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Synthesis and structural characterization of N-(*para*-substituted-phenyl)aza-15-crown-5 sodium heteropolymolybdotungstate

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Abstract—The title complexes of $[Na(N\text{-}(p\text{-}Rph)15C5)(Et_2O)]_2Na_2W_xMo_{8-x}O_{26}$ [(**1**): R = H, x = 0.26: (**2**): R = CH_3, x = 0.50] were synthesized by the reaction of N-(*p*-Rph)15-crown-5 with tetra-*n*-butylammonium polymolybdotungstate and a sodium cation and characterized by elemental analysis, IR, ^1H NMR and H,H-COSY NMR spectra and crystal structure determination of complex (**2**). The complexes can be described as having a two-dimensional $[Na_2W_xMo_{8-x}O_{26}]_\infty^{2-}$ anion framework in which the sodium is coordinated with six terminal O atoms of neighbouring β-octamolybdotungstates in octahedral geometry and a $[Na(N\text{-}(p\text{-}Rph)15C5(Et_2O)]^+$ complex cation in which the sodium cation shows pentahedral pyramidal coordination geometry, which is rarely observed. The packing of the complex cations and the two-dimensional anion framework were in different layers separately. The N-(*para*-substituted-phenyl)aza-15-crown-5 combined with the octamolybdotungstate anion with a ratio of W/Mo of 0.26/7.74 in complex (**1**) and 0.50/7.50 in complex (**2**), respectively, however the DB18C6 and DB24C8 chose the hexamolybdotungstate anion with a ratio of W/Mo of 4/2 and 1/5 to form the complexes $[Na(DB18C6)\,(CH_3OH)]_2W_4Mo_2O_{19}$ and $[Na(DB24C8)]_2W_1Mo_5O_{19}$. © 1997 Elsevier Science Ltd

Keywords: N-(*para*-substituted-phenyl)aza-15-crown-5; β-octamolybdotungstate; crystal; complex; coordination.

Both crown ether supermolecular complexes and polyoxometalate complexes have attracted considerable interest in view of their application prospects in materials science and life science. Furthermore, crown ether compounds have shown special molecular recognition as hosts when they choose guest molecules in chemical reactions, and polyoxometalate anions have given different structures and degrees of polymerization as the chemical environment is changed [1–3]. A new branch in chemistry is growing up in which the choice of crown ether compounds of polyoxometalate anions is studied while 'The Crown Ether Chemistry' is combined with 'The Polyoxometalate Chemistry'.

We have reported recently the complexes of dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) with hexaoxometalate (M = W and Mo) in which the differences in bond-type and distribution and occupation of W and Mo atoms have been observed owing to a change of radius of the crown ether [4–6]. As a part of our continued interest in the field of crown ether polyoxometalate complexes, we describe herein two new complexes of $[Na(N\text{-}(p\text{-}Rph)15C5)(Et_2O)]_2Na_2W_xMo_{8-x}O_{26}$ where R is H and x is 0.26 in complex (**1**) and R is CH_3 and x is 0.50 in complex (**2**).

RESULTS AND DISCUSSION

The title complexes were prepared by mixing N-(*para*-substituted-phenyl)aza-15-crown-5 [N-(*p*-Rph) 15C5], sodium chloride and tetra-*n*-butylammonium hexamolybdotungstate salt in a mixed sol-

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vent of CH_3OH and CH_3CN and crystallizing from DMF, CH_3OH and Et_2O.

The products were obtained as air-stable orange-yellow solids in yields of about 40%. Elemental analysis, IR and NMR data of the complexes were consistent with the expected structure.

The main features of the IR spectra of the two complexes were the $\nu_{C\text{–}O\text{–}C}$ absorption of complexes [1100 cm^{-1} in complex (**1**) and 1098 cm^{-1} in complex (**2**)] showing distinct red shifts in comparison with $\nu_{C\text{–}O\text{–}C}$ of the corresponding uncoordinated crown ether, which confirmed the coordination of the O atoms of the crown ether with sodium cation in the complexes. Four strong bands in the range 703–938 cm^{-1} were observed and assigned to the absorption of Mo═O and Mo—O in the β-octamolybdotungstate anion.

For the ^1H NMR assignment of the complexes, it was difficult in the range 3.2–3.6 because of the overlap of the peaks of the CH_2 protons of the crown ether and diethyl ether. Taking advantage of H,H-COSY NMR spectrum (Fig. 1), the peaks of the highest field in the range (which were covered partly by the peaks of DMSO solvent) were assigned to the CH_2 of diethyl ether first by the coupling correlation of CH_3 of diethyl ether. About the CH_2 of the crown ether, the chemical shift sequence should be $H_E \geqslant H_D \geqslant H_C > H_B > H_A$ according to the electronegativity of neighbouring atoms, and the peak of H_E should be a singlet based on the molecular symmetry. However, the peak at the lowest field in the range was a triplet which belonged to protons other than H_E. The H_A can be explained as that located at the region of the shielding of Π_7^8 consisting of six π electrons of benzene and a pair of *p* electrons of a N atom. The triplet of H_B can also be determined by the coupling correlation of H_A and H_B. Of the two singlets remaining, the peak downfield belonged to H_E and the one upfield was assigned to H_C and H_D according to the integrated results.

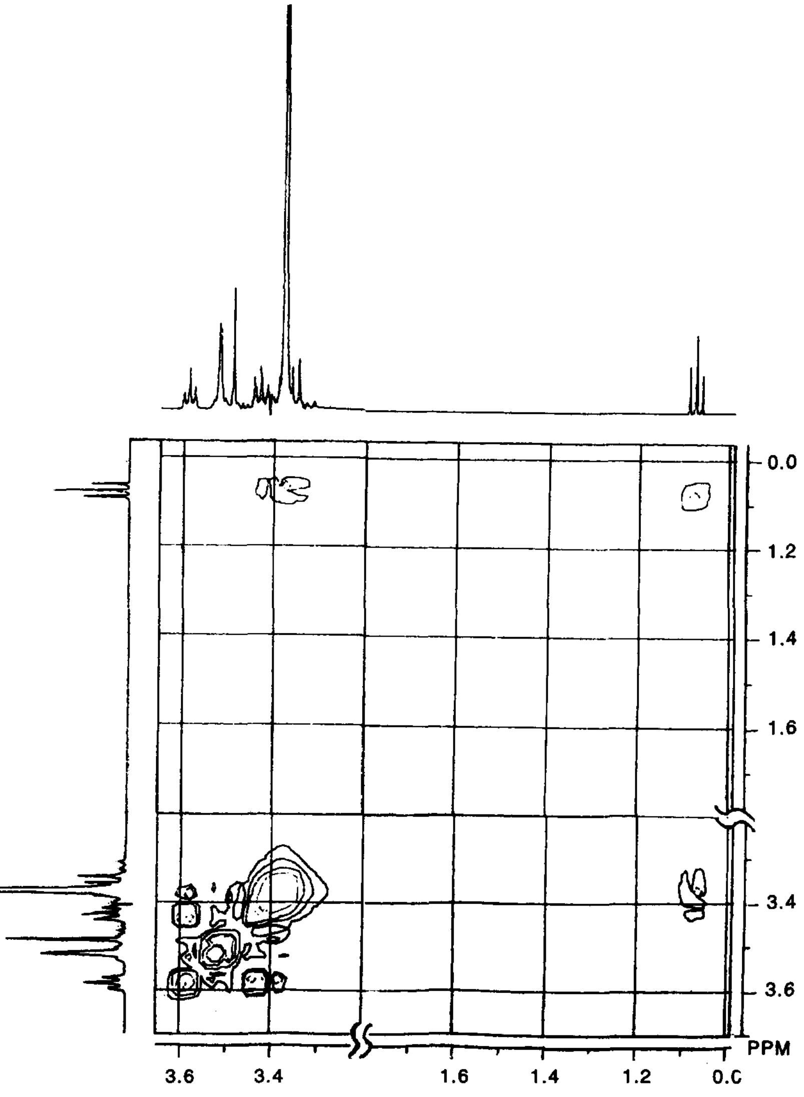

Fig. 1. The H,H-COSY spectrum of $[Na(N\text{-}(p\text{-}CH_3ph)(Et_2O)]^+$.

A single crystal X-ray diffraction analysis of the complex (**2**) showed that the complex consisted of two $[Na(N\text{-}(p\text{-}Rph)15C5)(Et_2O)]^+$ cations and one $[Na_2W_xMo_{8\text{-}x}O_{26}]^{2-}$ anion. There were two types of Na^+ cations in the complex according to their chemical environment and coordination geometry playing important roles. The ion Na(2) was coordinated to four O and one N atoms of N-(*p*-Rph)15C5 with the distances of Na—O of 2.42(2)—2.48(1) Å and Na—N of 2.79(1) Å in a distorted pentagon and also coordinated with the O atom of an Et_2O which was at the apex of a distorted pentagonal pyramid with a distance of Na—O of 2.410(8) Å (Fig. 2). The Na(1) ion was six-coordinated with a distorted octahedral environment being bonded to four terminal O atoms from the neighbouring octamolybdotungstate anion on the one side and two terminal O atoms of the neighbouring octamolybdotungstate on the other side with Na—O bond lengths of 2.377(8)–2.538(9) Å, by which the two-dimensional network anions structure of $[Na_2W_xMo_{8\text{-}x}]^{2-}_{\infty}$ was formed (Fig. 3).

The crystal was composed of parallel two-dimensional anion frameworks and the packing of the sodium N-(*para*-substituted-phenyl)aza-15-crown-5 complex cations were located only up and down the two-dimensional anion network with the orientation of *p*-Rph ligands toward the neighbouring anion networks. Compared with previous studies in which dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) chose hexamolybdotungstate to coordinate to constitute $[Na(DB18C6)(CH_3OH)]_2W_4Mo_2O_{19}$ and $[Na(DB24C8)]_2W_1Mo_5O_{19}$, it was revealed that not only the degree of the polymerization of the polymolybdotungstate varied with the structure of crown ether, but also the ratio of W/Mo changed. Furthermore, the occupation and distribution of W and Mo in the crystal lattice are quite different. In the $[Na(p\text{-}Rph)aza\text{-}15C5(Et_2OH)]_2W_xMo_{8\text{-}x}O_{26}$, only the position of M(1) and M(1a) are occupied by both W and Mo atoms [M(1) = 0.13W +0.87Mo in complex (**1**) and M(1) = 0.25W+ 0.75Mo in complex (**2**)]; whereas the occupation and distribution of W and Mo atoms are equal at every position of M in the $[Na(DB18C6)(CH_3OH)]_2W_4Mo_2O_{19}$ [M = (2/3)W+(1/3)Mo]; but in the complex of $[Na(DB24C8)]_2W_1Mo_5O_{19}$ the occupation and distribution of W and Mo atoms are unequal again [M(1) = 0.136W+0.864Mo, M(2) = 0.154W+0.846Mo and M(3) = 0.197W+0.803Mo] [5,6]. The reason which caused the differences in the occupation and distribution of W and Mo atoms and degree of polymerization in polymolybdotungstate is under investigation.

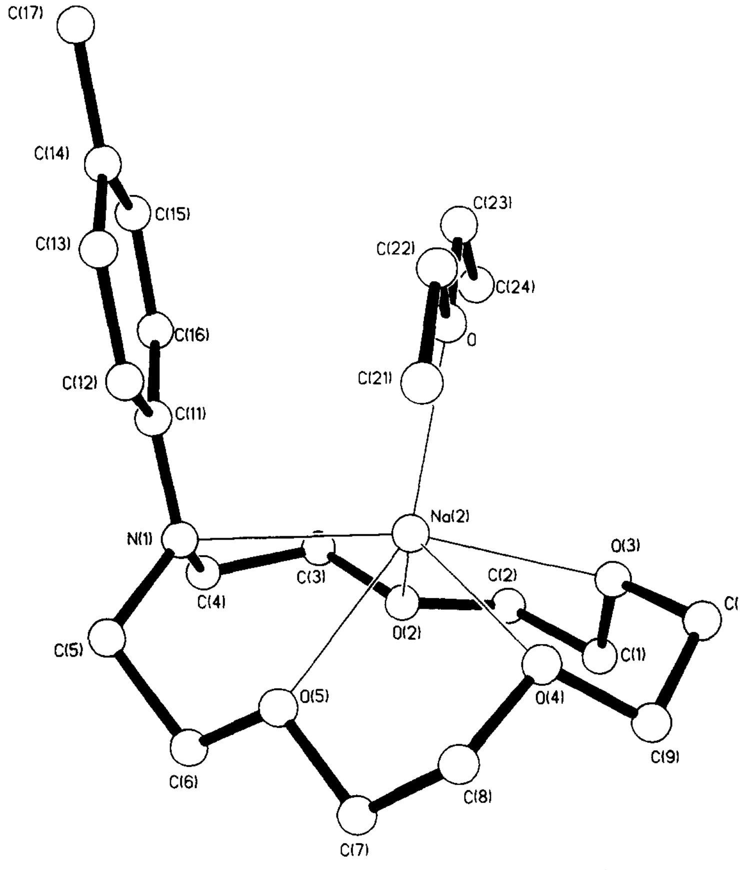

Fig. 2. The structure of $[Na(N\text{-}(p\text{-}CH_3ph)(Et_2O)]^+$.

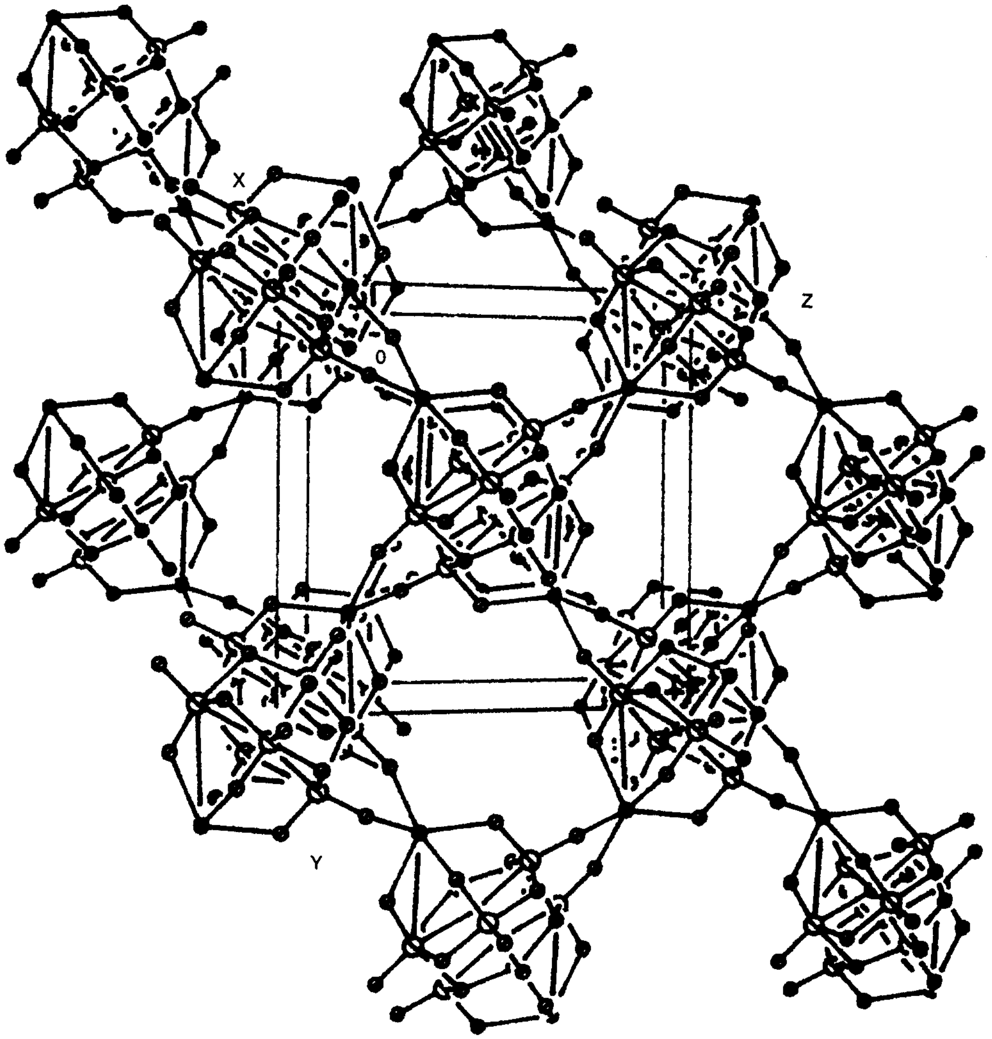

Fig. 3. The structure of $[Na_2M_8O_{26}]_\infty^{2-}$.

EXPERIMENTAL

Materials and methods

All reagents were used as received from commercial supplies. All manipulations were carried out in the laboratory atmosphere. Elemental C, H and N analysis and W, Mo analyses were performed on a Perkin–Elmer analyser and an ICP-AAS(ICP-8410) analyser. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 1600 Series FT IR spectrometer. ^1H NMR and H,H-COSY spectra were obtained using a Bruker AM-500 spectrometer using DMSO as solvent.

Preparation of title complexes

To a solution of equal mole ratios of $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ preadjusted to pH = 3.5 with chloric acid, $(n\text{-}Bu)_4NBr$ was added and stirred for 1 h, then a yellow powder of tetra-*n*-butylammonium hexamolybdotungstate was produced, filtered and dried in the air.

A mixture of N-(*p*-substituted-phenyl)aza-15-crown-5 prepared according to literature [7] and tetra-*n*-butylammonium hexamolybdotungstate produced above in appropriate volume of solution of CH_3OH and CH_3CN was stirred for 6 h and filtered, the filtrate was layered with Et_2O for 15 days and yellow crystals were obtained.

Complex (**1**). C, 23.5 (23.8); H, 3.1 (3.5); N, 1.4 (1.4); W, 2.4 (2.4); Mo, 36.1 (36.8)%. ^1H NMR (500 MHz DMSO) δ: 1.08 (3H, t, CH_3), 3.42 (2H, m, OCH_2), 3.61 (4H, t, H_A), 3.47 (4H, t, H_B), 3.49 (8H, s, H_C, H_D), 3.53 (4H, s, H_E), 6.56 (2H, m, H_a), 7.13 (2H, m, H_b), 6.55 (1H, m, H_C).

Complex (**2**) C, 24.7 (24.4); H, 3.1 (3.6); N, 1.5 (1.4); W, 4.2 (4.5); Mo, 34.4 (34.8)%. ^1H NMR (500 MHz DMSO) δ: 1.08 (3H, t, CH_3), 2.14 (3H, t, $phCH_3$), 3.42 (2H, m, OCH_2), 3.59 (4H, t, H_A), 3.48 (4H, t, H_B), 3.52 (8H, s, H_C, H_D), 3.53 (4H, s, H_E), 6.51 (2H, m, H_a), 6.93 (2H, m, H_b).

Table 1. Bond lengths (Å) of complex (**2**)

M(1)—Mo(2)[a]	3.213(1)	O(14)—Mo(4a)[b]	2.242(8)
M(1)—Mo(3)	3.218(2)	O(15)—Mo(2a)[b]	2.293(6)
M(1)—Na(1)	3.696(5)	O(16)—Na(1d)[b]	2.377(8)
M(1)—O(11)	2.145(7)	Na(2)—N(1)	2.79(1)
M(1)—O(13)	1.945(6)	Na(2)—O(2)	2.44(1)
M(1)—O(14)	1.772(8)	Na(2)—O(3)	2.42(1)
M(1)—O(15)	1.957(6)	Na(2)—O(4)	2.48(1)
M(1)—O(21)	1.703(7)	Na(2)—O(5)	2.43(1)
M(1)—O(11a)	2.310(6)	Na(2)—O	2.410(8)
Mo(2)—O(11)	2.325(6)	N(1)—C(4)	1.49(2)
Mo(2)—O(12)	1.717(7)	N(1)—C(5)	1.49(2)
Mo(2)—O(13)	2.019(6)	N(1)—C(11)	1.41(1)
Mo(2)—O(19)	1.892(8)	O(2)—C(2)	1.39(3)
Mo(2)—O(20)	1.712(7)	O(2)—C(3)	1.43(2)
Mo(2)—O(15a)[b]	2.293(6)	O(3)—C(1)	1.41(2)
Mo(3)—O(11)	2.344(6)	O(3)—C(10)	1.43(2)
Mo(3)—O(15)	2.000(7)	O(4)—C(8)	1.43(2)
Mo(3)—O(16)	1.705(7)	O(4)—C(9)	1.44(2)
Mo(3)—O(17)	1.912(7)	O(5)—C(6)	1.42(2)
Mo(3)—O(22)	1.700(7)	O(5)—C(7)	1.42(2)
Mo(3)—O(13a)[b]	2.289(7)	C(1)—C(2)	1.49(3)
Mo(4)—O(11)	2.422(7)	C(3)—C(4)	1.48(2)
Mo(4)—O(17)	1.912(7)	C(5)—C(6)	1.51(2)
Mo(4)—O(18)	1.69(1)	C(7)—C(8)	1.49(2)
Mo(4)—O(19)	1.936(8)	C(9)—C(10)	1.47(2)
Mo(4)—O(23)	1.723(7)	C(11)—C(12)	1.37(2)
Mo(4)—O(14a)[b]	2.242(8)	C(11)—C(16)	1.40(2)
Na(1)—O(20)	2.538(9)	C(12)—C(13)	1.40(2)
Na(1)—O(21)	2.48(1)	C(13)—C(14)	1.41(2)
Na(1)—O(22)	2.439(8)	C(14)—C(15)	1.36(2)
Na(1)—O(23)	2.463(8)	C(14)—C(17)	1.50(2)
Na(1)—C(12c)[b]	2.44(1)	C(15)—C(16)	1.36(2)
Na(1)—O(16e)[b]	2.377(8)	C(21)—C(22)	1.50(3)
O(11)—M(1a)[b]	2.310(6)	C(22)—O	1.41(2)
O(12)—Na(1b)[b]	2.44(1)	O—C(23)	1.43(2)
O(13)—Mo(3a)[b]	2.289(7)	C(23)—C(24)	1.50(2)
C—H	0.960		

[a] M(1) = 0.25W + 0.75Mo.

[b] $a = -x, -y, 1-z$; $b = 0.5-x, -0.5+y, 1-z$; $c = 0.5+x, 0.5-y, z$; $d = -0.5+x, 0.5-y, z$; $e = 0.5-x, 0.5+y, 1-z$; $f = -0.5+x, -0.5-y, z$.

Table 2. Bond angles (°) of complex (**2**)

Mo(2)—M(1)—Mo(3)[a]	91.8(1)	O(19)—Mo(2)—O(20)	101.5(4)
Mo(2)—M(1)—Na(1)	66.4(1)	M(1)—Mo(2)—O(15a)[b]	78.4(1)
Mo(3)—M(1)—Na(1)	64.8(1)	O(11)—Mo(2)—O(15a)	71.3(2)
Mo(2)—M(1)—O(11)	46.3(2)	O(12)—Mo(2)—O(15a)	90.8(3)
Mo(3)—M(1)—O(11)	46.7(2)	O(13)—Mo(2)—O(15a)	71.6(2)
Na(1)—M(1)—O(11)	62.1(2)	O(19)—Mo(2)—O(15a)	83.3(3)
Mo(2)—M(1)—O(13)	36.6(2)	O(20)—Mo(2)—O(15a)	161.1(3)
Mo(3)—M(1)—O(13)	126.2(2)	M(1)—Mo(3)—O(11)	41.8(2)
Na(1)—M(1)—O(13)	94.7(2)	M(1)—Mo(3)—O(15)	35.1(2)
O(11)—M(1)—O(13)	79.5(2)	O(11)—Mo(3)—O(15)	73.7(2)
Mo(2)—M(1)—O(14)	132.6(2)	M(1)—Mo(3)—O(16)	134.2(3)
Mo(3)—M(1)—O(14)	132.5(2)	O(11)—Mo(3)—O(16)	161.8(3)
Na(1)—M(1)—O(14)	139.3(2)	O(15)—Mo(3)—O(16)	99.1(3)
O(11)—M(1)—O(14)	158.0(3)	M(1)—Mo(3)—O(17)	118.5(2)
O(13)—M(1)—O(14)	95.9(3)	O(11)—Mo(3)—O(17)	76.7(3)
Mo(2)—M(1)—O(15)	125.6(2)	O(15)—Mo(3)—O(17)	145.9(3)
Mo(3)—M(1)—O(15)	36.0(2)	O(16)—Mo(3)—O(17)	103.8(3)
Na(1)—M(1)—O(15)	92.3(2)	M(1)—Mo(3)—O(22)	83.5(3)
O(11)—M(1)—O(15)	79.3(2)	O(11)—Mo(3)—O(22)	91.6(3)
O(13)—M(1)—O(15)	151.2(2)	O(15)—Mo(3)—O(22)	96.4(3)
O(14)—M(1)—O(15)	96.5(3)	O(16)—Mo(3)—O(22)	106.0(4)
Mo(2)—M(1)—O(21)	88.0(2)	O(17)—Mo(3)—O(22)	101.1(3)
Mo(3)—M(1)—O(21)	88.8(3)	M(1)—Mo(3)—O(13a)	78.8(2)
Na(1)—M(1)—O(21)	34.1(3)	O(11)—Mo(3)—O(13a)	71.5(2)
O(11)—M(1)—O(21)	96.2(3)	O(15)—Mo(3)—O(13a)	72.0(2)
O(13)—M(1)—O(21)	100.3(3)	O(16)—Mo(3)—O(13a)	90.4(3)
O(14)—M(1)—O(21)	105.8(3)	O(17)—Mo(3)—O(13a)	82.8(3)
O(15)—N(1)—O(21)	101.2(3)	O(22)—Mo(3)—O(13a)	161.5(3)
Mo(2)—M(1)—O(11a)	86.7(1)	O(11)—Mo(4)—O(17)	74.8(3)
Mo(3)—M(1)—O(11a)	86.1(2)	O(11)—Mo(4)—O(18)	164.0(4)
Na(1)—M(1)—O(11a)	138.5(2)	O(17)—Mo(4)—O(18)	102.3(4)
O(11)—M(1)—O(11a)	76.4(3)	O(17)—Mo(4)—O(19)	74.6(3)
O(13)—M(1)—O(11a)	78.5(2)	O(17)—Mo(4)—O(19)	145.8(4)
O(14)—M(1)—O(11a)	81.6(3)	O(18)—Mo(4)—O(19)	103.0(4)
O(15)—M(1)—O(11a)	77.8(2)	O(11)—Mo(4)—O(23)	89.7(3)
O(21)—M(1)—O(11a)	172.6(3)	O(17)—Mo(4)—O(23)	97.5(3)
M(1)—Mo(2)—O(11)	41.9(2)	O(18)—Mo(4)—O(23)	106.3(4)
M(1)—Mo(2)—O(12)	134.3(3)	O(19)—Mo(4)—O(23)	97.2(3)
O(11)—Mo(2)—O(12)	162.0(3)	O(11)—Mo(4)—O(14a)	70.5(2)
M(1)—Mo(2)—O(13)	35.1(2)	O(17)—Mo(4)—O(14a)	77.5(3)
O(11)—Mo(2)—O(13)	73.8(3)	O(18)—Mo(4)—O(14a)	93.5(4)
O(12)—Mo(2)—O(13)	99.3(3)	O(19)—Mo(4)—O(14a)	78.3(3)
M(1)—Mo(2)—O(19)	119.6(2)	O(23)—Mo(4)—O(14a)	160.3(3)
O(11)—Mo(2)—O(13)	77.8(3)	M(1)—Na(1)—O(20)	64.4(2)
O(12)—Mo(2)—O(19)	102.6(3)	M(1)—Na(1)—O(21)	22.7(2)
O(13)—Mo(2)—O(19)	146.8(3)	O(20)—Na(1)—O(21)	72.2(3)
M(1)—Mo(2)—O(20)	83.4(2)	M(1)—Na(1)—O(22)	65.1(2)
O(1)—Mo(2)—O(20)	91.7(3)	O(20)—Na(1)—O(22)	118.0(3)
O(12)—Mo(2)—O(20)	105.7(3)	O(21)—Na(1)—O(22)	74.9(3)
O(13)—Mo(2)—O(20)	96.2(3)	M(1)—Na(1)—O(23)	95.1(2)
O(20)—Na(1)—O(23)	74.5(3)	M(1)—O(21)—Na(1)	123.2(3)
O(21)—Na(1)—O(23)	117.7(3)	Mo(3)—O(22)—Na(1)	127.7(4)
O(22)—Na(1)—O(23)	76.6(3)	Mo(4)—O(23)—Na(1)	128.8(5)
M(1)—Na(1)—O(12c)	155.6(2)	N(1)—Na(2)—O(2)	65.4(4)
O(20)—Na(1)—O(12c)	140.0(3)	N(1)—Na(2)—O(3)	134.0(4)
O(21)—Na(1)—O(12c)	143.8(3)	O(2)—Na(2)—O(3)	68.6(4)
O(22)—Na(1)—O(12c)	94.1(3)	N(1)—Na(2)—O(4)	137.1(4)
O(23)—Na(1)—O(12c)	91.9(3)	O(2)—Na(2)—O(4)	119.1(4)
M(1)—Na(1)—O(16e)	106.4(3)	O(3)—Na(2)—O(4)	69.5(4)
O(20)—Na(1)—O(16e)	101.5(3)	N(1)—Na(2)—O(5)	67.1(3)
O(21)—Na(1)—O(16e)	84.1(3)	O(2)—Na(2)—O(5)	95.5(5)
O(22)—Na(1)—O(16e)	125.5(3)	O(3)—Na(2)—O(5)	119.7(4)
O(23)—Na(1)—O(16e)	154.0(3)	O(4)—Na(2)—O(5)	70.0(3)
O(12c)—Na(1)—O(16e)	74.5(3)	N(1)—Na(2)—O	108.9(4)

Table 2.—*Continued*

M(1)—O(11)—Mo(2)	91.8(3)	O(2)—Na(2)—O	132.8(3)
M(1)—O(11)—Mo(3)	91.5(2)	O(3)—Na(2)—O	100.7(4)
Mo(2)—O(11)—Mo(3)	163.4(3)	O(4)—Na(2)—O	96.8(3)
M(1)—O(11)—Mo(4)	164.2(3)	O(5)—Na(2)—O	126.7(4)
Mo(2)—O(11)—Mo(4)	86.2(2)	Na(2)—N(1)—C(4)	107.2(8)
Mo(3)—O(11)—Mo(4)	86.2(3)	Na(2)—N(1)—C(5)	105.0(7)
M(1)—O(11)—M(1a)	103.6(3)	C(4)—N(1)—C(5)	111.1(9)
Mo(2)—O(11)—M(1a)	98.0(2)	Na(2)—N(1)—C(11)	93.7(6)
Mo(3)—O(11)—M(1a)	97.1(2)	C(4)—N(1)—C(11)	119(1)
Mo(4)—O(11)—M(1a)	92.1(2)	C(5)—N(1)—C(11)	117(2)
Mo(2)—O(12)—Na(1b)	145.3(4)	Na(2)—O(2)—C(2)	113.4(8)
M(1)—O(13)—Mo(2)	108.2(4)	Na(2)—O(2)—C(3)	115.3(8)
M(1)—O(13)—Mo(3a)	110.6(3)	C(2)—O(2)—C(3)	112(1)
Mo(2)—O(13)—Mo(3a)	103.4(2)	Na(2)—O(3)—C(1)	110(1)
M(1)—O(14)—Mo(4a)	115.7(3)	Na(2)—O(3)—C(10)	110(1)
M(1)—O(15)—Mo(3)	108.8(3)	C(1)—O(3)—C(10)	116(1)
M(1)—O(15)—Mo(2a)	110.5(3)	Na(2)—O(4)—C(8)	110.3(9)
Mo(3)—O(15)—Mo(2a)	103.8(2)	Na(2)—O(4)—C(9)	111.4(7)
Mo(3)—O(16)—Na(1a)	151.4(5)	C(8)—O(4)—C(9)	111(1)
Mo(3)—O(17)—Mo(4)	116.8(4)	Na(2)—O(5)—C(6)	114.2(7)
Mo(2)—O(19)—Mo(4)	115.9(3)	Na(2)—O(5)—C(7)	110.8(9)
Mo(2)—O(20)—Na(1)	125.9(3)	C(6)—O(5)—C(7)	111.2(9)

[a] M(1) = 0.25 W + 0.75 Mo.

a = −*x*, −*y*, 1−*z*; *b* = 0.5−*x*, −0.5+*y*, 1−*z*; *c* = 0.5+*x*, 0.5−*y*, *z*; *d* = −0.5+*x*, 0.5−*y*, *z*; *e* = 0.5−*x*, 0.5+*y*, 1−*z*; *f* = −0.5+*x*, −0.5−*y*, *z*.

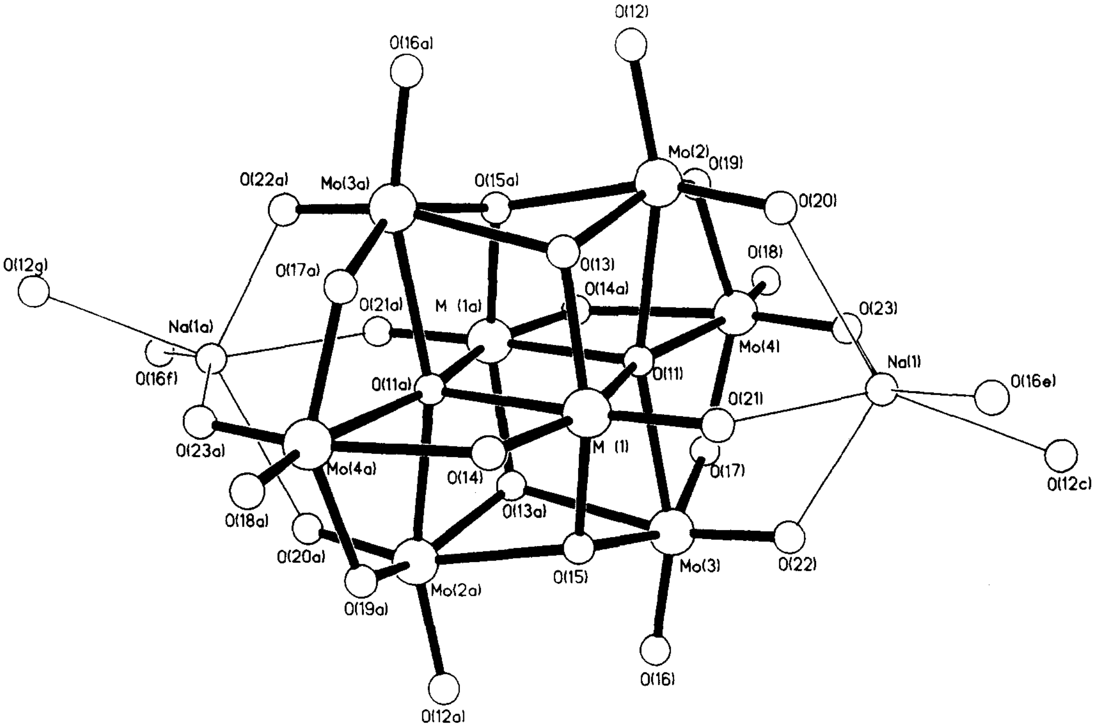

Fig. 4. The structure of $[Na_2M_8O_{26}]^{2-}$.

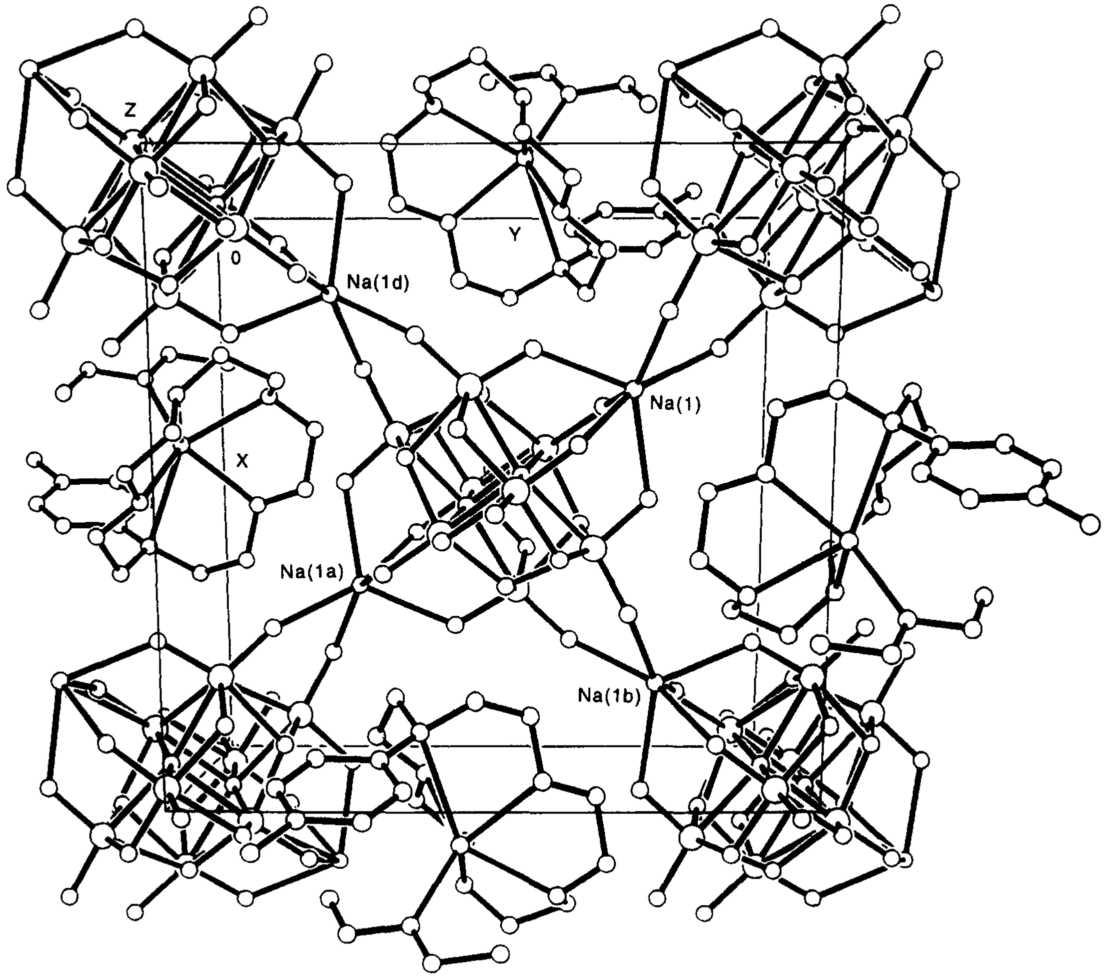

Fig. 5. The packing diagram of complex (**2**) viewed down the *c* axis.

Crystal data for complex (**2**). Yellow crystals from DMF–CH_3OH–Et_2O, $C_{42}H_{74}N_2Na_4O_{36}Mo_{7.5}W_{0.5}$, M = 2037.3, monoclinic, space group $P2_1/a$, $a = 14.590(4)$, $b = 13.817(3)$, $c = 17.639(3)$ Å, $\beta = 112.67(2)°$, $V = 3281(2)$ Å^3, $Z = 2$, $D_c = 2.12$ g/cm^3, $\mu = 2.37$ mm^{-1}, absorption corrections were made using DIFABS; $R = 0.045$, $Rw = 0.057$, and the goodness of fit was 0.98 for 3220 unique observed data and 414 parameters. Intensities were collected on a Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation $\lambda = 0.71073$ Å, θ–2θ scan mode, θ range 2.0–22.5°) at 293K, structure solution and refinement were performed on F using SHELXTL PLUS (VMS). Partial bond lengths and angles are listed in Tables 1 and 2, respectively. The structure of the complex cation, the sodium β-octamolybdotungstate anion and the two-dimensional anion framework are shown in Figs 2, 3 and 4. The packing diagram of complex (**2**) viewed down the *c* axis is presented in Fig. 5.

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