

# Synthesis and Structural Characterization of Manganese Carbonyl Incorporated Polyoxomolybdate

## $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{16}(\text{OCH}_3)_2\{\text{HOCH}_2\text{C}(\text{CH}_2\text{O})_3\}_2\{\text{Mn}(\text{CO})_3\}_2]$

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**Abstract** The polyoxoanion incorporated  $\{\text{Mn}(\text{CO})_3\}^+$  complex,  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{16}(\text{OCH}_3)_2\{\text{HOCH}_2\text{C}(\text{CH}_2\text{O})_3\}_2\{\text{Mn}(\text{CO})_3\}_2]$  (**1**), has been synthesized by the reaction of  $(n\text{-Bu}_4\text{N})_4[\text{Mo}_8\text{O}_{26}]$  with  $\text{Mn}(\text{CO})_5\text{Br}$  in methanol, in the presence of  $\text{C}(\text{CH}_2\text{OH})_4$ . The complex **1** has been characterized by IR, UV-Vis, X-ray single crystal diffraction, and TG. Crystal data for the complex **1**:  $\text{C}_{25}\text{H}_{48}\text{MnMo}_3\text{NO}_{16}$  (**1**), Triclinic  $P\bar{1}$ ,  $a=0.9405(3)$  nm,  $b=1.3351(4)$  nm,  $c=1.5455(4)$  nm,  $\alpha=103.206(5)^\circ$ ,  $\beta=102.165(5)^\circ$ ,  $\gamma=100.784(5)^\circ$ ,  $V=1.7896(9)$  nm<sup>3</sup>,  $Z=2$ ,  $R_1=0.0703$ ,  $wR_2=0.1495$ . The structure analysis of complex **1** shows that the complex consists of two tetrabutylammonium cations and a polyoxomolybdate anion that incorporates two *fac*- $\text{Mn}(\text{CO})_3^+$  units. The anion of complex **1** can be considered as the dimer of two rhomb-like anions by sharing of two corners.

**Keywords** Polyoxomolybdate; Manganese; Carbonyl

## 1 Introduction

Organometallic derivatives of polyoxometalates have attracted increasing interest in recent years because of the possibility of their combining the hard oxygen ligands with soft ligands to obtain novel structures and properties<sup>[1]</sup>. In addition, organometallic derivatives of polyoxometalates are potentially polyoxometalates-based catalysts or precatalysts<sup>[2,3]</sup>. Typical examples include the catalytic oxidation and reduction reactions of cyclohexene with  $[(1,5\text{-cod})\text{-IrP}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$  ( $\text{cod}=1,5\text{-cyclooctadiene}$ )<sup>[4,5]</sup>, and the syntheses of  $\text{C}_{n+1}$  carboxylic acids from  $\text{C}_n$  olefins by sequential one-pot hydroxylation and oxidation steps with  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})_4][\text{SiW}_{12}\text{O}_{40}]$  as a bifunctional catalyst<sup>[2,3,6,7]</sup>. However, a small portion of metal carbonyl derivatives of polyoxometalates, as a class of organometallic derivatives, have been reported so far<sup>[4–14]</sup>. Representative metal carbonyl complexes include the merely examples of polyoxoanion-supported metal carbonyl complexes  $[\text{M}(\text{CO})_3(\text{cis}\text{-Nb}_2\text{W}_4\text{O}_{19})]^{3-}$  ( $\text{M}=\text{Mn}$  or  $\text{Re}$ ),  $\{[\text{Rh}(\text{CO})_2]_3(\text{Nb}_2\text{W}_4\text{O}_{19})_2\}^{5-}$ ,  $\{[\text{Ir}(\text{CO})_2]_2\text{H}(\text{Nb}_2\text{W}_4\text{O}_{19})_2\}^{5-}$  etc. by

Klemperer and co-workers<sup>[8–14]</sup>,  $[\text{Re}(\text{CO})_3\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$ ,  $[\text{Ir}(\text{CO})_2\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{8-}$  by Finke<sup>[4]</sup> and  $[\text{M}_6\text{O}_{19}\{\text{M}'(\text{CO})_3\}_n]^{(8-n)-}$  ( $\text{M}=\text{Nb}$ ,  $\text{Ta}$ ;  $\text{M}'=\text{Mn}$ ,  $\text{Re}$ ;  $n=1,2$ ) by Pope<sup>[15]</sup>. Other types of metal carbonyl complexes comprise of polyoxomolybdate-incorporated metal carbonyl complexes  $[\text{Mo}_2\text{O}_5(\text{OCH}_3)_5\{\text{M}(\text{CO})_3\}_2]^-$  ( $\text{M}=\text{Mn}$  or  $\text{Re}$ ),  $[\text{Mn}(\text{H}_2\text{O})_2\{\text{Mo}_5\text{O}_{16}(\text{OCH}_3)_2\text{Mn}(\text{CO})_3\}_2]^{4-}$ ,  $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})\{\text{Mo}_5\text{O}_{13}(\text{OCH}_3)_4(\text{NO})\}]^{2-}$ ,  $[\text{Na}\{\text{Mo}_5\text{O}_{13}(\text{OCH}_3)_4(\text{NO})\}_2\{\text{Mn}(\text{CO})_3\}_2]^{3-}$  and so on, by Proust<sup>[2,3]</sup>. The remaining consists of metal carbonyl cation and polyoxoanion  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})(\text{CH}_3\text{CN})]_{8-n}\text{XM}_{12}\text{O}_{40}$ ,  $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})]_{8-n}\text{XM}_{12}\text{O}_{40}$  ( $\text{X}=\text{P}$ ,  $\text{Si}$ ;  $\text{M}=\text{Mo}$ ,  $\text{W}$ ), and so on, by Siedle<sup>[6,7]</sup>. Herein lies the synthesis and structural characterization of manganese tricarbonyl incorporated polyoxomolybdate  $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{16}(\text{OCH}_3)_2\{\text{HOCH}_2\text{C}(\text{CH}_2\text{O})_3\}_2\{\text{Mn}(\text{CO})_3\}_2]$ .

## 2 Experimental

### 2.1 Synthesis of Complex 1

All the reagents and solvents were purchased commercially and used without further purification.

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(*n*-Bu<sub>4</sub>N)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>] was prepared according to the literature method<sup>[16]</sup>.

0.365 g(0.25 mmol) of (*n*-Bu<sub>4</sub>N)<sub>4</sub>[Mo<sub>8</sub>O<sub>26</sub>], 0.074 g(0.5 mmol) of C(CH<sub>2</sub>OH)<sub>4</sub>, and 0.135 g(0.5 mmol) of Mn(CO)<sub>5</sub>Br, and 15 mL of methanol were stirred at room temperature until all the solids were dissolved(about half an hour). The solution turned to red and was cooled in an ice bath for 10 min. Then the clear red solution was allowed to stand at room temperature. After two days, orange block crystals suitable for X-ray diffraction were obtained(yield: 75% based on Mo).

## 2.2 General Methods

IR spectrum was recorded from KBr pellets on a Nicolet 170 FTIR spectrophotometer in a range of 4000—400 cm<sup>-1</sup>.

UV-Vis spectrum was obtained on a U-4100 spectrometer from 350—550 nm in CH<sub>3</sub>CN.

The TG curve was obtained with an Exstar 6000 analyzer in nitrogen gas atmosphere at a heating rate of 10 °C/min from room temperature to 900 °C.

## 2.3 Structure Determination

A suitable orange single crystal of complex 1 with the approximate dimensions 0.22 mm×0.16 mm×0.12 mm was selected and mounted on a glass fiber capillary. The data were collected on a Bruker APEX-II CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda=0.071073$  nm) at 293(2) K in a range of  $2.29^\circ \leq \theta \leq 25.05^\circ$ . A total of 6305(4981 unique,  $R_{\text{int}}=0.0183$ ) reflections were measured( $-11 \leq h \leq 10$ ,  $-12 \leq k \leq 15$ ,  $-18 \leq l \leq 18$ ). The structure was solved by a direct method and refined *via* full-matrix least-squares calculations with anisotropic thermal parameters for all the nonhydrogen atoms. The hydrogen atoms were geometrically fixed to ride on the parent atoms to which they are attached. All the calculations were performed *via* the SHELXTL-97 program<sup>[17]</sup>.

The crystallographic data for complex 1 are summarized in Table 1.

Selected bond lengths and bond angles for the title complex are shown in Table 2.

Crystallographic data for complex 1 were already deposited at the Cambridge Crystallographic Data Center as supplementary publications, with CCDC

reference number 675359.

**Table 1** Crystal data and structure refinement parameters for complex 1

Empirical formula	C <sub>25</sub> H <sub>18</sub> MnMo <sub>3</sub> NO <sub>16</sub>
Formula weight	961.40
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /nm	0.9405(3)
<i>b</i> /nm	1.3351(4)
<i>c</i> /nm	1.5455(4)
$\alpha$ /( $^\circ$ )	103.206(5)
$\beta$ /( $^\circ$ )	102.165(5)
$\gamma$ /( $^\circ$ )	100.784(5)
<i>V</i> /nm <sup>3</sup>	1.7896(9)
<i>Z</i>	2
<i>D<sub>c</sub></i> /( <i>Mg</i> ·m <sup>-3</sup> )	1.784
<i>F</i> (000)	968
Abs. coeff./mm <sup>-1</sup>	1.439
<i>T</i> /K	293(2)
Reflns. collected No.	6305
Independent reflns No.	4981
Data/restrain/parameters	6305/ 48/ 415
GOF on <i>F</i> <sup>2</sup>	1.071
Final <i>R</i> indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.0703, <i>wR</i> <sub>2</sub> =0.1495
<i>R</i> indices(all data)	<i>R</i> <sub>1</sub> =0.0888, <i>wR</i> <sub>2</sub> =0.1583

**Table 2** Selected bond lengths(nm) and bond angles( $^\circ$ ) for complex 1

Mo1—O2	0.1692(7)	Mo1—O1	0.1696(7)
Mo1—O11	0.1900(6)	Mo1—O12	0.2010(7)
Mo1—O7	0.2279(5)	Mo1—O8	0.2312(7)
Mo2—O3	0.1680(6)	Mo2—O10	0.1777(6)
Mo2—O4	0.1796(5)	Mo2—O9	0.2049(6)
Mo2—O8	0.2191(6)	Mo2—O7	0.2295(5)
Mo3—O6	0.1683(6)	Mo3—O5	0.1695(6)
Mo3—O11	0.1918(6)	Mo3—O4	0.2005(6)
Mo3—O10	0.2246(6)	Mo3—O7	0.2268(5)
Mn1—C3	0.1520(2)	Mn1—C2	0.1642(16)
Mn1—C1	0.1718(9)	Mn1—O9	0.2042(6)
Mn1—O12	0.2104(7)	Mn1—O8	0.2107(7)
Mo2—O4—Mo3	164.2(3)	Mo3—O7—Mo1	91.02(19)
Mo3—O7—Mo2	97.11(19)	Mo1—O7—Mo2	106.5(2)
Mo2—O8—Mo1	109.0(2)	Mn1—O9—Mo2	107.4(3)
Mo2—O10—Mo3	116.0(2)	Mo1—O11—Mo3	116.3(3)

## 3 Results and Discussion

### 3.1 Structure Description

A single-crystal structure analysis(Table 1) reveals that complex 1 is constructed from two tetrabutylammonium cations and a tricarbonyl manganese incorporated into a polyoxomolybdate anion, which is an octanuclear anionic cluster(Fig.1).

The anion of complex 1 is located at a crystallographic inversion center and consists of two tetranuclear [Mo<sub>3</sub>O<sub>8</sub>(OCH<sub>3</sub>){HOCH<sub>2</sub>C(OCH<sub>2</sub>)<sub>3</sub>}{MnCO<sub>3</sub>}]<sup>-</sup> moieties. The two equivalent halves of the anion are connected by two almost linear Mo—O—Mo bridges

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