Polyhedron 100 (2015) 290–295

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and X-ray crystallographic characterization of two different inorganic–organic hybrid isopolyoxomolybdates with α-dipropylammonium *N*,*N*-diisobutylacetamide by varying reaction conditions

Shikha Sharma [a], Sunil K. Ghosh [a,*], Mukesh Kumar [b,*], Joti N. Sharma [c]

[a] *Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*
[b] *Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*
[c] *Process Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

ARTICLE INFO

Article history:
Received 16 June 2015
Accepted 24 August 2015
Available online 29 August 2015

Keywords:
Inorganic–organic hybrid
Polyoxomolybdates
Crystal structure
Self assembly
H-bonding

ABSTRACT

Two new polyoxomolybdate based inorganic–organic hybrid compounds have been obtained from same ammonium ion ligand **1** and molybdate source just by altering reaction conditions. The new hybrid polyoxomolybdate complexes $(LH)_2[Mo_6O_{19}]$ **3** and $(LH)_4[Mo_8O_{26}]$ $(MeCN)_2$ **4** have distinct structural features revealed by X-ray crystallographic studies. The complex **3** contains two ammonium ligands to balance the charge on hexamolybdate dianion. The most striking feature of $(LH)_2[Mo_6O_{19}]$ is the presence of inter-ligand hydrogen bonding (N—H···O=C) between two ligands arranged in an antiparallel fashion that favors the formation of a net like structure which embeds the Mo_6O_{19} dianion. The complex **4** contains four ammonium ligands to balance the charge on β-octamolybdate tetraanion. Interestingly, complex **4** exhibits strong hydrogen-bonding interactions between ammonium ligand and octamolybdate anion (N—H···O—Mo) and no inter-ligand H-bonding interaction. The different structural features of hybrid compounds **3** and **4** suggest that different polyoxomolybdate clusters play a key role in the process of assembling of ligands.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Molybdenum compounds are popular target for studies because of their importance in biological systems [1–3], interesting structural features [3,4] and extensive applications in various fields of sciences [5]. Besides normal compounds and complexes, Mo forms extensive range of oxometalate clusters consists of isopolyacids or heteropolyacids [3–6]. The Lindqvist anionic hexamolybdate $[Mo_6O_{19}]^{2-}$ has been structurally characterized as isolated salt in solid state [7]. The interesting aspects of structure chemistry of the octamolybdate anion, $[Mo_8O_{26}]^{4-}$ is seen in varied structural patterns in the solid state [8]. Seven isomeric forms viz. α–η of octamolybdates, $[Mo_8O_{26}]^{4-}$ are known [8–10]. The structures differ in the types of polyhedron that fuse to form the cluster and in the linkage between polyhedra.

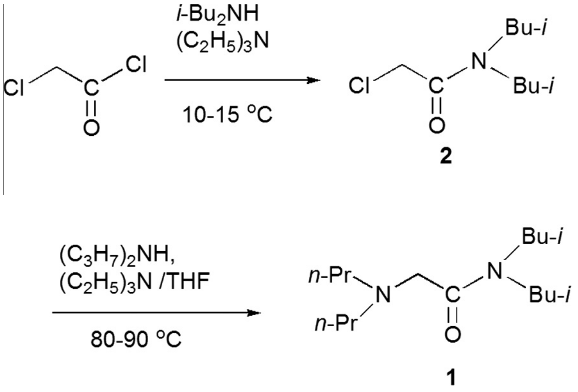
Several research attempts have been made to functionalize the polyoxomolybdates (POMs) with an organic component which gives rise to the formation of inorganic–organic hybrid materials where POMs work as building blocks. As the POM anions contain many oxygen atoms which act as good hydrogen bond acceptors, fictionalization of these POMs with organic molecules having many hydrogen atoms give rise to interesting supramolecular chemistry [11–13]. The supramolecular interactions are mediated by various type of hydrogen bonds like O—H···O, N—H···O, C—H···O, O—H···N, etc. [11,12].

Quaternary ammonium salt such as Aliquat and tertiary amine like Alamines are generally used for extraction of Mo from weakly acidic aqueous medium [14–16]. Crystal structure of POM anion with Bu_4N^+ as a mixed $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$, i.e., $[n\text{-}Bu_4N]_8[Mo_6O_{19}]_2[\alpha\text{-}(Mo_8O_{26})]$ [17] has been reported recently. Crystals of $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$ have also been made using different organic ligands [12,18–20]. Complexes of POM with organic amino type ligands associated with transition metals such as Cu or Co have been prepared and characterized by X-ray crystallography [21–24]. But, individual complexes of $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$ with the same ligand are not known. Recently, we have developed α-dipropylamino *N*,*N*-diisobutylacetamide (L) **1** (Scheme 1) as an

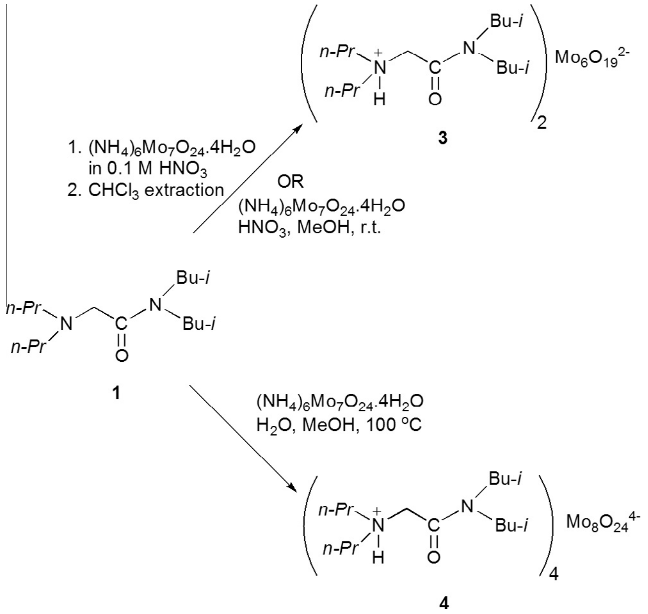
---

* Corresponding authors. Tel.: +91 22 25595012; fax: +91 22 25505151.
E-mail address: ghsunil@barc.gov.in (S.K. Ghosh).

http://dx.doi.org/10.1016/j.poly.2015.08.029
0277-5387/© 2015 Elsevier Ltd. All rights reserved.



Scheme 1. Synthesis of α-dipropylamino *N*,*N*-diisobutylacetamide **1**.



Scheme 2. Synthesis of metal–ligand complexes **3** and **4**.

amine based extractant for Mo with an aim for its recovery from spent nuclear fuel dissolved in nitric acid where other amine based extractants did not work [25]. Considering the great importance of inorganic–organic hybrid materials of polyoxomolybdates, we herein report the condition dependent crystal engineered syntheses of $(LH^+)_2[Mo_6O_{19}]^{2-}$ and $(LH^+)_4[Mo_8O_{26}]^{4-}$ complexes and their X-ray crystallographic characterization.

2. Results and discussion

α-Dipropylamino *N*,*N*-diisobutylacetamide **1** was synthesized following our reported procedure [25] from the commercially available starting materials as described in Scheme 1. For this, chloroacetyl chloride was reacted with diisobutylamine in the presence of triethylamine to give the amide **2** which was subsequently reacted with diisopropylamine to give the desired α-dipropylamino *N*,*N*-diisobutylacetamide **1** in very good overall yield.

When the chloroform solution of ligand **1** was repeatedly contacted with fresh solution of $(NH_4)_6Mo_7O_{24}·4H_2O$ in 0.1 M aqueous HNO_3 and the resultant organic phase was concentrated, a yellow precipitate was obtained which on crystallization from acetonitrile provided a yellow complex $(LH)_2[Mo_6O_{19}]$ **3** (Scheme 2). The same complex **3** was achieved when a 0.5 M nitric acid solution of $(NH_4)_6Mo_7O_{24}·4H_2O$ and a methanolic solution of ligand **1** were mixed and stirred at room temperature. Interestingly, when $(NH_4)_6Mo_7O_{24}·4H_2O$ was dissolved in water, mixed with a methanolic solution of ligand **1** and heated at 100 °C, a colorless complex $(LH)_4[Mo_8O_{26}]$ **4** was formed.

Table 1
Crystallographic data and details of structure refinement for complexes **3** and **4**.

	3	4
Empirical formula	Mo_6O_{19}, $2(C_{16}H_{35}N_2O)$	Mo_8O_{26}, $4(C_{16}H_{35}N_2O)$, $2(C_2H_3N)$
Formula weight	1422.56	2351.46
T (K)	293(2)	293(2)
λ (Å)	1.5418	1.5418
Crystal system	monoclinic	triclinic
Space group	$I2/a$	$P\bar{1}$
a (Å)	24.8703(11)	11.8091(11)
b (Å)	11.1774(3)	12.1612(11)
c (Å)	20.4442(9)	18.2009(13)
α (°)	90	77.755(7)
β (°)	119.195(6)	81.247(7)
γ (°)	90	87.642(7)
V (Å^3)	4961.2(4)	2524.6(4)
Z	4	1
D_{calc} (g/cm^3)	1.905	1.547
μ (mm^{-1})	12.706	8.471
$F(000)$	2840.0	1200.0
Crystal size (mm^3)	0.4585 × 0.288 × 0.1217	0.5939 × 0.3818 × 0.1877
θ max (°)	69.865	70.096
Reflections collected/unique	8318/4616	16607/9390
R_{int}	0.0621	0.0809
Data/restraints/parameters	4616/48/332	9390/24/535
Goodness-of-fit on F^2	1.010	1.133
R_1/wR_2 [$I \geqslant 2\sigma(I)$]	0.0943/0.2491	0.1100/0.2873
R_1/wR_2 (all data)	0.1161/0.2800	0.1319/0.3204
Residuals (e Å^{-3})	1.92, −3.29	3.48, −2.54

2.1. Synthesis of complex $(LH)_2[Mo_6O_{19}]$ **3** (route A)

A solution of acetamide **1** (271 mg, 1 mmol) in chloroform (5 mL) was repeatedly contacted with fresh solution of $(NH_4)_6Mo_7O_{24}·4H_2O$ (46 mg, 0.037 mmol) in 0.1 M aqueous HNO_3 (5 mL). The chloroform extract was concentrated under reduced pressure to give a yellow precipitate of metal ligand complex. The precipitate was triturated with 10% ethyl acetate–hexane solution to remove excess ligand **1**. The solid residue was then crystallized from acetonitrile to obtain the yellow crystalline complex **3** (603 mg, 85%). IR (KBr): $\bar{\nu}$ 3450, 3109, 2960, 2877, 1643 (C=O), 1464, 1387, 1257, 1157, 953 (Mo=O), 800, 592 (Mo—O—Mo), 436 cm^{-1}.

2.2. Synthesis of Mo crystal $(LH)_2[Mo_6O_{19}]$ **3** (route B)

A solution of $(NH_4)_6Mo_7O_{24}·4H_2O$ (84 mg, 0.068 mmol) in 0.5 M HNO_3 (3 mL) was added to a solution of acetamide **1** (55 mg, 0.204 mmol) in MeOH (2 mL) and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the light yellow precipitate was washed with 10% ethyl acetate–hexane solution to remove the excess ligand **1**. The yellow powder was crystallized from acetonitrile to give yellow crystals of complex **3** (79 mg, 81%).

2.3. Synthesis of Mo crystal $(LH)_4[Mo_8O_{26}]$ $(MeCN)_2$ **4**

A solution of $(NH_4)_6Mo_7O_{24}·4H_2O$ (42 mg, 0.034 mmol) in water (2 mL) was added to a solution of acetamide **1** (64 mg, 0.238 mmol) in MeOH (1 mL). The reaction mixture was stirred at 100 °C for 3 h, brought to room temperature and concentrated under reduced pressure. The solid residue was washed with 10% ethyl acetate–hexane solution to remove the excess ligand **1**. The

Download English Version:

https://daneshyari.com/en/article/1335944

Download Persian Version:

https://daneshyari.com/article/1335944

Daneshyari.com