

Synthesis and Characterization of Molybdenum(VI) Complexes with 1,10-Phenanthroline

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Received: August 02, 2011 / Accepted: November 01, 2011 / Published: April 25, 2012.

Abstract: The development of routes and strategies for the design and preparation of complexes of 4d metals in moderate oxidation states is of great importance in magnetochemistry, bioinorganic chemistry, materials chemistry and solid-state chemistry. Bidentate ligands containing N or O donors especially phenanthroline have been widely used to form complexes with interesting structural motif. Reaction of $M(CO)_6$ ($M = Cr, Mo, W$) with phenanthroline has been done in 1935 and produced an interesting stereo structure, but the reaction of $MoO_2(acac)_2$ ($acac = acetylacetonato$) with phenanthroline has not been studied yet. So, in this research, first of all $MoO_2(acac)_2$ was prepared, and then it reacted with bidentate nitrogen donor to lead to produce the complex of $[MoO_2L_2]$ ($L = Phen$) and different aspects of this complex were studied. This complex is very active and highly selective epoxidation catalyst. The structure of the product was characterized by various spectral techniques such as elemental analysis, 1H NMR, ^{13}C NMR and IR spectroscopy.

Key words: Dioxomolybdenum, $acac$, phenanthroline, complexes.

1. Introduction

A large number of bi-dentate, tri-dentate, tetra-dentate ligands containing oxygen, nitrogen and sulphur donor atoms have been complexes to the $Cis-MoO_2$ moiety [1], especially bidentate ligands containing N or O donors especially phenanthroline have been widely used to form complexes with interesting structural motif [2-3]. The chemistry of dioxomolybdenum has been receiving increasing attention over the past two decade due to its important catalytic versatile in the field of chemistry and biochemistry [1, 3-5]. Molybdenum plays an important role in biological systems especially in catalyzing two electron oxidation of purine, aldehyde, sulfite, and format with participating in acting of redox reactions associated with enzymes such as nitrogenase, aldehyde oxidase, xanthine dehydrogenase, nitrate reductase [6]. During enzymatic reaction, Mo center cycles between

the formal oxidation state of IV, V, and VII. Transition metal compounds with multiple metal-ligand bonds show a fascinating variety of structures and reactivities, and therefore, they have become a very active field of chemical research. The most important elements forming multiple bonds with transition metals are oxygen, nitrogen, and carbon [7-8]. These ligands can be various aliphatic and aromatic with multiple metal ligands bonds which show a fascinating variety of structures and reactivities. In this work [9], $MoO_2(Phen)_2$ was prepared as a new complex of this group, and then the structure of complex has been characterized with IR, 1H NMR, ^{13}C NMR and UV.

2. Experiment

2.1 Preparation of $[MoO_2(acac)_2]$

To make ready $MoO_2(acac)_2$, $(NH_4)_6Mo_7O_{24} \cdot H_2O$ (15 g) was added to water (50 mL) as solvent, while they were stirred after that acetylacetonate (20 mL) was added, pH of solution was balanced by $(HNO_3$ 10%) to 3.5, then solution on stirrer was putted for 2 hr.

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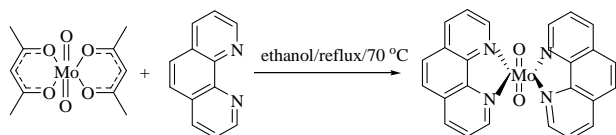
The product which was filtered off and washed by ethanol and ice-cold water was dried in vacuo [10].

2.2 Synthesis of $[MoO_2(phen)_2]$

For preparing slightly complex, direct reaction of $MoO_2(acac)_2$ (1.6 g) with phenanthroline (0.9010 g) in ethanol which was achieved by heating was refluxed and stirred for 2 h. The deep blue deposit (1.05 g) has been gotten and then was washed by ice-cold water (Scheme 1).

3. Results and Discussion

In this research, a new complex $MoO_2(phen)_2$ based on Mo with desired structure has been synthesized. The deep blue crystal was obtained by the reaction of



Scheme 1 Synthesis of $[MoO_2(phen)_2]$.

phenanthroline in ethanol as solvent. Its IR spectrum showed a shift for peaks at 1950 cm^{-1} and 2100 cm^{-1} for free phenanthroline, as shown in Fig. 1. When this was compared by IR spectrum of the complex, a new peak which appeared at 915 cm^{-1} was assigned to ($\nu_{Mo=O}$) stretching, as shown in Fig. 2. The movement of peaks for complex at 1579 cm^{-1} and 1624 cm^{-1} in comparing with free phenanthroline to lower region accrued.

In investigating 1H NMR spectrum to proof synthesizing of the complex, the chemical shift was observed in region 7.75-9.1 ppm in all of peaks for phenanthroline, 7.79 ppm (s, 2H), 7.98 ppm (s, 2H), 8.48 ppm (s, 2H), 9.1 ppm (s, 2H) to 7.78 ppm (s, 2H), 7.99 ppm (s, 2H), 8.49 ppm (s, 2H), 9.1 ppm (s, 2H) (Fig. 2), respectively, and four new peaks appear in 7.78 ppm (s, 2H), 7.99 ppm (s, 2H), 8.49 ppm (s, 2H) and 9.1 ppm (s, 2H) which were compared to 1H NMR of $MoO_2(acac)_2$ (Figs. 3 and 4). At the end, all of observation strongly suggests that this new complex is realized.

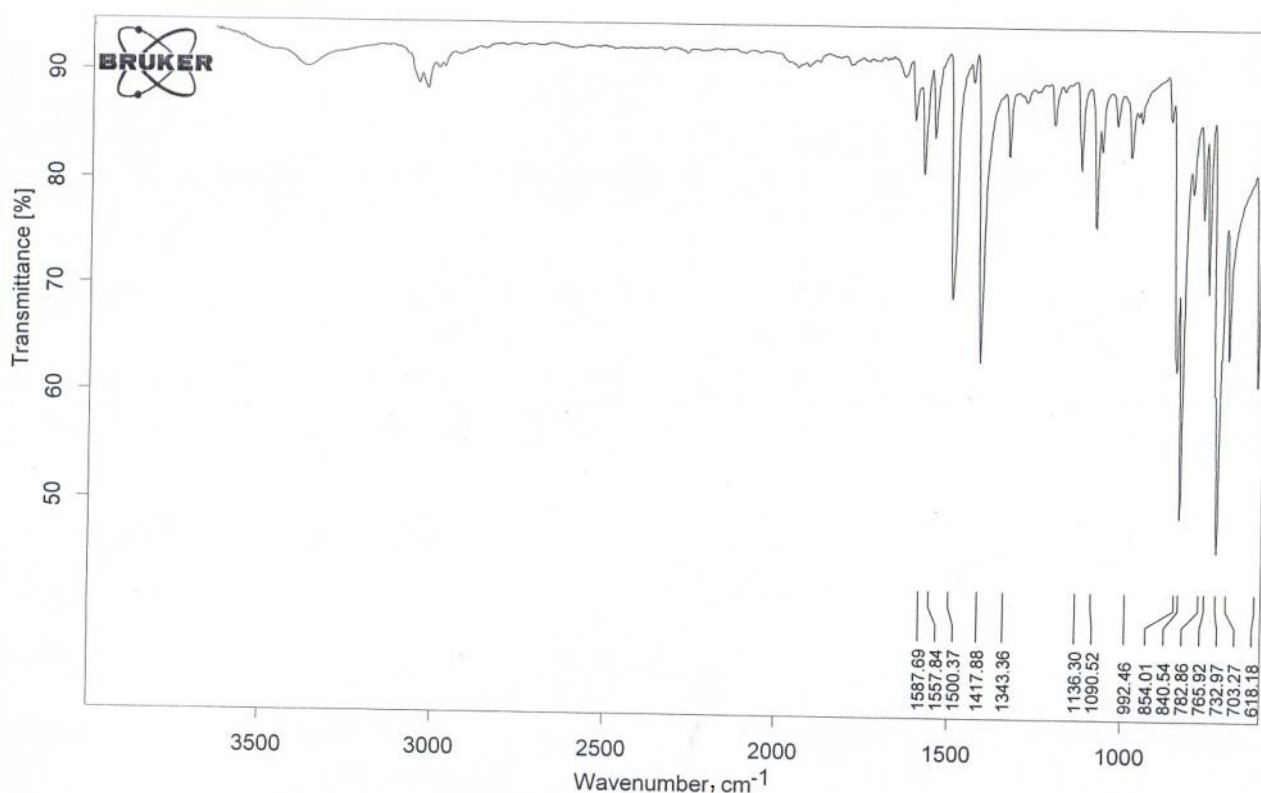
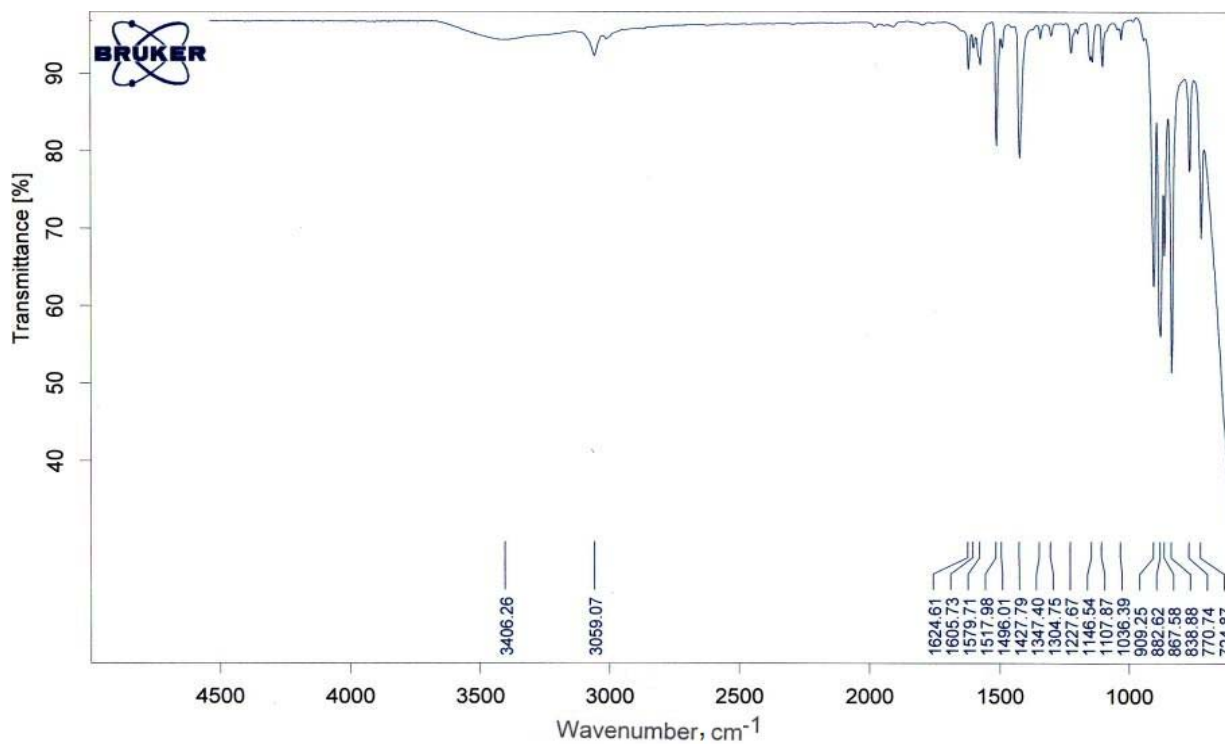
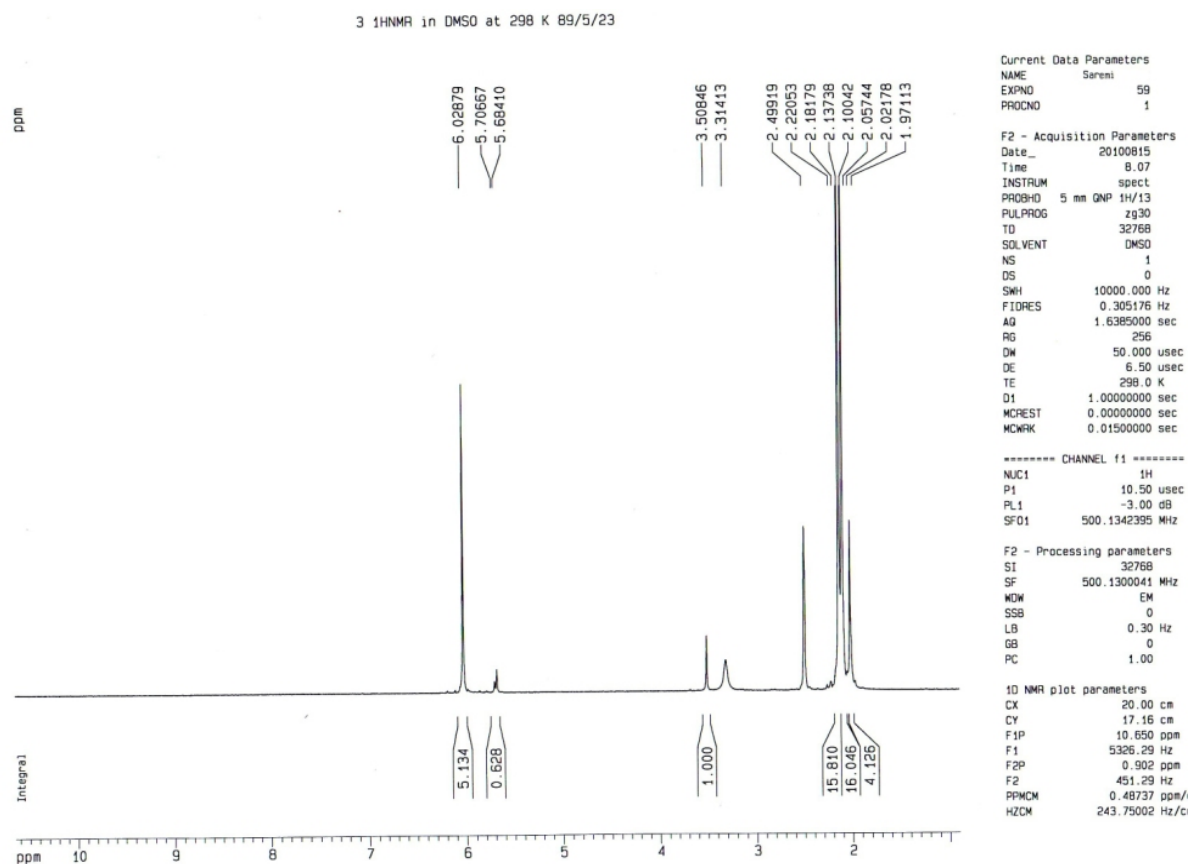


Fig. 1 IR of phenanthroline.

Fig. 2 IR of $\text{MoO}_2(\text{phen})_2$.Fig. 3 ^1H NMR of $\text{MoO}_2(\text{acac})_2$.

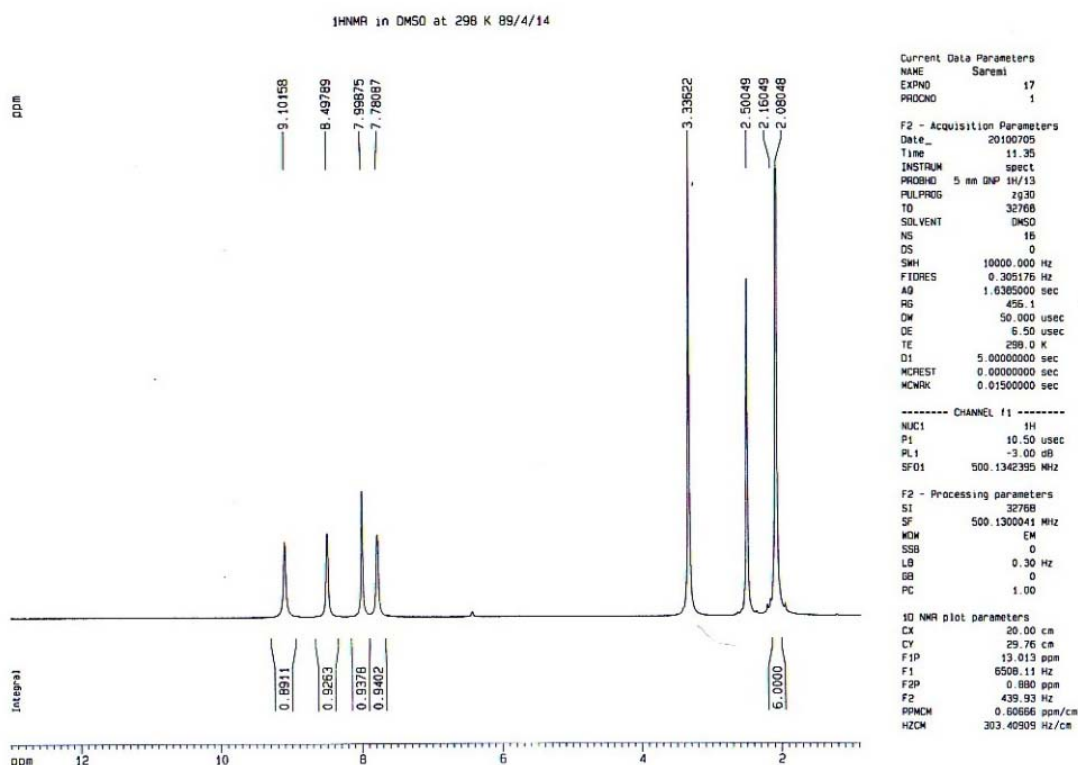


Fig. 4 ^1H NMR of $\text{MoO}_2(\text{phen})_2$.

4. Conclusions

In this work, a new molybdenum(VI) complex was synthesized and characterized by various spectral techniques such as elemental analysis, IR and ^1H NMR spectroscopy. In order to corroborate synthesis of this new complex, its IR and proton ^1H NMR spectroscopy with its initial materials spectroscopies were compared.

As well, the influence of the terminal oxo ligands together with the bidentate nitrogen donor ligands on the Mo centre obviously keeps the compounds on a quite stable level of electron density.

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