Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2579-2582

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18347

Synthesis and Structure of Two Supramolecular Compounds Based on Macrocyclic Nickel(II) Complex and $[Mo_8O_{26}]^{4-}$

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Received: 19 June 2014; *Accepted*: 10 September 2014; *Published online*: 30 March 2015; AJC-17083

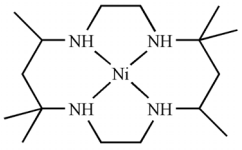
Two supramolecular structures with the formula $[NiL]_2[Mo_8O_{26}]\cdot 2H_2O$ (**1**) and $[NiL][Na_2Mo_8O_{26}]$ (**2**) (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) were synthesized and characterized by elemental analyses and IR spectra. The crystal structures were determined by the X-ray diffraction. The crystal of complex **1** is orthorhombic: space group Pbca, a = 17.812 (2), b = 15.942 (2), c = 19.295 (3) Å, V = 5478.8(12) Å^3, Z = 4. The crystal of complex **2** is triclinic: space group P-1, a = 10.022(19), b = 10.717(2), c = 11.110(2) Å, α = 87.930(3)°, β = 72.115(3)°, γ = 62.383(3)°, V = 998.2(3) Å^3, Z = 1. In both complexes, the $[NiL]^{2+}$ and $[Mo_8O_{26}]^{4-}$ monomers are connected through intermolecular hydrogen bonding to generate two-dimensional sheets.

Keywords: Macrocyclic nickel(II) complexes, Molybdenum cluster, Hydrogen bonding.

INTRODUCTION

Building novel materials based on the well-known structural polyoxometalate types continues to be focus of much attention, not only because of their fascinating structures but also their potential applications in catalysis, medicine, ion exchange, gas storage, molecular electronics and biological chemistry [1-3]. Recently, many extended structures have been constructed using transition metal complexes and polyoxo-molybdate clusters such as $[Mo_8O_{26}]^{4-}$ as building blocks [4-9].

In our previous reported[10-16], some polyoxometalate materials with 1D, 2D and 3D structures were obtained by the reactions of $[ML](ClO_4)_2$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, M = Cu, Ni and Zn, **Scheme-I**) with polyoxovanadates and molybdenum phosphates. In continuation of our research on the constructions of polyoxometalate materials, we employ polyoxomolybdates and nickel(II) macrocyclic complexes as building blocks. Herein, we report the preparation and structures of two 2D supramolecular complexes $[NiL]_2[Mo_8O_{26}]\cdot 2H_2O$ (**1**) and $[NiL][Na_2Mo_8O_{26}]$ (**2**).



$[NiL]^{2+}$

Scheme-I: Sketch of a Ni(II) complex cation

EXPERIMENTAL

The macrocyclic ligand (L) and its nickel(II) complexes were prepared according to the literature method[17,18]. All of the other chemicals are commercially sourced and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyzer. IR spectra were recorded in the 4000-400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer.

Synthesis of $[NiL]_2[Mo_8O_{26}]\cdot 2H_2O$ (1): A mixture of $NiL(ClO_4)_2$ (0.108 g, 0.2 mmol), MoO_3 (0.096 g, 0.67 mmol) and H_2O (18 mL) was added to a Teflon-lined reactor and heated at 170 °C for 4 days. Yellow block-shaped crystals of **1** were obtained in 31 % yield. Anal. found: C, 20.31; H, 4.24; N, 6.03 %. Calcd. for $C_{32}H_{76}N_8O_{28}Mo_8Ni_2$ (**1**): C, 20.17; H, 4.02; N, 5.88 %. IR (KBr, ν_{max}, cm^{-1}): (Mo=O and Mo-O-Mo) 942-708.

Synthesis of $[NiL][Na_2Mo_8O_{26}]$ (2): A mixture of $NiL(ClO_4)_2$ (0.108 g, 0.2 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.083 g, 0.67 mmol) and H_2O (18 mL) was adjusted to pH = 6.5 with 1 mol/L HCl and added to a Teflon-lined reactor and heated at 130 °C for 5 days. Yellow block-shaped crystals of **2** were obtained in 40 % yield. Anal. found: C, 12.69; H, 2.49; N, 3.33 %. Calcd.

for $C_{16}H_{36}N_4O_{26}Mo_8Na_2Ni$ (**2**): C, 12.22; H, 2.31; N, 3.56 %. IR (KBr, ν_{max}, cm^{-1}): (Mo=O and Mo-O-Mo) 945-711.

X-Ray crystal structure determination: Single-crystal data for **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer equipped with MoK_α radiation (λ = 0.71073 Å) at 173(2) K. Empirical absorption corrections were applied by using the SADABS program[19]. Both structures were studied using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (expect those of nitrogen atoms and water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of the macrocyclic nitrogen atoms were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXTL system of computer programs[20]. For complex **1**, a total of 23282 reflections were collected in the range of $2.01 < \theta < 27.03°$, of which 5966 were independent (R_{int} = 0.0366) and 4539 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. The final R = 0.0333 and wR = 0.0709 for 4539 observed reflections with $I > 2\sigma(I)$ and R = 0.0521 and wR = 0.0774 for 5966 independent reflections, S = 1.096, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta\rho)_{max}$ = 1.063 and $(\Delta\rho)_{min}$ = -1.032 e/Å^3. For complex **2**, a total of 7607 reflections were collected in the range of $2.16 < \theta < 26.04°$, of which 3827 were independent (R_{int} = 0.0211) and 2864 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. The final R = 0.0332 and wR = 0.0866 for 2864 observed reflections with $I > 2\sigma(I)$ and R = 0.0527 and wR = 0.1091 for 3827 independent reflections, S = 1.077, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta\rho)_{max}$ = 0.990 and $(\Delta\rho)_{min}$ = -0.842 e/Å^3. The crystallographic data for the title compound is summarized in Table-1. Selected bond lengths are listed in Table-2. Hydrogen bond parameters are given in Table-3.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **1** AND **2**

Compound	**1**	**2**
Empirical formula	$C_{32}H_{76}N_8O_{28}Mo_8Ni_2$	$C_{16}H_{36}N_4O_{26}Mo_8NiNa_2$
Formula weight	1905.95	1572.70
Temperature (K)	173(2)	173(2)
Crystal system	Orthorhombic	Triclinic
Space group	Pbca	P-1
a/Å	17.812(2)	10.0222(19)
b/Å	15.942(2)	10.717(2)
c/Å	19.295(3)	11.110(2)
α/°	90	87.930(3)
β/°	90	72.115(3)
α/°	90	62.383(3)
V/Å^3	5478.8(12)	998.2(3)
Z	4	1
D_c/Mg cm^{-3}	2.311	2.616
μ/mm^{-1}	2.528	2.999
F (000)	3670	754
Crystal size (mm)	0.42 × 0.36 × 0.21	0.36 × 0.21 × 0.13
θ Range for data collection	2.01-27.03	2.16-26.04
Reflections collected/unique	23282/5966 (0.0366)	7607/3827 (0.0211)
Completeness to θ	9.3 %	96.8 %
Goodness-of-fit on F^2	1.096	1.077
Final R indices [I >2σ(I)]	0.0333, 0.0709	0.0332, 0.0866
R indices (all data)	0.0521, 0.0774	0.0527, 0.1091
Max. peak/hole (e. Å^{-3})	1.063/-1.032	0.990/-0.842

RESULTS AND DISCUSSION

The molecular structures of **1** and **2** are shown as Figs. 1 and 2, respectively. X-ray crystal structural analysis reveals that complex **1** contains two $[NiL]^{2+}$ cation, one β-$[Mo_8O_{26}]^{4-}$ anion and two water molecules (Fig. 1). Selected bond distances and

TABLE-2
SELECTED BOND LENGTHS (Å)

1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Ni(1)–N(1)	1.943(4)	Ni(1)–N(2)	1.931(4)	Ni(1)–N(3)	1.945(5)
Ni(1)-N(4)	1.948(4)	Mo(1)-O(1)	1.960(3)	Mo(1)-O(2)	1.691(3)
Mo(1)-O(3)	1.753(3)	Mo(1)-O(12)^A	1.934(3)	Mo(1)-O(13)	2.358(3)
Mo(1)-O(13)^A	2.130(3)	Mo(2)-O(4)	1.694(4)	Mo(2)-O(5)	1.719(4)
Mo(2)-O(3)	2.270(3)	Mo(2)-O(10)	1.919(4)	Mo(2)-O(13)	2.495(3)
Mo(2)-O(6)	1.910(4)	Mo(3)-O(8)	1.694(4)	Mo(3)-O(6)^A	1.901(3)
Mo(3)-O(7)	1.696(3)	Mo(3)-O(13)^A	2.323(3)	Mo(4)-O(9)	1.699(4)
Mo(3)-O(12)	2.346(3)	Mo(4)-O(10)	1.906(4)	Mo(4)-O(12)	2.000(3)
Mo(4)-O(11)	1.702(3)	O(1)-Mo(3)	2.010(3)	O(1)-Mo(4)	2.366(3)
Mo(4)-O(13)	2.325(3)	-	-	-	-
2					
Mo(1)-O(1)	1.704(5)	Mo(1)-O(2)	1.708(5)	Mo(1)-O(3)	1.884(5)
Mo(1)-O(9)^B	2.301(5)	Mo(1)-O(12)	2.005(5)	Mo(1)-O(13)	2.329(4)
Mo(2)-O(9)	1.946(5)	Mo(2)-O(10)	1.747(5)	Mo(2)-O(11)	1.688(5)
Mo(2)-O(12)	1.945(5)	Mo(2)-O(13)	2.152(4)	Mo(2)-O(13)^B	2.366(5)
Mo(3)-O(6)	1.879(5)	Mo(3)-O(7)	1.707(5)	Mo(3)-O(8)	1.710(5)
Mo(3)-O(9)	2.014(5)	Mo(3)-O(12)^B	2.314(5)	Mo(3)-O(13)	2.283(4)
Mo(4)-O(3)	1.931(5)	Mo(4)-O(4)	1.700(5)	Mo(4)-O(5)	1.693(5)
Mo(4)-O(6)	1.945(5)	Mo(4)-O(10)^B	2.280(5)	Mo(4)-O(13)	2.479(4)
Ni(1)-N(1)	1.949(6)	Ni(1)-N(2)	1.964(5)	-	

Symmetry codes: A: -x, 1-y, 1-z; B: 2-x , 2-y, 1-z

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠DHA
		1		
N(3)-H(3A)...O(1W)$^{\#1}$	0.930	1.97	2.807(7)	148.5
O(1W)-H(1WA)...O(2)$^{\#2}$	0.865	2.05	2.847(6)	153.0
O(1W)-H(1WB)...O(5)$^{\#3}$	0.866	2.06	2.901(7)	163.0
		2		
N(2)-H(2B)...O(2)$^{\#4}$	0.930	2.20	3.029(8)	148.1

Symmetry codes: #1:-x + 1/2, y-1/2, z; #2: -x + 1/2, -y + 1, z + 1/2; #3: -x, y + 1/2, -z + 3/2; #4: x, y-1, z-1

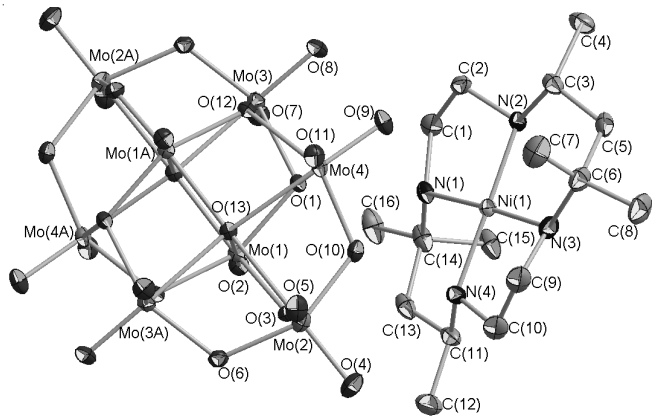


Fig. 1. ORTEP diagram of **1** with 30 % probability displacement ellipsoids (H atoms and water molecule are omitted for clarity), the symmetry codes for the generated atoms: A (-x, 1-y, 1-z)

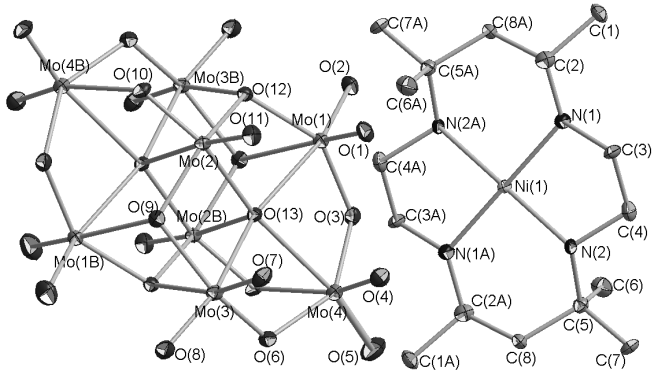


Fig. 2. ORTEP diagram of **2** with 30 % probability displacement ellipsoids (H and Na atoms are omitted for clarity), the symmetry codes for the generated atoms: B (2-x, 2-y, 1-z), C (1-x, 1-y, -z)

angles of complex **1** are shown in Table-1. In the cation, each Ni(II) atom lies on an inversion center and is coordinated with four macrocyclic nitrogen atoms in the equatorial plane. The average Ni-N distance is 1.942(4) Å. Presently three different octamolybdate isomers (α, β, γ) $[Mo_8O_{26}]^{4-}$ have been isolated and structurally characterized[21]. The β-$[Mo_8O_{26}]^{4-}$ anion is built up from eight MoO_6 distorted octahedral that share edges and corners through six μ_2-, four μ_3- and two μ_5-oxygen atoms. The molybdenum center in $[MoO_6]$ octahedron has Mo-O bonds in the range of 1.691(3)-1.719(4) Å for fourteen terminal oxygen atoms (O_t), 1.910(4)-2.270(3) Å for six μ_2 bridging oxygen atoms (O_b) and 1.960(3)-2.495(3) Å for six μ_3 and μ_5 center oxygen atoms (O_c). The $[MoO_6]$ octahedron units have O-Mo-O angles in the ranges of 71.45(12)-175.76(15). The β-$[Mo_8O_{26}]^{4-}$ anions are connected by N-H···O (2.807(7) Å) and O-H···O (2.847(6) and 2.901(7) Å) (Table-2) intermolecular hydrogen bonds between oxygen atoms [O(2) and O(5)] of β-$[Mo_8O_{26}]^{4-}$ and secondary amine (N3) of macrocyclic ligand L and free water molecule [O(1W)] to form a two-dimensional sheet (Fig. 3).

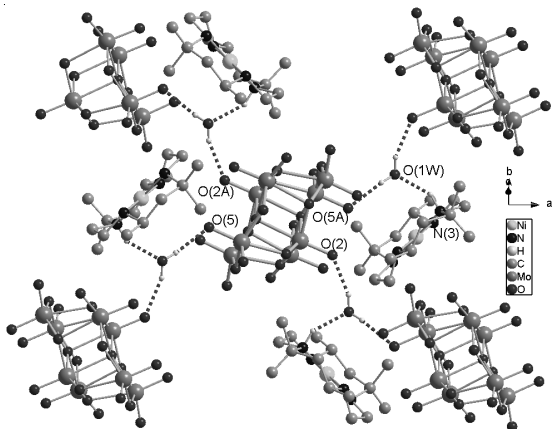


Fig. 3. Side view of two-dimensional hydrogen bonded sheet in complex **1**

The structure of complex **2** consists of one $[NiL]^{2+}$ cation, one β-$[Mo_8O_{26}]^{4-}$ anion and two sodium ions (Fig. 2) and the Ni-N bonds in the range of 1.949(6)-1.964(5) Å. The β-$[Mo_8O_{26}]^{4-}$ anion is similar to those in complex **1**. The V-O_b and V-O_c bond lengths [1.747(5)-2.479(4) Å] are longer than the V-O_t distances [1.688(5)-1.710(5) Å]. The $[MoO_6]$ octahedron units have similar O-Mo-O angles in the ranges of 71.24(17)-173.70(2). A one-dimensional chain is formed through the connecting of β-$[Mo_8O_{26}]^{4-}$ with Na^+ and the four-coordinated $[NiL]^{2+}$ locate between two adjacent chains and link two chains through N-H···O (2.807(7) Å) (Table-2) intermolecular hydrogen bonds between oxygen atoms [O(2)] of β-$[Mo_8O_{26}]^{4-}$ and secondary amine [N(2)] of macrocyclic ligand L to generate a two-dimensional sheet (Fig. 4).

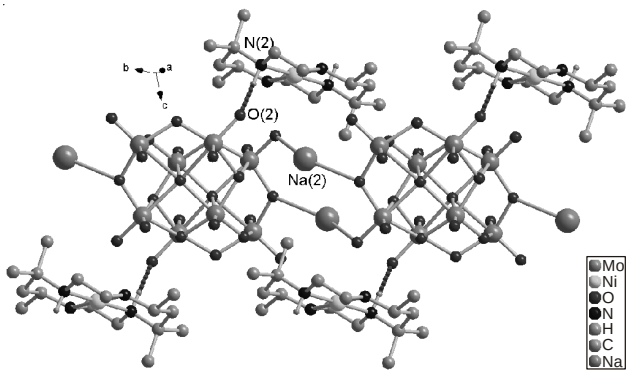


Fig. 4. Side view of two-dimensional hydrogen bonded sheet in complex **2**

The infrared spectra of **1** and **2** show characteristic bands near 940 cm^{-1} attributed to the Mo=O group, bands between 840 and 710 cm^{-1} due to the Mo-O-Mo group and bands near 3100 cm^{-1} are associated with the N-H stretching vibration and bands between 1635 and 1460 cm^{-1} are assigned to the C-C and C-N stretching vibrations of the organic amines, respectively.

Conclusion

In this work, we have successfully obtained two supramolecular structures from $NiL(ClO_4)_2$ with polyoxoanion of $[Mo_8O_{26}]^{4-}$ *via* hydrogen bonding. In both complexes **1** and **2**, the $[NiL]^{2+}$ and $[Mo_8O_{26}]^{4-}$ monomers are connected through intermolecular hydrogen bonding to generate two-dimensional sheets. The results have demonstrated that hydrogen bonds play a key role in supramolecular assemblies.

Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC 965563 for 1 and 965561 for 2. Copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk

ACKNOWLEDGEMENTS

This work was financially Supported by the Project for Undergraduate Research Study and Innovative Experiment of Hunan Provincial (2013-191) and National Undergraduate Training Programs for Innovation and Entrepreneurship (201310551158), the Key Laboratory of Functional Organometallic Materials of Hunan Province College (13K10), the Scientific Research Fund of Hunan Provincial Education Department (13B029), the Construct Program of the Key Discipline in Hunan Province (2011-76) and the Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province (2012-318) and the Program for Excellent Talents in Hunan University of Science and Engineering.

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