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Synthesis and Characterization of Dioxotungsten (VI) and Dioxomolybdenum (VI) Complexes of Chelating Hydrazone via Their Oxoperoxo Complexes

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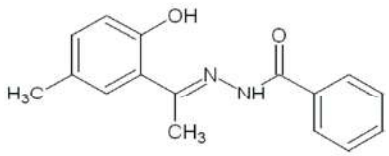
Abstract: This paper deals with the synthesis of dioxotungsten (VI) and dioxomolybdenum (VI) complexes with chelating hydrazone derived from 2-hydroxy-5-methylacetophenone and benzoyl hydrazide through abstraction of oxygen from the corresponding oxoperoxo complexes. They have characterized by elemental analysis, IR and ^{1}H-NMR studies.

Key words: Hydrazone · Spectroscopic Studies · Oxoperoxo Complexes

INTRODUCTION

There has been growing interest in the study of dioxotungsten (VI) and dioxomolybdenum (VI) hydrazones complexes because of their physiological activity, coordinative capability and applications in analytical chemistry [1-5]. The metal carrier $[MoO_2(acac)_2]$ (Hacac = acetylacetone) has played an important role through its ligand exchange reactions, in the development of the chemistry of dioxomolybdenum (VI) cation [6]. The facile synthesis and successful use of such a metal for dioxotungsten (VI) cation, $[WO_2(acac)_2]$, has only been reported [7]. Recently it has been shown that oxoperoxo complexes of tungsten and molybdenum can be converted to the corresponding dioxo species through a abstraction of an oxygen using triphenyl phosphene [8]. These oxoperoxo complexes can be made readily using MO_3 (M = W or Mo), H_2O_2 and the ligand. We have now extended the feasibility of this method to other oxoperoxo complexes of tungsten and molybdenum with 2-hydroxy-5-methylacetophenone benzoylhydrazone (H_2L).



(H_2L)

MATERIALS AND MATHODS

All the chemicals and solvents used were of analytical grade and were used without further purification. 2-hydroxy-5-methylacetophenone and benzoyl hydrazide were prepared according to methods reported in literature [9]. Tungsten and molybdenum were estimated gravimetrically after decomposing the complex with concentrated nitric acid by standard method [10].

Physical Measurements: Elemental analysis was carried out with a Carlo Erba 1108 analyser. The IR spectra were recorded on a 621 Perkin Elmer grating spectrophotometer as KBr disc. ^{1}H-NMR spectra were obtained in DMSO-d_6 using a Bruker Ac250 spectrometer, using TMS as reference.

Synthesis of Acid Hydrazone (H_2L): Benzoyl hydrazide (50 mmol) was dissolved in a ~100 ml of ethanol. To this was added 2-hydroxy-5-methylacetophenone (50 mmol) and the mixture was refluxed on a water bath for 3-4 h. A solid mass was separated after cooling and it was then filtered, washed with ethanol and diethyl ether to remove unreacted ligand and subsequently dried in vacuo over anhydrous $CaCl_2$. It was crystallized from ethanol. Yield: 70% and M.P. = 173°C.

Preparation of $[WO(O_2)L(H_2O)]$ (1): A filtered solution of peroxotungstic acid, prepared in situ, by stirring WO_3H_2O (0.50g, 2 mmol) in H_2O_2 (30%, 25 ml) for 15 h, was added to

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a hot ethanolic solution (30 ml) of H_2L (0.52g, 2 mmol) with stirring. The stirring was continued for 2 h while cooling the reaction in an ice bath. The yellow complex separated was filtered, washed with ethanol-water (3:2 v/v), followed by diethyl and recrystallized from 95% ethanol. Yield: 63%.

Preparation of $[Mo(O)_2L(H_2O)]$ (2): The orange yellowish complex, 2 was prepared in same as described for complexes 1 using peroxomolybdic acid and H_2L and recrystallized from 95% ethanol. Yield: 65%.

Preparation of $[WO_2L(CH_3OH)]$ (3): A solution of PPh_3 (0.39g, 1.5 mmol) in10 ml methanol was added to a suspension of $[WO(O_2)(L)(H_2O)]$ (0.52g, 1 mmol) in 40 ml methanol and the reaction mixture was reflux on an oil bath for 15 h. After cooling the flask at ambient temperature, the separated yellow complex was filtered, washed with methanol and dried in vacuo. Yield: 65%.

Preparation of $[MoO_2L]$ (4): This complex was prepared as described for 3 using $[Mo(O_2)L(H_2O)]$ (0.42g, 1 mmol) and PPh_3 (0.39g, 1.5 mmol). Yield: 65%.

The complexes 3 and 4 were also prepared by the reaction of H_2L with $[WO(acac)_2]$ or $[MoO_2(acac)_2]$, respectively, following the literature procedure [11].

RESULTS AND DISCUSSION

The reaction of WO_3 or MoO_3 with excess of 30% aqueous of H_2O_2 generates in situ peroxotungstic or peroxomolybdic acid, respectively. These peroxo species readily react with alcoholic solution of H_2L which on crystallization from 95% ethanol give the corresponding oxoperoxo complexes having the general formula $[MO(O_2)L(H_2O)]$ (M = W or Mo). Both the complexes are stable and do not explode on heating but decomposed ~190°C. These complexes exhibit their IR active modes namely, the symmetric M  stretch (γ_2) at ~575 cm^{-1}, the antisymmetric M  stretch (γ_3) at ~695 cm^{-1} and the stretching O-O (γ_1) at ~890 cm^{-1} [12, 13]. In addition, complexes 1 and 2 display the ν(M=O) mode at 965 and 960 cm^{-1}, respectively. These oxoperoxo complexes readily undergo oxygen transfer reaction with PPh_3 in anhydrous methanol to give the corresponding dioxo complexes of formulae $[WO_2L(CH_3OH)]$ and $[MoO_2L]$. The formation of a representative dioxotungsten (VI) complex may be represented by the following reaction:

$$[WO(O_2)L(H_2O)]+PPh_3 \xrightarrow{\text{Ethanol}} [WO_2L(CH_3OH)]+OPPh_3+H_2O$$

The presence of two bands at ca 950 cm^{-1}, characteristic of the cis-MO_2 group [14] and the absence of the bands due to the metal-peroxo grouping in the IR spectra, clearly indicate the formation of the $[MO_2]^{2+}$ complexes. In addition, complex 4 shows an additional broad band at 770 cm^{-1} due to weakened ν(Mo=O) as a result of Mo-O → Mo interaction. The formation of $OPPh_3$ is also evident by the presence of an IR band at 1190 cm^{-1} due to ν(P=O) mode in the yellowish white powder recovered from the filtrate after separating the dioxo complexes.

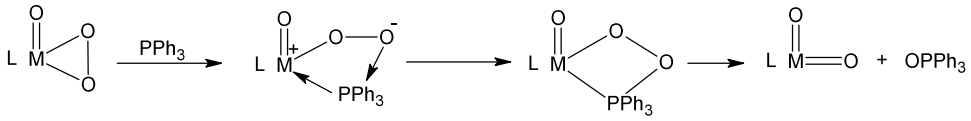
The ligand exhibits two resonances at 11.10 and 12.90 ppm (singlet, 1H each) due to NH and phenolic protons, respectively. The absence of both the resonance upon complexation suggests the coordination of the enolic oxygen (due to enolization of the ketonic group) and the phenolic oxygen atoms to the metal after proton replacement. A sharp singlet at 2.5 ppm due to the methyl protons of the *o*-hydroxyacetophenone moiety shifts downfield due to coordination of the azomethine nitrogen. The signal due to methyl protons of methanol in $[WO_2L(CH_3OH)]$ appears separately at 3.30 ppm.

The H_2L shows IR bands at 3236, 2912(b), 1647, 1604 and 1512 cm^{-1} due to ν(NH), ν(OH), ν(C=O), ν(C=N) and ν(C-O) (phenolic) modes, respectively. The ν(NH) and ν(C=O) disappear in the spectra of the complexes indicating the destruction of the carbonyl moiety as a result of enolization and subsequent coordination of the enolic oxygen after proton replacement. A new band appearing in the region 1235-1245 cm^{-1} is assigned to the ν(C-O) (enolic) mode [15, 16]. The shift of the ν(C-O) (phenolic) stretch to higher frequency by 9-13 cm^{-1} while shift of the ν(C=N) stretch to lower frequency by 9-25 cm^{-1} in the complexes indicates the coordination of the phenolic oxygen and azomethine nitrogen atoms to the metal ion [17, 18]. Thus the spectral data suggest the dibasic tridentate behavior of the ligand. A broad band ~3400 cm^{-1} in the peroxo complexes may be due to coordinated water, while in 3 this may be due to coordinated methanol. The coordination of methanol is further supported by the appearance of a new band at 1008 cm^{-1} in 3; the ν(C-O) stretch in methanol appears is 1035 cm^{-1} [19].

Although triphenylphosphine (or its derivatives) has played very important role in stabilizing and isolating $[MO]^{2+}$ and $[M_2O_3]^{4+}$ species through abstraction of an oxygen from the corresponding $[MO]^{2+}$ (M= W or Mo) complexes [20], isolation of dioxo species $[MO]^{2+}$,

fromoxoperoxo complexes using triphenylphosphine have been reported [21]. We have extended the application of triphenylphosphine in isolating $[MO]^{2+}$ (M= W or Mo) complexes of H_2L from their corresponding oxoperoxo complexes. The IR spectral data clearly indicate the conversion of oxoperoxo complexes to the dioxo one. The IR as well as NMR spectral data of these complexes also compare well with the authentic samples, prepared by the reaction of $[MO_2(acac)_2]$ and H_2L.

As H_2L behaves as dibasic tridentate ligand, the structure of seven coordinated peroxo complexes may be considered as reported for $[MoO(O_2)(Pydc)(H_2O)]$ (Pydc = pyridine-2,6-dicarboxylate (2^-)] [22]. Since the equatorial plane in this pentagonal bipyramidal structure is formed by the tridentate ligand and the peroxo group, the formation of cis-dioxo group in the complexes 3 and 4 can easily be explained through the following reaction path:



Where,

M = W or Mo

L= ligand

Table 1: Elemental analysis of the ligand and its metal complexes

		Elemental analysis % Found (Calcd)			
Compound	Formula weight	C	H	N	M
H_2L	268.29	71.53(71.53)	6.00(6.01)	10.32(10.44)	--
$[WO(O_2)L(H_2O)]$	516.14	37.10 (37.23)	3.05 (3.12)	5.21 (5.43)	36.03 (35.62)
$[Mo(O)_2L(H_2O)]$	428.24	44.31 (44.87)	3.25 (3.77)	6.48 (6.54)	22.98 (22.40)
$[WO_2L(CH_3OH)]$	514.17	38.95 (39.71)	3.15 (3.53)	5.18 (5.45)	34.89 (35.75)
$[MoO_2L]$	394.23	48.98 (48.75)	3.20 (3.58)	7.01 (7.11)	25.03 (24.34)

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