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An Alkali Metal−Crown Ether Complex Supported by a Keggin Anion through the Three Terminal Oxygen Atoms in a Single M_3O_{13} Triplet: Synthesis and Characterization of $[\{Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)\}_3\{PMo_{12}O_{40}\}]$

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Introduction

Polyoxometalates have received great attention because they have potential applications in sorption clathration, catalysis, electric conductivity, magnetism, and photochemistry.[1−9] Recently, a number of inorganic or organometallic complexes supported by polyoxoanions have been reported, such as $[La(Mo_8O_{26})_2]$,[5−10] $[\{Cu(4,4'\text{-}bipy)\}_4(Mo_8O_{26})]$,[11] $[Cu(en)_2(Mo_8O_{26})]$,[12] $[(CO)_3Mn(cis\text{-}Nb_2W_4O_{19})]$, [13] $[CpRh\cdot P_2W_{15}NbO_{62}]$,[7−14] and $[\{C_5Me_5\}Rh_2(Mo_{13}O_{40})]^{2+}$ [15], in which the polyoxoanions contain sufficient charge density at their surface oxygen atoms to coordinate metals and organometallics.[16] It is believed that surface activation, for the typical Keggin polyoxoanions, may be achieved by replacing Mo(VI) or W(VI) centers by one or more metals (Nb, V) with lower valence, such as $\{(CpTi)[\beta\text{-}(SiW_9V_3O_{40})]\}^{4+}$ [17,18] or $\{[(1,5\text{-}COD)Ir][\beta\text{-}(SiW_9Nb_3O_{40})]\}^{6+}$,[19] or by reducing the anions, such as $[PW_{12}O_{40}Ni(2,2'\text{-}bipy)_2(H_2O)]^{3-}$.[20] To our knowledge, inorganic or organometallic complexes supported by the typical Keggin $PMo_{12}O_{40}^{3-}$ unit have not been reported.

Table 1. Crystal Data and Structure Refinement for the Complex

empirical formula	C66 H81 Mo12 N3 Na3 O58 P
fw	3095.56
temp	293(2) K
wavelength	0.71073 Å
cryst syst	rhombohedral
space group	*R*3
unit cell dimensions	$a = 14.6000(17)$ Å
	$b = 14.6000(17)$ Å
	$c = 14.6000(17)$ Å
	$\alpha = 109.300(17)°$
	$\beta = 109.300(17)°$
	$\gamma = 109.300(17)°$
volume	2410.8(5) Å^3
Z, Calcd density	1, 2.132 Mg/m^3
absorption coeff	1.639 mm^{-1}
F(000)	1514
Data/restraints/parameters	4345/1/429
GOF on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0289, wR2 = 0.0728
R indices (all data)	R1 = 0.0307, wR2 = 0.0734

Here we report the synthesis and characterization of an alkali metal−crown ether complex supported by the α-Keggin $PMo_{12}O_{40}^{3-}$ anion. The complex, $[\{Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)\}_3\{PMo_{12}O_{40}\}]$, has an unusual structure in which the polyoxoanion is coordinated to three $[Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)]^+$ ions through the three terminal oxygen atoms in a single M_3O_{13} triplet.

Experimental Section

Physical Measurement. C, H, and N elements were analyzed on a Perkin−Elmer 240C elemental analyzer, and other elements were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. Infrared spectra were recorded with KBr pellets on a Magna FT−IR 560 spectrometer. ^{1}H NMR spectra were taken on a Bruker Am-500 spectrometer operating at 500M Hz, using DMSO as solvent.

Preparation. The complex, $[\{Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)\}_3\{PMo_{12}O_{40}\}]$, was synthesized by the solid-state reaction at room temperature as orange blocks in 15% yield based on molybdophosphate acid. A mixture of dibenzo-18-crown-6 (0.36 g), NaCl (0.058 g), and $H_3PMo_{12}O_{40}\cdot 24H_2O$ (0.6 g) was ground in an agate mortar for 30 min, then 20 mL of acetonitrile solvent was added. The mixture was vibrated by ultrasonic waves and kept in the tube for 5 days. The orange blocks were picked out from the mixture. Anal. Calcd for the complex: C, 25.58; H, 2.62; N, 1.36; Na, 2.23; P, 1.00; Mo, 37.19. Found: C, 25.67; H, 2.82; N, 1.41; Na, 2.15; P, 0.98; Mo, 37.08. IR (cm^{-1}): 2929(w), 1503(m), 1454(m), 1252(m), 1213(sh), 1126(m), 1061(s), 958(s), 880(m), and 806(s). ^{1}H NMR(ppm): 6.94(4H), 6.86(4H), 4.05(8H), 3.34(8H), and 2.07(3H).

X-ray Crystallography. An orange crystal with dimensions 0.50 × 0.42 × 0.38 mm was affixed to the end of a glass capillary and mounted on the goniometric head of a Siemens P4 four-circle diffractometer. Accurate cell dimensions were obtained by least-squares refinement of 25 centered reflections [λ(Mo Kα) = 0.71073 Å]. These cell parameters, together with selected information related to the crystallographic experiment, are given in Table 1. During data collection (θ /2θ scans, bisecting geometry), the intensities of three standard reflections were measured every 97 reflections; no significant changes in those intensities were observed. An empirical absorption correction from ψ scan was applied (1.639 mm^{-1}). Intensities ($2\theta = 4.82-50.04°$) were measured for 5171 reflections, of which 4345 unique reflections [$I > 2\sigma(I)$] were used for further computation.

The structure was solved by direct methods and completed by a series Fourier synthesis and least-squares refinement. Anisotropic thermal parameters were used to refine all atoms other than hydrogen. Hydrogen atoms were placed in the idealized positions with *U*(eq) set at 1.2 *U*(eq)

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Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**. *U*(eq) Is Defined as One-Third of the Trace of the Orthogonalized $\mathbf{U}_{ij}$ Tensor.

	x	y	z	*U*(eq)
Mo(1)	622(1)	−20732(1)	−10870(1)	22(1)
Mo(2)	−1016(1)	−21942(1)	−13937(1)	27(1)
Mo(3)	−844(1)	−23786(1)	−12723(1)	28(1)
Mo(4)	−3820(1)	−23645(1)	−15285(1)	31(1)
P(1)	−2341(1)	−22341(1)	−12341(1)	17(1)
Na(1)	3946(1)	−19475(1)	−9690(1)	39(1)
O(1)	69(2)	−24204(2)	−12859(3)	39(1)
O(2)	−998(2)	−23161(2)	−13632(2)	27(1)
O(3)	−14(2)	−21028(2)	−12416(2)	22(1)
O(4)	2000(2)	−20130(2)	−10445(2)	30(1)
O(5)	−1293(3)	−21293(3)	−11293(3)	18(1)
O(6)	−4834(2)	−23668(2)	−14662(2)	29(1)
O(7)	599(2)	−20580(2)	−9567(2)	21(1)
O(8)	−2460(2)	−23158(2)	−15263(2)	30(1)
O(9)	169(2)	−22233(2)	−11482(2)	25(1)
O(10)	−4737(3)	−24452(3)	−16655(2)	41(1)
O(11)	−1518(2)	−20959(2)	−14073(2)	30(1)
O(12)	−2200(2)	−25088(2)	−13708(2)	29(1)
O(13)	−176(2)	−21819(2)	−14491(2)	38(1)
O(14)	3806(3)	−19998(3)	−8119(2)	45(1)
O(15)	−2433(2)	−22238(2)	−13373(2)	20(1)
O(16)	3288(2)	−20936(3)	−11616(2)	41(1)
O(17)	3896(2)	−18082(2)	−8086(2)	40(1)
O(18)	3821(3)	−18792(3)	−11160(3)	47(1)
O(19)	4969(3)	−17356(2)	−9050(3)	46(1)
O(21)	3493(2)	−21451(2)	−9915(2)	43(1)
N(1)	5832(4)	−19106(5)	−8919(5)	84(2)
C(1)	3416(4)	−19630(4)	−12263(4)	47(1)
C(2)	2665(4)	−20744(4)	−12435(4)	43(1)
C(3)	2680(4)	−22032(4)	−11832(4)	50(2)
C(4)	3351(4)	−22208(4)	−10935(4)	52(1)
C(5)	3943(4)	−21546(4)	−8983(4)	43(1)
C(6)	4204(4)	−22388(4)	−8999(5)	56(2)
C(7)	4600(5)	−22435(5)	−8021(5)	66(2)
C(8)	4755(5)	−21672(5)	−7068(5)	74(2)
C(9)	4504(5)	−20812(5)	−7049(5)	60(2)
C(10)	4111(4)	−20766(4)	−8008(4)	41(1)
C(11)	3888(4)	−19203(4)	−7174(4)	49(1)
C(12)	3399(4)	−18551(4)	−7545(4)	41(1)
C(13)	5026(4)	−17279(4)	−7412(4)	46(1)
C(14)	5317(4)	−16601(4)	−7952(4)	44(1)
C(15)	5034(3)	−16928(4)	−9745(4)	41(1)
C(16)	5621(4)	−15799(4)	−9383(4)	49(1)
C(17)	5678(4)	−15461(4)	−10160(5)	59(2)
C(18)	5169(4)	−16228(4)	−11254(3)	68(2)
C(19)	4539(4)	−17350(4)	−11633(3)	65(2)
C(20)	4456(3)	−17709(4)	−10872(4)	41(1)
C(21)	6653(4)	−19024(4)	−8776(4)	52(2)
C(22)	7727(5)	−18917(7)	−8602(5)	93(3)

for the non-hydrogen atom. The final cycle of refinement gave R1 = 0.0289 and wR2 = 0.0728. In the final difference map, the deepest hole was −0.709 eÅ^{-3} and the highest peak was 0.670 eÅ^{-3}. Final atomic coordinates and bond lengths for the complex are listed in Table 2 and in Table 3, respectively.

Results and Discussion

In the IR spectra of the complex, four intense bands at 1061, 958, 880, and 806 cm^{-1} are attributed to ν as(P−O$_a$), ν as(Mo═O$_t$), ν as(Mo−O$_b$−Mo), and ν as(Mo−O$_c$−Mo), respectively (O$_t$ = terminal oxygen, O$_b$ = bridged oxygen of two octahedral sharing a corner, and O$_c$ = bridged oxygen sharing an edge), showing the polyoxoanion has an α-Keggin structure. Features at 2929, 1503, 1454, 1252, 1213, and 1126 cm^{-1} are characteristic of dibenzo-18-crown-6. In comparison with the free crown ether molecules, ν(C−O) in the complex is shifted from 1230 cm^{-1} to 1213 cm^{-1}, which demonstrates that the crown ether molecules are coordinated to metal ions. The ^{1}H NMR spectrum contains four sharp signals in a relative ratio of intensities 1:1:2:2 (6.94, 6.86, 4.05, and 3.34 ppm), which are assigned to the hydrogen atoms of dibenzo-18-crown-6. Compared with those of free dibenzo-18-crown-6, the ^{1}H NMR signals of the crown ether protons in the complex are not obviously shifted. The signal at 2.07 ppm is attributed to the −CH$_3$ of acetonitrile.

Table 3. Bond Lengths [Å] and Angles [deg] for the Complex[a]

Mo(1)−O(4)	1.689(3)	Mo(1)−O(9)	1.843(3)
Mo(1)−O(7)	1.855(3)	Mo(1)−O(3)	1.962(3)
Mo(1)−O(7)#1	1.980(3)	Mo(1)−O(5)	2.425(3)
Mo(2)−O(13)	1.672(3)	Mo(2)−O(11)	1.851(3)
Mo(2)−O(3)	1.858(2)	Mo(2)−O(8)	1.975(3)
Mo(2)−O(2)	1.977(3)	Mo(2)−O(15)	2.432(3)
Mo(3)−O(1)	1.680(3)	Mo(3)−O(2)	1.840(3)
Mo(3)−O(12)	1.851(3)	Mo(3)−O(9)	1.976(3)
Mo(3)−O(11)#2	1.984(3)	Mo(3)−O(15)#2	2.428(3)
Mo(4)−O(10)	1.677(3)	Mo(4)−O(6)#2	1.858(3)
Mo(4)−O(8)	1.859(3)	Mo(4)−O(6)	1.975(3)
Mo(4)−O(12)#1	1.975(3)	Mo(4)−O(15)	2.416(3)
P(1)−O(15)#2	1.531(3)	P(1)−O(15)#1	1.531(3)
P(1)−O(15)	1.531(3)	P(1)−O(5)	1.542(5)
Na(1)−O(4)	2.374(3)	Na(1)−N(1)	2.390(5)
Na(1)−O(16)	2.505(4)	Na(1)−O(17)	2.586(4)
Na(1)−O(19)	2.604(4)	Na(1)−O(21)	2.616(4)
Na(1)−O(18)	2.628(4)	Na(1)−O(14)	2.693(4)
O(4)−Na(1)−N(1)	170.2(2)	O(4)−Na(1)−O(16)	81.21(12)
N(1)−Na(1)−O(16)	96.08(19)	O(4)−Na(1)−O(17)	78.56(12)
N(1)−Na(1)−O(17)	104.88(18)	O(16)−Na(1)−O(17)	158.86(13)
O(4)−Na(1)−O(19)	109.00(14)	N(1)−Na(1)−O(19)	80.50(18)
O(16)−Na(1)−O(19)	121.46(15)	O(17)−Na(1)−O(19)	60.85(12)
O(4)−Na(1)−O(21)	86.52(12)	N(1)−Na(1)−O(21)	83.77(19)
O(16)−Na(1)−O(21)	65.66(12)	O(17)−Na(1)−O(21)	118.76(14)
O(19)−Na(1)−O(21)	163.32(12)	O(4)−Na(1)−O(18)	86.21(13)
N(1)−Na(1)−O(18)	101.2(2)	O(16)−Na(1)−O(18)	64.50(12)
O(17)−Na(1)−O(18)	107.83(14)	O(19)−Na(1)−O(18)	59.23(11)
O(21)−Na(1)−O(18)	130.17(12)	O(4)−Na(1)−O(14)	85.30(13)
N(1)−Na(1)−O(14)	88.2(2)	O(16)−Na(1)−O(14)	121.91(13)
O(17)−Na(1)−O(14)	62.49(12)	O(19)−Na(1)−O(14)	116.39(12)
O(21)−Na(1)−O(14)	57.27(11)	O(18)−Na(1)−O(14)	168.28(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 = $z + 1$, $x - 2$, $y + 1$, #2 = $y + 2$, $z - 1$, $x - 1$.

As shown in Figure 1, the novel molecular complex [{Na(dibenzo-18-crown-6)(MeCN)}$_3${PMo$_{12}$O$_{40}$}] consists of an α-Keggin heteropolyanion, [PMo$_{12}$O$_{40}$]$^{3-}$, and three cations, [Na(dibenzo-18-crown-6)(MeCN)]$^+$. As in other Keggin structures,[1] the polyoxoanion is formed from twelve MoO$_6$ octahedra and one PO$_4$ tetrahedron. For PO$_4$, the P−O distances are in the range of 1.531(3)−1.542(3) Å, while the O−P−O angles vary from 109.13(11) to 109.81(11)°. The Mo−O distances can be grouped into three sets: Mo−O$_t$ 1.672(3)−1.689(8) Å, Mo−O$_a$ 2.416(3)−2.432(3) Å, and Mo−O$_b$ 1.840(3)−1.984(3) Å. There are alternating "short" and "long" Mo−O$_b$−Mo bonds (mean of 1.851 and 1.975 Å, respectively) which result from small displacements of Mo atoms from the mirror planes of the M$_3$O$_{13}$ triplets.[1] In the molecule, the Na$^+$ ions are coordinated to dibenzo-18-crown-6 molecules with Na−O (crown ether) of 2.505(4)−2.693(4) Å. The Na$^+$ ion is nearly located on the plane defined by the crown ether oxygen atoms (−0.088 Å). Except for this, the Na$^+$ ion is coordinated to MeCN molecules, with Na−N 2.390(4) Å and Na(1)−N(1)−C(21) 166.1(1)°. The unusual feature here is that the Keggin structural unit, [PMo$_{12}$O$_{40}$]$^{3-}$, is coordinated to Na$^+$ cations via the three terminal oxygen atoms in a single M$_3$O$_{13}$ triplet, forming a novel neutral and discrete molecule, with Na−O 2.374(3) Å, the Na(1)−O(4)−Mo(1) 169.9(2)°, and O(4)−Na(1)−N(1) 170.2(2)°.

Using an empirical bond valence calculation,[21] $S = \exp[(1.907-R)/0.37]$ (S = bond valence, R = bond length), the S

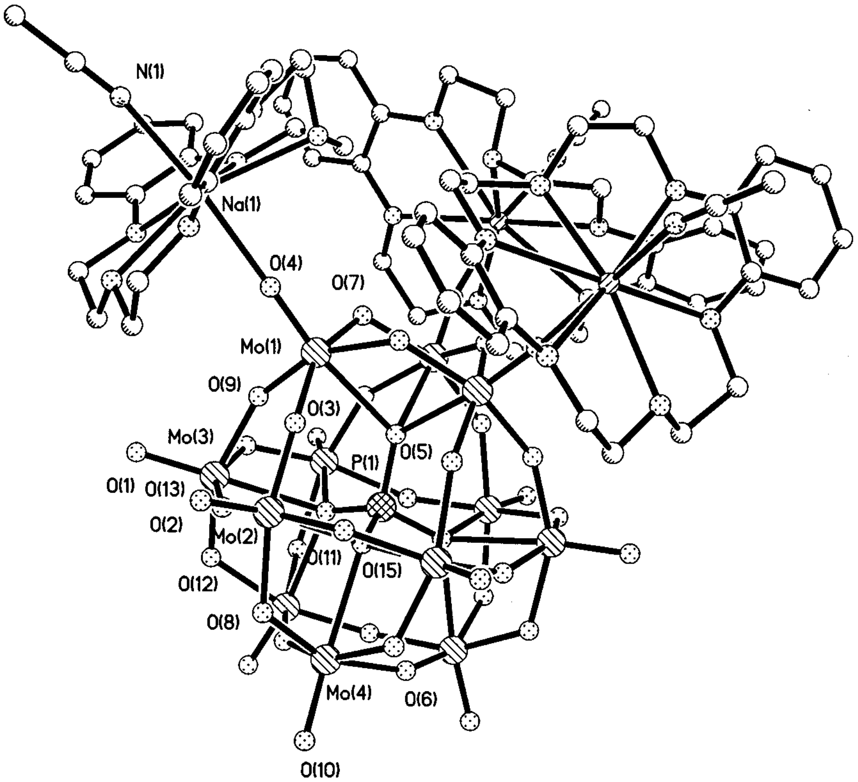

Figure 1. The structure of the alkali metal complex supported by the Keggin anion [{Na(dibenzo-18-crown-6)(MeCN)}$_3${PMo$_{12}$O$_{40}$}].

values for the Mo atoms are in the range of 6.07−6.17. The average value for the calculated oxidation state of Mo is 6.09, which is consistent with ESR results. This shows that the [PMo$_{12}$O$_{40}$]$^{3-}$ anion is in the high oxidation state. The bond valences are in the range of 1.80−1.88 for the terminal oxygen atoms of the Keggin polyoxoanion, and the average bond valence value is 1.85, which indicates that the terminal oxygen atoms are capable of coordinating to metal ions to some extent.

There are many examples[22−33] in which Na$^+$ ions are coordinated to the terminal oxygen atoms of polyoxometalate anions in the crystal, although the coordination interactions have not been identified in solution. The interactions are more obvious for Na$^+$ ions than for other alkali metal ions, possibly because Na$^+$ ions have a suitable ionic radius. Generally, each Na$^+$ ion is octahedrally coordinated to six O atoms (including those of water molecules), but complexes with coordination numbers of five or seven have been also found in some structures.[32,33] In this structure, each Na$^+$ ion coordinates one N atom from MeCN and seven O atoms, of which one is a polyoxoanion and six are crown ether O atoms.

In the crystal of two-electron reduced [K(18-crown-6)]$_2$-[N(PPh$_3$)$_2$][HPMo$_{12}$O$_{40}$]·8MeCN·18-crown-6,[34] there is no coordinative interaction between K$^+$ ions and terminal oxygen atoms of the polyoxoanions. [K(18-crown-6)]$^+$ ions fill the holes formed by the polyoxoanions packing and interact electrostatically with [HPMo$_{12}$O$_{40}$]$^{4-}$ anions. Each [K(18-crown-6)]$^+$ ion is shared by the adjacent polyoxoanions. In this work, however, each [Na(dibenzo-18-crown-6)]$^+$ ion is assigned to a polyoxoanion with the Na−O distance of 2.374(3) Å. Three [Na(dibenzo-18-crown-6)]$^+$ ions in the complex molecule are unevenly distributed over a PMo$_{12}$O$_{40}$$^{3-}$ anion and coordinated to the three terminal oxygen atoms in a single M$_3$O$_{13}$ triplet, although the twelve terminal oxygen atoms of the Keggin anion are in the same circumstance and there are the electrostatic repulsive forces among the Na$^+$ ions. We think that the unusual structure is derived from the coordinative interactions between the Na$^+$ ions and the terminal oxygen atoms of the Keggin anion and the van der Waals forces among organic components. The van der Waals forces lead to the aggregation of the crown ether molecules in the complex molecule (Figure 1) and in the crystal (Figure 2), as found in other molecules based on crown ethers and polyoxometalates.[35,36] This gives overall stability to the structure. The complex, [{Na(dibenzo-18-crown-6)(MeCN)}$_3$-{PMo$_{12}$O$_{40}$}], is a neutral and discrete molecule, which is packed in the crystal via van der Waals forces (Figure 2). The disposition of crown ether molecules is not regular like that in other compounds,[35,36] owing to the coordination between the Na$^+$ ions and the terminal oxygen atoms of the Keggin anion.

Conclusions

An alkali metal−crown ether complex supported by the typical Keggin PMo$_{12}$O$_{40}$$^{3-}$ anions has been synthesized and characterized for the first time. It was found that the terminal oxygen atoms of the typical Keggin PMo$_{12}$O$_{40}$$^{3-}$ anion are

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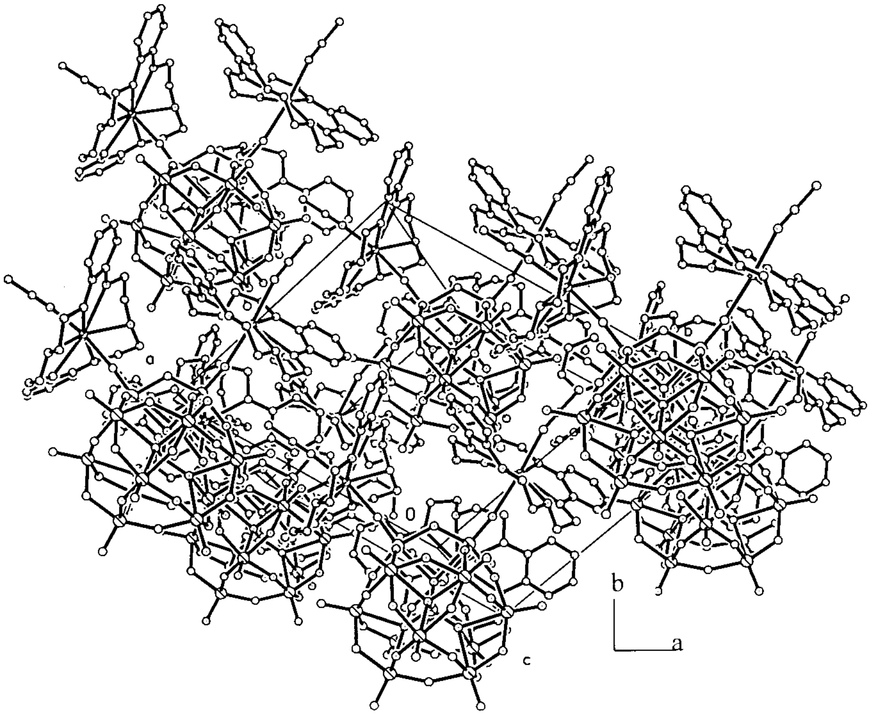

Figure 2. Packing diagram viewed down the *c* axis for the complex.

capable of coordinating to metal ions. It is interesting to note that the Keggin structural unit $[PMo_{12}O_{40}]^{3-}$ is coordinated to Na^+ cations through the three terminal oxygen atoms in a single M_3O_{13} triplet, forming a neutral and discrete molecule. The unusual structure is formed due to the coordinative interactions between the terminal oxygen atoms of the Keggin anion and the Na^+ ions and the van der Waals forces among organic components.

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Supporting Information Available: Crystal data and structure refinement details, atomic coordinates, bond lengths and bond angles, isotropic displacement parameters, coordinates and isotropic displacement parameters of hydrogen atoms, molecular structure diagram with atomic labeling, and IR and ^1H NMR spectra for the complex (12 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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