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Synthesis and Characterization of a Mononuclear Mo(IV) Oxo Complex $(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$

MOHAMMAD ASIM ANSARI, JAYANTHI CHANDRASEKARAN and SABYASACHI SARKAR*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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Abstract

Reaction of $(Et_2NH)_2MoOS_3$ with elemental sulfur results in the formation of a known complex ion $[MoO(S_4)_2]^{2-}$. Here, sulfur, an external oxidant, induces the electron transfer from ligated sulfur to metal. The reaction of $[MoO(S_4)_2]^{2-}$ with dibenzoyl acetylene results in the formation of a dithiolene complex ion, $[MoO(S_2C_2(COPh)_2)_2]^{2-}$ having the metal in the same oxidation state. This pentacoordinated, air stable, diamagnetic compound undergoes irreversible one electron oxidation at 0.84 V and irreversible reduction at −1.76 V. The XPS data of $[MoO(S_4)_2]^{2-}$ is also discussed.

Introduction

The molybdenum center of the molybdenum hydroxylases appears to cycle between +4, +5 and +6 during its catalytic process [1, 2]. EXAFS data for reduced xanthine oxidase and reduced sulfite oxidase indicate the presence of a terminal oxo ligand, two or three thiolate ligands and one oxygen or nitrogen donor ligand in the Mo(IV) coordination sphere [3]. Thus, Mo(IV) oxo complexes are of considerable importance though less explored as compared to Mo(V) and Mo(VI) oxo complexes. In this paper, we report the synthesis of a new complex $(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$ and improved methods of preparation of the starting materials.

Experimental

H_2MoO_4 was used as received. Dibenzoyl acetylene (DBA) was prepared by a literature method [4]. Solvents and other reagents were of analytical grade and distilled before use.

C, H and N were analysed at the microanalytical laboratory, IIT, Kanpur and sulfur was estimated gravimetrically as $BaSO_4$. Infrared spectra as CsI pellets were recorded on a Perkin-Elmer model 580 spectrophotometer. Electronic spectra were recorded on a Schimadzu (UV 190) double beam spectrophotometer. ^1H NMR and ^{13}C NMR spectra were taken on Varian EM-390, 90 MHz and Varian CFT-20, 400 MHz spectrometers, respectively, in DMSO-d_6. The X-ray diffractogram was obtained on a ISO-BEBYFLEX X-200 diffractometer using Cu Kα radiation source. XPS measurements were carried out on an ESCALAB 510 photo-electron spectrometer using the Al Kα line (1486.6 eV) radiation taking carbon ($1s_{1/2}$) binding energy (285.0 eV) as standard. Cyclic voltammograms (CV) were recorded on a PAR model 370-4 electrochemistry system, 174A polarographic analyzer, 175-universal programmer, REO074, X-Y recorder. All the experiments were done under a nitrogen atmosphere in a three electrode configuration using platinum and glassy-carbon working electrodes in the positive and negative potential region and referenced to a saturated calomel electrode (SCE).

Preparations

$(Et_2NH_2)_2MoOS_3$ *(1)*

H_2MoO_4 (1.62 g, 0.1 mol) was dissolved in H_2O (10 ml) and Et_2NH (10 ml) was added to it. The resulting solution was stirred well and filtered. H_2S gas was passed over the surface of the above filtrate for 5–7 min. Addition of iso-propanol (30 ml) and ether (10 ml) to the above solution and keeping it at 5 °C for 2 h gave reddish orange crystals. These were quickly washed with cold iso-propanol and ether and dried under vacuum. Yield 2.53 g (~71%).

$(Et_4N)_2[MoO(S_4)_2]$ *(2)*

A solution of $(Et_2NH_2)_2MoOS_3$ (356 mg, 1 mmol) in CH_3CN (20 ml) was stirred with Et_4NBr (420 mg, 2 mmol) and elemental sulfur (160 mg, 5 mmol) for 30 min and left overnight to yield a golden yellow crystalline product. The product was filtered, washed with H_2O, ethanol, CS_2 and ether and dried under vacuum. Yield 552 mg (~88%).

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical and Spectral Data of Compounds 1, 2 and 3

Compound	Analysis, found (calc.) (%)				IR frequencies (cm^{-1})		Electronic absorptions λ_{max} (ϵ) (nm)
	C	H	N	S	ν(Mo=O)	Other important vibrations	
$(Et_2NH_2)_2[MoOS_3]$ (1)	26.96 (26.92)	6.74 (6.51)	7.86 (7.68)	26.96 (26.98)	860	480 (ν(Mo–S))	310 (7950) 392 (6150) 462 (3950)
$(Et_4N)_2[MoO(S_4)_2]$ (2)	30.57 (30.62)	6.36 (6.29)	4.45 (4.38)	40.76 (40.79)	930	420, 375, 335 (ν(Mo–S_4))	316 (6620) 475 (sh) 555 (sh)
$(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$ (3)	59.50 (59.62)	6.19 (6.10)	2.89 (2.80)	13.22 (13.28)	950	1660 (ν(C=O)) 1490 (ν(C=C))	310 (sh) 338 (sh) 400 (5700)

TABLE II. XPS Data for some Relevant Systems

System	S(2p) (eV)	S($2s_{1/2}$) (eV)	Mo($3d_{5/2}$) (eV)	Mo($3d_{3/2}$) (eV)
S_8	164.2			
Cs_2MoS_4	162.2	227.6	230.7	231.7
$(Et_4N)_2[MoO(S_4)_2]$	162.7	226.2	229.5	233.0

$(Et_4N)_2[MoO(S_2C_2(COPh)_2)_2]$ (3)

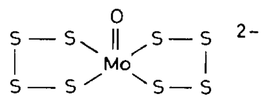
2 (314 mg, 0.5 mmol) was taken in DMF (5 ml) and dissolved by warming on a water bath for 10 min. Dibenzoyl acetylene (234 mg, 1 mmol) was added to this solution and warmed for a further 10 min on the water bath. The solution was cooled and iso-propanol (50 ml) was added. The oily mass so obtained was dissolved in CH_3CN (10 ml), then absolute ethanol (20 ml) and isopropanol (10 ml) were added to it. Keeping the solution for 2 days at room temperature resulted in the separation of a dark brown crystalline product which was washed with ethanol and ether and dried under vacuum. Yield 190 mg (39%).

Results and Discussion

The analytical and spectral data of all the compounds are listed in Table I. Though the preparation of $(NH_4)_2MoOS_3$ and $(Et_4N)_2MoOS_3$ are reported in the literature [5, 6], the purity and yield of these compounds have always been a problem. The synthesis of a dialkylaminium salt of oxo trithiomolybdate is reported here for the first time. The pure compound is obtained in high yield when H_2S is passed over the surface of a solution of molybdic acid in a mixture of water and diethylamine for 5–7 min. If H_2S is bubbled into the solution or the gas is passed over the surface for a longer time, tetrathiomolybdate, $[MoS_4]^{2-}$ is obtained. The presence of tetrathiomolybdate in trace amounts in the preparation of $[MoOS_3]^{2-}$ can be detected from the electronic spectrum of the compound as $(Et_2NH_2)_2[MoOS_3]$ gives charge transfer bands at 462, 392 and 310 nm (Table I) whereas $(Et_2NH_2)_2[MoS_4]$ gives bands at 468 and 318 nm.

Formation of the complex $(Et_4N)_2[MoO(S_4)_2]$ from $[MoOS_3]^{2-}$ using sulfur as an external oxidant is a good example of induced electron transfer reaction [7]. Conversion of Mo(VI) to Mo(IV) requires two electrons which are supplied by the sulfur atoms ligated to the metal ion. The electron balanced reactions are shown below:

$$[MoOS_3]^{2-} + \tfrac{5}{8}S_8 \xrightarrow[CH_3CN]{\text{room temperature}}$$



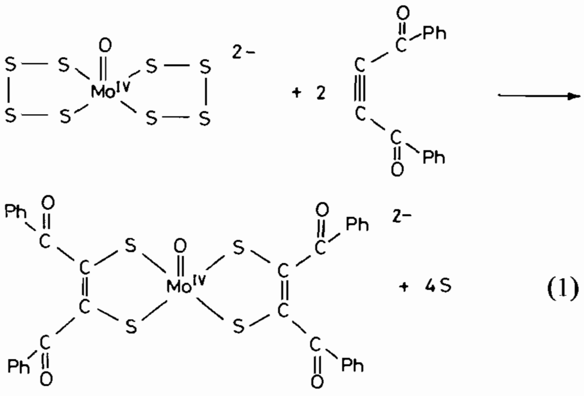
$$3S^{2-} + 5S \longrightarrow 2S_4^{2-} + 2e$$

$$Mo(VI) + 2e \longrightarrow Mo(IV)$$

Comparison of X-ray powder diffractogram suggests that **2** is isostructural with $[MoS(S_4)_2]^{2-}$ [8]. XPS (Table II) of **2** shows a broad band (FWHM 3.06

eV) responsible for S(2p) which can readily be resolved to give two sets of S(2p) binding energies in the ratio 1:1 at 162.6 and 163.4 eV. The bands responsible for S(2s), Mo($3d_{5/2}$) and Mo($3d_{3/2}$) are overlapping. However, a better resolution shows three distinct bands at 226.5, 229.5 and 233.0 eV arising from S(2s), Mo($3d_{5/2}$) and Mo($3d_{3/2}$), respectively. This data suggests that the binding energy of S(2p) in **2** is higher than the uncoordinated MoS_4^{2-} [9] but less than the elemental sulfur S_8 [10].

Reaction of $[MoO(S_4)_2]^{2-}$ with dibenzoyl acetylene results in the reduction of acetylene and the formation of the dithiolene complex **3*** as shown in eqn. (1):



(1)

Insertion of acetylene does not take place across the Mo–S bond, instead it follows the cycloaddition process as found in the case of $[MoS(S_4)_2]^{2-}$ [12].

Spectroscopic data are given in Table I. ν(Mo=O) in compounds **1**, **2** and **3** appears at 860, 930 and 960 cm^{-1}, respectively. This indicates that the Mo=O bond order increases as we go from **1** to **3**. The absorptions at 1490 and 1660 cm^{-1} have been assigned to ν(C=C) and ν(C=O) on the basis of earlier works [13–15]. The electronic absorption bands of **3** at 400 and 338 nm are assigned to ligand to metal charge transfer and the band at 310 nm is attributed to intra-ligand charge transfer. Chemical shifts for different carbon atoms are presented in Table III. None of the signals obtained in the ^{13}C NMR spectrum represent a carbon attached to a metal atom [16]. ^1H NMR gives a triplet (1.08 δ) and a quartet (3.14 δ) for the methyl and methylene protons of the cation and a multiplet (7.3–7.9 δ) for the phenyl groups of the anion.

3 undergoes one electron irreversible oxidation at 0.84 V and irreversible reduction at –1.76 V showing the high redox stability of the complex (Fig. 1).

TABLE III. ^{13}C NMR (DMSO-d_6) Chemical Shifts for 3

Chemical shift δ (ppm)	Assignment
193.92	CO
148.53	C=C
137.56	Ph
132.11	Ph
129.02	Ph
127.85	Ph
51.40	CH_3 (cation)
40.63–38.89	DMSO
6.96	CH_2 (cation)

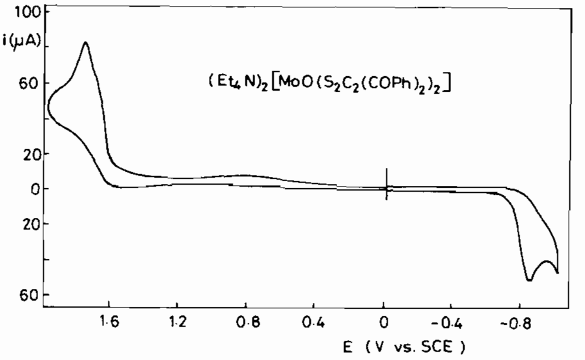


Fig. 1. Cyclic voltammogram (8.2 × 10^{-4} M in CH_3CN, supporting electrolyte $[Et_4N]ClO_4$, scan rate 0.05 V s^{-1}.

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*Preliminary reports of a similar complex with dicarbomethoxy acetylene (DMA) were presented at the Fifth International Conference on 'The Chemistry and Uses of Molybdenum' [11].

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