$ and $M(3)$. Nothing in the present study allows us to give an explanation for the distribution.

Finally, the two independent half-amines are situated so that the middle C–C bond of each amine molecule is centered on the two-fold axis. The first is on a general position, the second half-amine is partly lying on the mirror [N(2) and C(5)], and the rest of the molecule [C(4) and C(6)] is disordered on each side of the mirror. From this, one can easily calculate the stoichiometry to be one Keggin anion to three hexanediamine molecules.

The Keggin structure is confirmed by the FT-IR spectra for which the two peaks at 1059 and 964 cm^{-1} are very typical for Keggin anions (24) and can be attributed to the $v_{as}(P–O_i)$ and $v_{as}(M–O_t)$ (M = Mo, W) bands, respectively. The two other peaks at 844 and 787 cm^{-1} can be assigned to the $v_{as}(M–O_c–M)$ and $v_{as}(M–O_e–M)$ vibrations. This allows us to confirm the existence of the two types of oxygens O_c and O_e that could not be distinguished by single crystal X-ray diffraction.

From the low pH of the solution during the hydrothermal synthesis (pH $\leq$ 2), only a diprotonated state for the

This type of disorder in Keggin anions has been observed (20) and discussed (21) previously: the structure contains normal α-type Keggin (22, 23) anions, disordered over two positions related by a 90° rotation about the molecular fourfold axis, where the metal and oxygen atoms of the two molecules are almost superposed (usually between 0.2 and 0.6 Å from each other). The consequences of such a model are that the inner PO_4^{2-} tetrahedra is disordered and the thermal ellipsoids for the oxygen atoms are unusually elongated (Fig. 1 and Table 2). The individual $[PM_{12}O_{40}]^{6-}$ molecules can then be described as usual α-type Keggin ions, formed of four tetrahedrally corner-shared M_3O_{13} units consisting of three edge sharing MO_6 distorted octahedra, the tungsten atoms forming a cubo-octahedral framework. The oxygen atoms can be classified into four groups: O_t bonded to one M atom $[d(M–O_t)_{aver} = 1.64(3)$ Å], O_c bridging two M atoms in the different units, O_e shared by two M inside each unit $[d(M–O_{c–e})_{aver} =$

TABLE 3
Selection of Bond Lengths (Å) and angles for $[PMo_{4.27}W_{7.73}O_{40}^{6-}][H_3N(CH_2)_6NH_3^{2+}]_3$

Bond distances

Anion

$M(1)$–$O(1)$	1.62 (2)	$M(3)$–$O(13)$	1.93 (2)
$M(1)$–$O(12)$	1.88 (2)	$M(3)$–$O(33)$	1.91 (1)
$M(1)$–$O(13)$	1.89 (2)	$M(3)$–$O(34)$	1.89 (2)
$M(2)$–$O(2)$	1.68 (1)	$M(4)$–$O(4)$	1.60 (2)
$M(2)$–$O(12)$	1.93 (2)	$M(4)$–$O(24)$	1.90 (2)
$M(2)$–$O(22)$	1.88 (1)	$M(4)$–$O(34)$	1.92 (2)
$M(2)$–$O(23)$	1.84 (2)	$P(1)$–$O(5)$	1.55 (2)
$M(2)$–$O(24)$	1.91 (2)	$P(1)$–$O(6)$	1.49 (3)
$M(3)$–$O(3)$	1.64 (2)	$P(1)$–$O(7)$	1.57 (3)

Amine 1		Amine 2	
N(1)–C(1)	1.34 (4)	N(2)–C(4)	1.45 (6)
C(1)–C(2)	1.54 (5)	C(4)–C(5)	1.43 (7)
C(2)–C(3)	1.50 (4)	C(5)–C(6)	1.55 (8)
C(3)–C(3)	1.40 (6)	C(6)–C(6)	1.5 (1)

Bond angles

Anion

O(1)–$M(1)$–O(12)	101.7 (8)	O(13)–$M(3)$–O(14)	87.2 (7)
O(12)–$M(1)$–O(12)	156.5 (15)	O(23)–$M(3)$–O(34)	155.5 (9)
O(1)–$M(1)$–O(13)	99.9 (8)	O(33)–$M(3)$–O(34)	87.5 (8)
O(12)–$M(1)$–O(13)	89.4 (8)	O(4)–$M(4)$–O(24)	101.6 (11)
O(1)–$M(1)$–O(13)	99.8 (8)	O(24)–$M(4)$–O(24)	87.8 (9)
O(12)–$M(1)$–O(13)	86.7 (9)	O(4)–$M(4)$–O(34)	101.5 (9)
O(13)–$M(1)$–O(13)	160.1 (15)	O(24)–$M(4)$–O(34)	156.8 (10)
O(2)–$M(2)$–O(12)	102.8 (9)	O(4)–$M(4)$–O(34)	101.7 (9)
O(2)–$M(2)$–O(22)	102.4 (14)	O(24)–$M(4)$–O(34)	87.1 (8)
O(12)–$M(2)$–O(22)	154.8 (15)	O(34)–$M(4)$–O(34)	88.7 (9)
O(2)–$M(2)$–O(22)	102.4 (14)	$M(1)$–O(12)–$M(2)$	138.6 (12)
O(2)–$M(2)$–O(23)	100.3 (9)	$M(1)$–O(13)–$M(3)$	137.6 (13)
O(12)–$M(2)$–O(23)	88.5 (8)	$M(2)$–O(22)–$M(2)$	140.2 (21)
O(22)–$M(2)$–O(23)	87.9 (12)	$M(2)$–O(23)–$M(3)$	140.0 (12)
O(2)–$M(2)$–O(24)	102.8 (10)	$M(2)$–O(24)–$M(4)$	139.1 (12)
O(12)–$M(2)$–O(24)	85.0 (9)	$M(3)$–O(33)–$M(3)$	139.1 (16)
O(22)–$M(2)$–O(24)	88.6 (11)	$M(3)$–O(34)–$M(4)$	138.8 (11)
O(23)–$M(2)$–O(24)	156.8 (10)	O(5)–$P(1)$–O(5)	180.0
O(3)–$M(3)$–O(13)	102.7 (10)	O(5)–$P(1)$–O(5)	69.7 (14)
O(3)–$M(3)$–O(23)	102.6 (10)	O(5)–$P(1)$–O(5)	110.3 (14)
O(13)–$M(3)$–O(3)	86.6 (7)	O(5)–$P(1)$–O(6)	110.4 (9)
O(3)–$M(3)$–O(33)	100.2 (7)	O(5)–$P(1)$–O(6)	69.6 (9)
O(13)–$M(3)$–O(33)	157.1 (12)	O(5)–$P(1)$–O(7)	72.5 (8)
O(23)–$M(3)$–O(33)	89.0 (9)	O(5)–$P(1)$–O(7)	107.5 (8)
O(3)–$M(3)$–O(33)	100.2 (11)	O(6)–$P(1)$–O(7)	69.3 (15)
O(13)–$M(3)$–O(33)	157.1 (12)	O(6)–$P(1)$–O(7)	110.7 (15)
O(23)–$M(3)$–O(33)	89.0 (9)	O(7)–$P(1)$–O(7)	180.0

Amine 1		Amine 2	
N(1)–C(1)–C(2)	117.6 (33)	N(2)–C(4)–C(5)	107.5 (50)
C(1)–C(2)–C(3)	112.5 (31)	C(4)–C(5)–C(6)	121.3 (34)
C(2)–C(3)–C(3)	116.5 (41)	C(5)–C(6)–C(6)	105.0 (60)

[a] M can be either Mo or W.

diamine can reasonably be considered and therefore the Keggin anion must have a charge of (6-). Since most Mo(VI) or W(VI) Keggin salts are colorless (23, 25), this charge, together with the black color and the metallic luster of the crystals (26, 27), suggests a mixed valence compound with both Mo/W(V) and Mo/W(VI), as observed by Hölscher *et al.* (14) in their reduced Dawson anion salt. The presence of paramagnetic Mo/W(V) in the compound was confirmed by ESR with the observation of a strong signal ($g = 1.983$) typical of Mo/W(V) (28), slightly larger than the g value obtained for the molybdotungstate Keggin anion reduced by only one electron for which $1.913 \leq g_{||} \leq 1.935$ and $1.934 \leq g_{\perp} \leq 1.953$ (29, 30). The determination of the degree of delocalization of the electrons in this Keggin ion is out of the scope of this paper, but since molybdenum is more easily reduced than tungsten (31, 32) it is very likely that the 3 electrons should be mainly localized on the molybdenum sites. Similar behavior has been observed in a mixed valent molybdenotungsten phosphate bronzes in which all molybdenum atoms are reduced (15). This is also suggested by the high g value obtained for our compound. Indeed, pure W phases show a much lower value: for α-$[PW_{12}O_{40}]^{n-}$ (33), $g = 1.827$, and α-$[PMo_{12}O_{40}]^{n-}$ (34), $1.938 < g < 1.949$.

When compared to the mixed valent Keggin polyoxometallate involving molybdenum and tungsten, $K_6Mo_3W_9PO_{40}$, obtained by Leclaire *et al.* (12), one can note in both cases that: (i) the anion's charge is 6-, indicating a 3 electron reduction; (ii) the partial reduction of Mo(VI) and W(VI) is made possible by the presence of metallic molybdenum and tungsten in the reaction mixture. Indeed, hydrothermal synthesis, achieved under similar conditions but without any metallic reducing agent present in the reaction mixture, leads to some W(VI), poorly colored, α-type Keggin ammonium salts (13); (iii) even though the initial ratio between Mo and W was close to 50/50, tungsten atoms predominate in the final compound.

The structure, represented in Figs. 2 and 3, has a lamellar organization formed from alternating organic–inorganic planes with their normal parallel to c. The ratio between the two cell parameters that are parallel to the layer $a/b = 0.51 \approx 1/2$ is far from the required value of $1/\sqrt{3}$ needed to describe the plane of the Keggin anion as being close packed. This close packed organization within the inorganic plane is often observed in such salts when the use of a large cation induces a segregation of the molecules into organic and inorganic planes (13, 35). In our case, the organic molecules slightly interdigitate the inorganic planes, moving the polyanions away from each other. Thus the first sphere of coordination of the Keggin anion is formed from six NH_3^+ groups [$d(P(1)-N(1)) = 5.58(2)$ Å ($\times 4$); $d(P(1)-N(2)) = 5.61(3)$ Å ($\times 2$)]; the first oxygen atom of the closest Keggin anion is found at $d(P(1)-O(3)) = 6.60(3)$ Å (see Fig. 4) and therefore we can conclude that there are no direct anion–anion interactions.
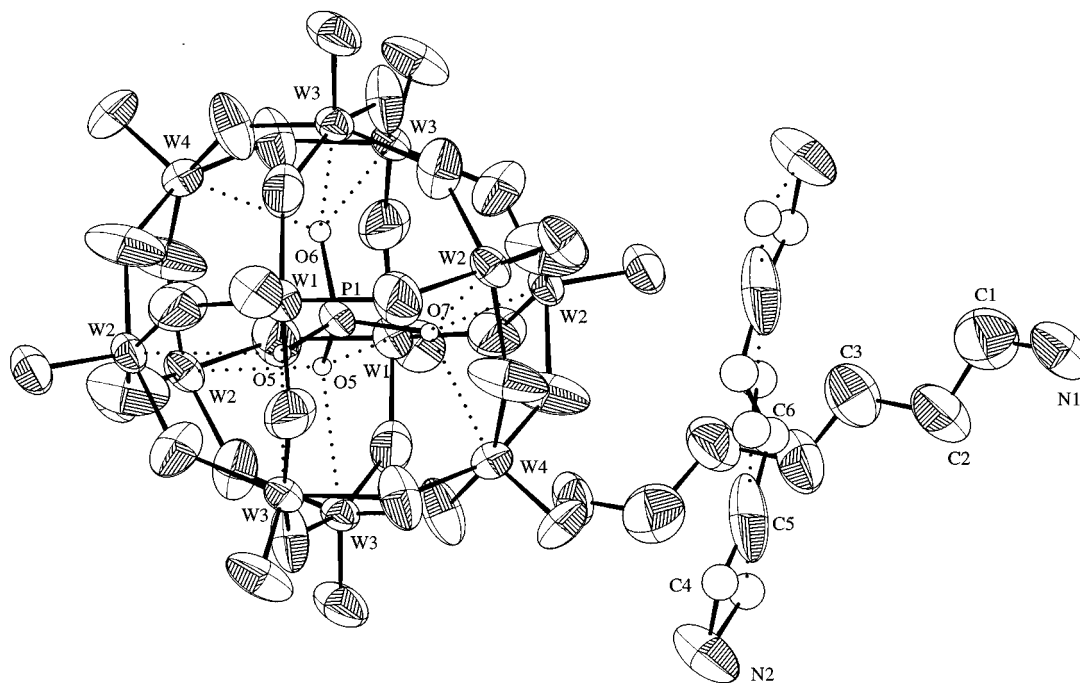
FIG. 1. The Keggin anion and the two protonated diamines represented by thermal motion ellipsoids with 50% probability. For clarity, only nonhydrogen atoms and one of the two possible orientation of the PO_4^{2-} tetrahedra are shown.

Finally, attempts to solubilize this salt in usual polar solvents were unsuccessful. But, since Keggin anion salts have now been obtained by hydrothermal synthesis with quite a few different ammonium cations, we expect that the use of a cation such as tetrabutylammonium should routinely yield soluble salts containing this mixed valence Keggin anion.
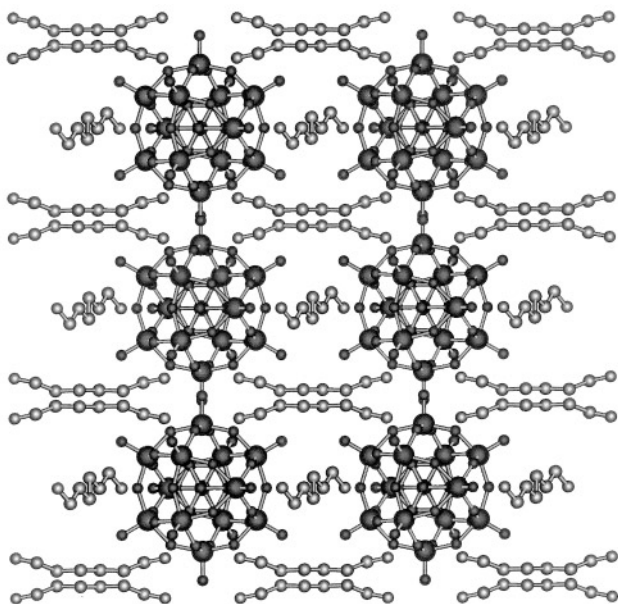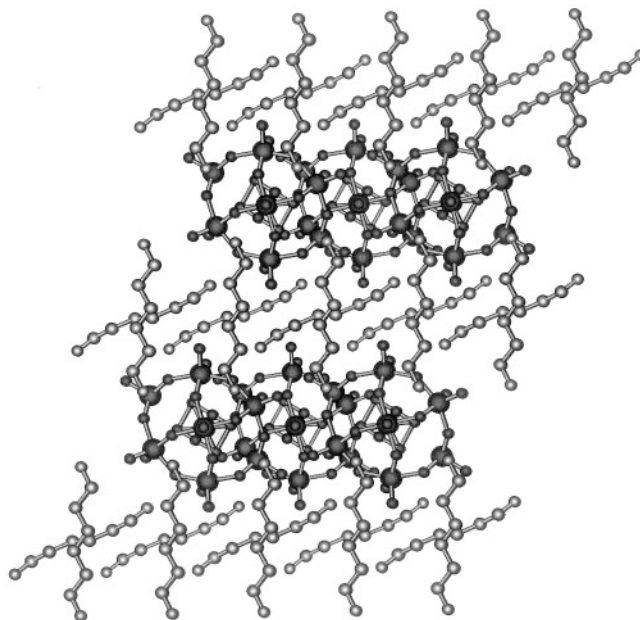

FIG. 2. View of the structure along the 100 axis.
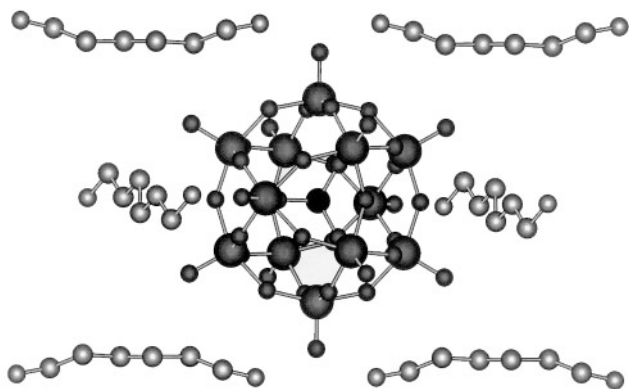

FIG. 3. View of the structure along the 010 axis.

FIG. 4. The Keggin anion and its six surrounding organic cations.

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