

Title

**Dioxomolybdenum (VI) Complexes with
o-Phenylenediamine and 4-Methyl-o-
Phenylenediamine Ligands: Synthesis and
Catalytic Activity in Oxidation of Alcohols**

Authors

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Abstract

Two new dioxomolybdenum (VI) complexes $[\text{MoO}_2(\text{acac})\text{LL}']$ (I) and $[\text{MoO}_2\text{L}_2\text{L}_2'']$ (II) $[\text{L}=\text{OC}(\text{CH}_3)\text{CHCOCH}_3$, $\text{L}'=\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$, $\text{L}''=\text{NH}_2\text{C}_6\text{H}_3(\text{CH}_3)\text{NH}_2$] with diamine o-Phenylenediamine (OPDA) and 4-Methyl-o-Phenylenediamine (4-Me-OPDA) ligands have been synthesized and characterized. Compounds (I) (61% yield) and (II) (62% yield) were obtained from the reactions of $\text{MoO}_2(\text{acac})_2$ [acac=acetyl acetonato] with 1 equiv. of OPDA and 4-Me-OPDA. ^1H , ^{13}C NMR, IR spectral data indicated that the ligands acted as unidentate and structures of both compounds were six-coordinated. The dioxomolybdenum (VI) complexes (I) and (II) are efficient catalysts for oxidation of alcohols with H_2O_2 as an oxidant.

Key words

Dioxomolybdenum (VI) complexes; Diamine ligands; Structures; Oxidation catalysis.

Introduction

The chemistry of dioxomolybdenum (VI) complexes has received considerable attention in recent years [1-5]. The various ligands with different donor properties into dioxomolybdenum give complexes which exhibit intriguing lability differences. There is extensive literature on the use of dioxomolybdenum (VI) complexes as catalysts in some important industrial processes [6-8], as well as their role in some biological processes [9-10]. With these advantages, we have extended our study to two new dioxo complexes of molybdenum (VI) with *o*-Phenylenediamine (OPDA) and 4-Methyl-*o*-Phenylenediamin (4-Me-OPDA) ligands.

OPDA and 4-Me-OPDA can react as bidentate NH donor ligands with transition metals. The variety of possible molybdenum complexes with wide choice of OPDA and 4-Me-OPDA ligands and coordination environments has prompted us to undertake research in this area. Wilkinson and *et al.* reported the complexes $\text{Cr}(\text{O}_3\text{SCF}_3)_4[(\text{H}_2\text{N})_2\text{C}_6\text{H}_4]$, $\text{CrCl}_2[(\text{HN})_2\text{C}_6\text{H}_4](\text{PMe}_2\text{Ph})_2$ [11] and the binuclear tungsten complex $\{\text{WCl}_3[(\text{HN})(\text{H}_2\text{N})\text{C}_6\text{H}_4]\}_2[\mu\text{-}1,2\text{-}(\text{N})_2\text{C}_6\text{H}_4]$ [12]. Therefore, the chemistry of these ligands has been focused mainly on Cr and W, whereas the reports on molybdenum with OPDA are still rare and there have not been any reports on the synthesis of compounds (I) and (II).

We have successfully employed the synthesized complexes as catalysts to generate acids from alcohols which are an industrial aspect of this project.

We report here the synthesis of these complexes and identify them by ^1H , ^{13}C NMR, IR spectroscopy and elemental analysis. Finally, we study their conductivity and catalytic reaction of the synthesized

dioxomolybdenum (VI) complexes.

Experimental

IR spectra (as KBr discs) were recorded with a Perkh Elmer Spectrum GX. ^1H , ^{13}C NMR spectra were recorded with a BRUKER Specto Spin 500 MHz spectrometer. Carbon, Hydrogen and Nitrogen analysis were carried out by C.H.N-O-Rapid Heraeus Elemental analyzer. Conductivities of 10^{-3} M solutions of the complexes in dimethyl sulphoxide (DMSO) were measured at 25 °C using a Conductivity Meter ES-14 (HORIBA).

Reagents

Ammonium heptamolybdate tetrahydrate, acetyl acetone (acacH), 1, 2-Phenylenediamine, 4-methyl-1, 2-Phenylenediamine and 1-butanol were used as received from commercial (Merck). Solvents: ethanol, ether, and tetrahydrofuran (THF), were dried and distilled before use by standard methods. DMSO and MF were used as received without any further purification.

Preparation of complexes

Preparation of $\text{MoO}_2(\text{acac})_2$. This complex was prepared from ammonium heptamolybdate tetrahydrate and acetyl acetone following the procedure of reference [13].

General method for the preparation of complexes $[\text{MoO}_2(\text{acac})\text{LL}'](\text{I})$, $[\text{MoO}_2\text{L}_2\text{L}'''](\text{II})$, $(\text{L}=\text{OC}(\text{CH}_3)\text{CHCOCH}_3$, $\text{L}'=\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$, $\text{L}''=\text{NH}_2\text{C}_6\text{H}_3\text{CH}_3\text{NH}_2$). $\text{L}'\text{,L}''$ (5 mmol) was dissolved in 150 ml ethanol by refluxing on a water bath and 1.65 g (5 mmol) of solid $\text{MoO}_2(\text{acac})_2$ was added to the ligands solution. The mixture was refluxed for 3 h and the violet precipitate filtered, and washed successively with water and ether and finally dried in vacuo over P_4O_{10} .

Reaction of (I) and (II) with 1-butanol (reaction A)

Compound (I) and (II) (0.015 mol) were suspended in 20 cm³ of dioxane, and a stoichiometric amount of 1-butanol was added. The mixture was refluxed at 60°C for 24 h. The mixture of the reaction was filtered and filtrate distilled. The butyric acid was identified from its boiling point and IR spectroscopy [(I) 90% and (II) 89%].

Catalytic reaction of (I) and (II) and H₂O₂ with 1-butanol (reaction B)

A 25 cm³ quantity of 1-butanol (20.22 g, 0.273 mol) was dissolved in 20 cm³ of tetrahydrofuran (THF) and 1 g of the synthesized complexes (I) and (II) was added followed by 25 cm³ of 30% H₂O₂. The mixture was kept under reflux at 90 °C for 24 h. The mixture of the reaction was filtered and the filtrate distilled. The butyric acid was identified from its boiling point and IR spectroscopy [(I) 88% and (II) 85% yield].

Results and discussion

Starting material MoO₂(acac)₂ was prepared according to the literature [12]. Addition of one equivalent of the ligands to the solution of complex MoO₂(acac)₂ precursor in solvent ethanol resulted in intense violet precipitate. The various times and temperatures of reaction showed that no differences were occurred in type of the structure and 61% for

(I) and 62% for (II) yield of compounds.

IR spectra data are presented in Table 1. The precursor complex of MoO₂(acac)₂ has two sharp bands in 904 and 933 cm⁻¹ which are related to symmetrical and anti symmetrical stretching vibration of Mo=O, respectively. These bands in the complexes (I) and (II) appear in 901, 946 and 899, 942cm⁻¹, respectively. The ν(Mo—O) band observed at 407cm⁻¹ for MoO₂(acac)₂ is shifted to upper frequencies in I, II (Table 1.), indicating that oxygen atom coordination remained in the produced complexes. The ν(Mo—N) band appears at 409 cm⁻¹ in the far-IR spectra of the both complexes. Besides, two sharp bands observed at 3224, 3288cm⁻¹ and 3215, 3290cm⁻¹ for the complexes I and II, respectively, are due to stretching vibration of NH₂ which in turn show the coordination by the amine nitrogen atom. In spite of the fact that the ligands OPDA and 4-Me-OPDA are potentially bidentate, the coordination occurs via the amine nitrogen atom.

The presence of ν(C=N) band in the both complexes and its absence in MoO₂(acac)₂ are indications delocalization electrons in the ring o-Phenylenediamine connected to molybdenum atom. The ν(C=O) band observed at 1586 cm⁻¹ for MoO₂(acac)₂ and 1598, 1600 cm⁻¹ for (I), (II) respectively. The ν(C=C) band which appears at 1502 cm⁻¹ for MoO₂(acac)₂ and pairs 1477, 1515 cm⁻¹ and 1523, 1472 cm⁻¹ for (I), (II) complexes,

Table 1- IR spectral data for the Mo(VI) complexes ν [band maxima (cm⁻¹)]

Compound	ν (C=N)	ν (Mo=O)	ν (Mo—O)	ν (C=O)	ν (C—O)	ν (C=C)	ν (Mo—N)	ν (N—H)
(I)[MoO ₂ (acac)LL']	1630	901 946	468	1598	1047 1279	1515 1477	409	3224 3288
(II)[MoO ₂ L ₂ L ₂ "]	1640	899 942	480	1600	1045 1254	1523 1472	409	3215 3290
[MoO ₂ (acac) ₂]	—	904 933	407	1586	1022 1262	1502	—	—

respectively (Table 1) indicates two different delocalization electrons in complexes (I), (II).

^1H , ^{13}C NMR spectra which were obtained in DMSO-d_6 solutions at room temperature are presented in Table 2. The ^{13}C NMR spectra of complexes (I), (II) showed clearly 14 and 24 carbon resonances, respectively. The carbon resonances (Table 2) are assigned to $\text{C}=\text{O}$ (176.0, 174.5 ppm), $\text{C}-\text{O}$ (95.8, 95.1 ppm), CH_3 (19.0, 18.6 ppm), $\text{C}=\text{C}$ (119.1, 157.8 ppm), aromatic carbons (100 - 150 ppm) in the compounds (I), (II), respectively. Thus, we resulted in the compound (I), (II) via

have yet connect acac ligand to molybdenum atom. The ^1H NMR resonances were somewhat broad, and consistent to ^{13}C NMR showed two different resonances for NH_2 groups, that is, sharp resonances 4.80 and 5.00 ppm for NH_2 and broad resonances 9.30 and 9.49 ppm for NH_2 groups coordinated to Mo atom for compounds (I) and (II), respectively. Therefore, the way OPDA and 4-Me-OPDA ligands are connected to $\text{MoO}_2(\text{acac})_2$ complex is considerable interest because the bidentate ligands with two electron-donating nitrogen atom of, only one nitrogen from NH_2 groups is coordinated and

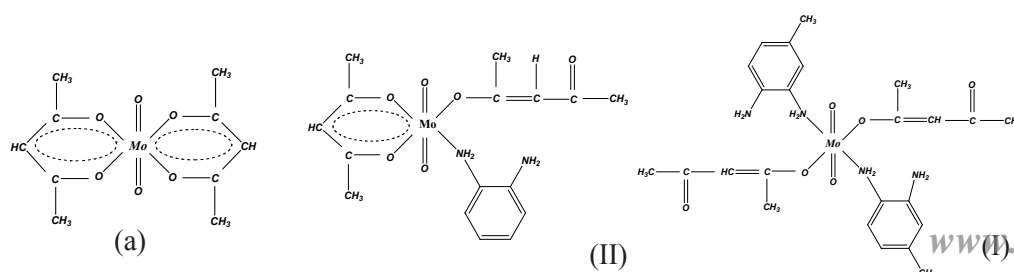
Table 2- ^1H , ^{13}C NMR Spectral data for the complexes (I), (II) δ [band maxima (ppm)]

Compound	^1H NMR	^{13}C NMR
(I) $[\text{MoO}_2(\text{acac})\text{LL}']$	1.20(3H,s), 2.27(3H,s), 2.48(3H,s) 4.35(1H,s), 4.80(2H), 5.11(1H,s) 6.42(1H,d,d), 6.86(1H,d,d), 7.17(1H,d) 7.18(1H,d), 9.30(2H)	19.0, 176.0, 115.5, 28.1, 95.8 133.9, 25.0, 118.1, 158.4, 129.0 124.3, 127.0, 123.4, 140.2
(II) $[\text{MoO}_2\text{L}_2\text{L}_2'']$	2.04(3H,s), 2.22(3H,s), 2.28(3H,s), 2.46(3H,s) 2.74(3H,s), 2.97(3H,s), 4.82(1H,s), 5.00(2H) 5.30(1H,s), 6.20(1H,s), 6.29(1H,d), 6.64(1H,d), 6.96(1H,d), 7.04(1H,s), 7.10(1H,d) 9.49(2H)	18.6, 174.5, 157.8, 23.8, 95.1, 23.9 95.8, 158.3, 175.8, 19.4, 138.8, 123.3, 126.7, 133.3, 25.9, 128.6, 133.3, 139.9, 125.4, 26.0, 130.7, 127.0, 123.7, 137.7

acts as a unidentate ligand. We suggest that acac ligand ring opens up and OPDA connects to Mo atom.

The analytical data are presented in Table 3. the molar conductance values show that two complexes are non-electrolytes in DMSO indicating that ligands are covalently bonded. Consideration

of the molar conductance in the different parts of the reactions have not exhibited any ionic species and indicating that ligands are covalently bonded, therefore we conclude that these reactions must exist with retention configuration and coordination number. These data are consistent with six fold coordination of molybdenum (VI) complexes and probably with the distorted octahedral geometry.



Scheme 1- structure $\text{MoO}_2(\text{acac})_2$ (a) and proposed structures for compound (I), (II)

Table 3- Analytical data and other Physical properties of the dioxo complexes

Compound	Colour	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Molar Conductance (ohm ⁻¹ cm ² mol ⁻¹)
		Calc.	Found	Calc.	Found	Calc.	Found	
(I) [MoO ₂ (acac)LL']	Violet	44.34	44.26	22.17	22.03	6.46	6.29	0
(II) [MoO ₂ L ₂ L ₂ "]	Deep Violet	50.70	49.45	16.90	16.66	9.86	9.59	0

Although we were not able to obtain, a single crystal to account for the NMR and IR results, two structures (I), (II) are proposed as shown in Scheme 1.

The catalytic activity of the two dioxomolybdenum (VI) complexes with respect to the peroxidic oxidation of alcohols has been tested for 1-butanol as substrate. Controlled experiments showed that practically no oxidation was formed without catalyst. In the presence of the Mo (VI) complexes was obtained as the only product with yields after 24 h of 88% for (I) and 85% for (II). Another important advantage of the heterogeneous catalysts is that the catalyst can be easily separated from the products and recycled. Based on these results, compounds (I) and (II) seem to be suitable catalysts for oxidation of alcohols.

References

- [1] Dinda, R.; Ghosh, S.; Falvello, L.R.; Tomas, M.; Mak, T.C.W.; *Polyhedron*; 25, 1375-2382; 2006.
- [2] Lehtonen, A.; Kessler, V.G.; *Inorg. Chem. Commun.*; 7, 691-693; 2004.
- [3] Fronczek, F.R.; Luck, R.L.; Wang, G.; *Inorg. Chem. Commun.*; 5, 384-387; 2002.
- [4] Lehtonen, A.; Sillanpaa, R.; *Polyhedron*; 26, 5293-5300; 2007.
- [5] Bruno, S.M.; Balula, S.S.; Valente, A.A.; Almeida, Paz, F.A.; Pillinger, M.; Sousa, C.; Klinowski, J.; Freire, C.; Ribeiro Claro, P.; Goncalves, I. S.; *J. Mol. Cat. A: Chem*; 270, 185-194; 2007.
- [6] Mancka, M.; Plass, W.; *Inorg. Chem. Commun*; 10, 677-680; 2007.
- [7] Petrovski, Z.; Valente, A.A.; Pillinger, M.; Dias, A.S.; Rodrigues, S.S.; Romao, C.C.; Goncalves, I.S.; *J. Mol. Cat. A: Chem*; 249, 166-171; 2006.
- [8] Kühn, F.E.; Zhao, J.; Abrantes, M.; Sun, W.; Afonso, C.A.M.; Branco, L.C.; Goncalves, I. S.; Pillinger, M.; Romao, C.C.; *Tetrahedron Lett.*; 46, 47-52; 2005.
- [9] Rousso, L.; Friedman, N.; Sheves, M.; Ottolenghi, M.; *Biochemistry*; 34, 12059-12065; 1995.
- [10] Bassov, T.; Sheves, M.; *Biochemistry*; 25, 5249-5258; 1986.
- [11] Leung, W.-H.; Danopoulos, A.A.; Wilkinson, G.; Hussain-Bates, B and Hursthouse, M.B.; *J. Chem. Soc. Dalton Trans*; 2501; 1991.
- [12] Redshaw, C.; Wilkinson, G.; Hussain-Bates, and Hursthouse, M.B; *J. Chem. Soc. Dalton Trans*; 555; 1992.
- [13] Chen, J.J.; McDonald, J.W.; Newton W.E.; *Inorg. Chem*; 15, 2612-2615; 1976.