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# Structural Features of $MoO_2$–Complexes of Thiosemicarbazones and Semicarbazones

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Synthesis, characterization and spectral features of six-co-ordinated dioxomolybdenum (VI) complexes of the type $[MoO_2(\overset{\frown\frown\frown}{XNNX})]$ (where $H\overset{\frown\frown\frown}{XNNX}H$ represents the thiosemicarbazone and semicarbazone moiety, X = O or S) are reported. These have been characterized by elemental analysis, conductance measurements, molecular weight determinations and magnetic studies. Based on IR, $^1$HNMR, $^{13}$CNMR and electronic spectral studies, an octahedral geometry with as $-MoO_2$ structure has been proposed. The antibacterial and antifungicidal activities of two representative ligands and their dioxomolybdenum complexes have also been evaluated and discussed.

## INTRODUCTION

Molybdenum exhibits a large number of stable and accessible oxidation states as well as varying coordination numbers from four to eight. The study of dioxomolybdenum (VI) complexes has thrived for several years because of the interest in modeling the molybdenum oxidases, enzymes that catalyze a number of biologically important oxotransfer reactions, such as the conversion of nitrate to nitrite, sulfite to sulfate and xanthine to uric acid[1] etc. Stiefel[2] and Holm[3] have demonstrated that the coordination gemetries of Mo (VI) species can be manipulated by the steric constant of the donor ligand system. Recently much interest has been shown in the synthesis of metal chelates with oxygen/sulphur containing ligands, as these possess cytotoxic activity.

In previous communications from these laboratories considerable amount of work with transition as well as non-transition metals[4,5] have been reported with oxygen, nitrogen and or sulfur containing ligands. The marked biological activity of molybdenum thio complexes as antibacterial agents and their role in enzymes in the bio-systems prompted us to stydy the dioxomolybdenum (VI) complexes with the biologically active thiosemicarbazones and semicarbazones and the results of these investigations are being presented in this paper.

## EXPERIMENTAL

All the chemicals of analytical grade were used and solvents were dried by

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the standard methods. The ligands were prepared by the condensation of benzil, biacetyl and glyoxal with thiosemicarbazide or semicarbazide hydrochloride (in the presence of sodium acetate) in 1 : 1 molar ratio in ethanol. These were recrystallized from the same solvent and dried in vacuo. Their important physical properties and analytical data are given Table-1.

TABLE 1
PHYSICAL PROPERTIES AND ANALYTICAL DATA OF LIGANDS.

| Sl. No | Ligand/Colour | m. pt. (°C) | Analysis % Found (Calcd) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| 1. | Benzil thiosemicarbazone<br>$C_{16}H_{14}N_6S_2$, (Yellow) | 78 | 53.90<br>(53.90) | 4.50<br>(4.49) | 23.62<br>(23.69) |
| 2. | Biacetyl thiosemicarbazone<br>$C_6H_{10}N_6S_2$, (Yellow) | 210 | 31.00<br>(31.03) | 5.20<br>(5.17) | 36.25<br>(36.20) |
| 3. | Glyoxal thiosemicarbazone<br>$C_4H_6N_6S_2$, (Cream) | 220 | 23.50<br>(23.52) | 3.90<br>(3.92) | 41.12<br>(41.17) |
| 4. | Benzil semicarbazone<br>$C_{16}H_{14}N_6O_2$, (Yellow) | 91 | 62.32<br>(62.20) | 4.90<br>(4.93) | 25.01<br>(25.92) |
| 5. | Biacetyl semicarbozone<br>$C_6H_9N_6O_2$, (Cream) | 213 | 36.21<br>(36.00) | 6.12<br>(6.00) | 42.09<br>(42.00) |
| 6. | Glyoxal semicarbazone<br>$C_4H_6N_6O_2$, (Yellow) | 270 | 25.52<br>(25.53) | 4.31<br>(4.25) | 44.60<br>(44.68) |

Bis (acetylacetonato) dioxomolybdenum (VI) was prepared according to the literature method[6].

*Synthesis of Complexes:* To a calculated amount of 1 mol of $MoO_2(acac)_2$ in dry MeOH (40 $cm^3$) the requisite amount of (1 mol) of ligand was added. The resulting mixture was refluxed for 1–6 hrs. After the completion of the reaction, the solvent was removed and the residue dried in vacuo for 3 hrs. The purity of complexes was checked by TLC using toluene and methanol (70 : 30) as solvent. The spot of product found to be different in comparison to reactant. The physical properties and analytical data of the resulting complexes are recorded in Table-2.

Conductivity measurements were made with a conductivity bridge type 305 Systronics model. Molecular weights were determined by the Rast Camphor method. The magnetic susceptibility measurements were carried out by the Gouy's method at the room temperature using $NiCl_2$ as the standard. IR spectra were recorded on a Perkin Elmer 577 grating spectrophotometer in Nujol mulls using KBr optics. The electronic spectra were obtained on a Pye Unicam SP8–100 spectrophotometer in dry methanol. $^1H$ NMR spectra were recorded on Jeol FX–900 spectrometer in DMSO–$d_6$ using TMS as the internal standard $^{13}C$ NMR spectra were recorded in MeOH at 22.49 MHz. Molybdenum was determined gravimetrically as bis(8–hydroxyquinolinato)dioxomolybdenum(VI). Carbon and hydrogen analyses were carried out at the microanalytical laboratory of the Department. Nitrogen was determined by the Kjeldhal's method.

TABLE 2
ANALYSES AND PHYSICAL CHARACTERISTICS OF THE DIOXOMOLYBDENUM (VI) COMPLEXES

| Compound/Colour | Mol. wt. Found | m. pt. (°C) | Analysis % Found (Calcd) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | Mo | N |
| $[MoO_2(C_{16}H_{14}N_6S_2)]$ (Green solid) | 498<br>(481) | 250 | 39.89<br>(39.83) | 2.85<br>(2.90) | 19.91<br>(19.90) | 17.40<br>(17.42) |
| $[MoO_2(C_{16}H_{10}N_6S_2)]$ (Green solid) | 372<br>(357) | 240 | 20.15<br>(20.11) | 1.80<br>(1.81) | 29.10<br>(29.01) | 25.42<br>(25.45) |
| $[MoO_2(C_4H_6N_6S_2)]$ (Green solid) | 320<br>(329) | 220 | 14.51<br>(14.54) | 2.70<br>(2.79) | 26.81<br>(26.80) | 23.41<br>(23.46) |
| $[MoO_2(C_{16}H_{14}N_6O_2)]$ (Blue solid) | 410<br>(409) | 140 | 42.64<br>(42.67) | 3.10<br>(3.11) | 21.38<br>(21.32) | 18.70<br>(18.66) |
| $[MoO_2(C_6H_{10}N_6O_2)]$ (Light green solid) | 315<br>(325) | 172 | 22.09<br>(22.08) | 3.11<br>(3.06) | 29.46<br>(29.43) | 25.71<br>(25.77) |
| $[MoO_2(C_4H_6N_6O_2)]$ (Dark green solid) | 312<br>(297) | 180 | 16.10<br>(16.11) | 2.10<br>(2.01) | 32.26<br>(32.20) | 28.25<br>(28.19) |

## RESULTS AND DISCUSSION

The reactions of molybdenum acetyl acetonate with semicarbazones (HONOH) and thiosemicarbazones (HONOH) in 1 : 1 molar ratio in methanol proceed with the liberation of two acetyl acetone molecules as indicated below.

$$MoO_2(acac)_2 + H\overset{\frown\frown\frown}{SNNS}H \rightarrow MoO_2\,(\overset{\frown\frown\frown}{SNNS}) + 2C_5H_8O_2$$

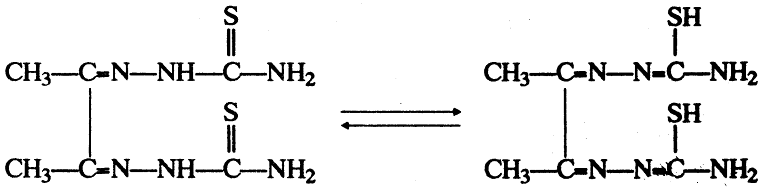
$$MoO_2(acac)_2 + H\overset{\frown\frown\frown}{ONNO}H \rightarrow MoO_2\,(\overset{\frown\frown\frown}{ONNO}) + 2C_5H_8O_2$$

These reactions are quite facile and completed after 4–6 hours of refluxing. The resulting complexes are obtained in the form of coloured solids. The molecular weight determinations show their monomeric nature. These are soluble in most of the common organic solvents and the molar conductance measurements (8–10 $ohm^{-1}cm^2mol^{-1}$) show that these are non electrolytes. All these derivatives are diamagnetic in nature.

The electronic spectra of the ligands exhibit three bands around *ca.* 275, 285 and 330 nm. The bands at *ca.* 275 and 285 nm are, possibly due to the $\pi - \pi^*$ transitions of benzene ring. The band around 330 nm may be due to $n - \pi^*$ transitions of the non-bonding electrons present on the nitrogen of the azomethine group. The first two bands remain unchanged in the corresponding complexes, wereas the third one under goes red shift due to the coordination of nitrogen to the central metal atom[7].

In the IR spectra of the ligands a broad and strong peak at *ca..* 3270 $cm^{-1}$ due to the hydrogen bonded NH[8] disappears in the metal complexes indicating its coordination with the metal atom. The $\nu C=N$ in the ligands appears at 1590–1600 $cm^{-1}$ and it undergoes a shift to the lower frequency in the complexes indicating that the unsaturated nitrogen of the azomethine linkage is cordinating to the molybdenum atom. The $\nu_{as}$ $NH_2$ and $\nu_{sym}$ $NH_2$ which appears around *ca..* 3420 and 3360 $cm^{-1}$ respectively in the ligands remain unchanged in the spectra of the complexes.

The bands due to $\nu(C=O)$, $\nu(C=S)$ and $\nu NH$ do not appear in the IR spectra of ligands in the solution state and which are observed in the IR spectra in KBr optics. This may be attributed to the existance of two tautomeric forms *viz.* amide or thioamide form in the solid state and hydroxylamine or thiolimine form in the solution state as shown below:



(thioamide form) (thiolimine form)

On complex formation these bands completely disappear showing thereby that the ketonic oxygen and thiolic sulphur are taking part in chelate formation[9]. Several new bands appearing at 460–440 $cm^{-1}$, 350–300 $cm^{-1}$ and 340–360 $cm^{-1}$ in the complexes may be attributed to $\nu(Mo-N)$, $\nu(Mo-S)$ and $\nu(Mo-O)$ respectively[10,11]. The $\nu_{sym}(O=Mo=O)$ and $\nu_{asy}(O=Mo=O)$ bands are observed in the range 920–890 $cm^{-1}$ in the complexes[12].

In the $^1H$ NMR spectra of the complexes, the disappearance of the signals at $\delta$ 10.08 and $\delta$ 11.23 ppm assignable to NH protons in the spectra of ligands clearly indicates its deprotonation. The proton signal for the azomethine proton observed at $\delta$ 8.32 – 7.32 ppm in the ligands gets shifted downfield in the spectra of Mo (VI) complexes. This deshielding is possibly due to the donation of the lone pair of electrons by the azomethine nitrogen to the central molybdenum atom resulting in the formation of coordinate band (Table-3).

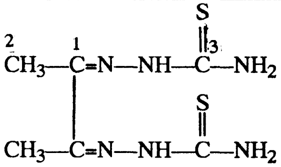
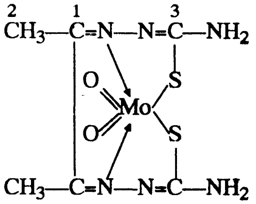
A signal observed at $\delta$ 191.20 ppm in the $^{13}C$ –NMR spectrum of biacetyl thiosemicarbazone due to carbon atom attached with thiolo group is shifted to $\delta$ 174.97 ppm in the spectrum of Mo (VI) complex and thus further substantiating the bonding pattern discussed above (Table 4).

TABLE 3
$^1$H NMR SPECTRAL DATA[a] (δ, ppm) OF LIGANDS AND THEIR DIOXOMOLYBDENUM (VI) COMPLEXES

| Sl.No. | Compound | Aromatic | NH | -NH$_2$ | Azomethine |
|---|---|---|---|---|---|
| 1. | $C_{16}H_{16}N_6S_2$ | 7.90–6.82 m | 11.23 s | 2.58 bs | 8.20 s |
| 2. | $[MoO_2(C_{16}H_{14}N_6S_2)]$ | 8.00–7.32 m | — | 2.60 bs | 8.34 s |
| 3. | $C_{16}H_{16}N_6O_2$ | 8.32–8.00 m | 10.08 s | 2.48 bs | 8.40 s |
| 4. | $[MoO_2(C_{16}H_{14}N_6O_2)]$ | 8.40–7.80 m | — | 2.54 bs | 8.60 s |

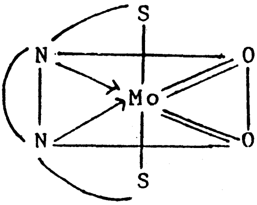
s = singlet, bs = broad singlet; m = multiplet complex; a = solvent – DMSO – d$_6$

TABLE 4
$^{13}$C NMR SPECTRAL DATA[a] OF BIACETYL THIOSEMICARBAZONE AND ITS DIOXOMOLYBDENUM COMPLEX

| Structure | Chemical Shift in δ, ppm | | |
|---|---|---|---|
| | 1 | 2 | 3 |
|  | 178.57 | 26.20 | 191.29 |
|  | 174.17 | 27.29 | 187.97 |

a = Solvent MeOH

Thus on the basis of above evidences the following tentative structure of MoO$_2$(C$_4$H$_6$N$_6$S$_2$) can be proposed.



(Where SNNS = donor set of the ligand).

The antibacterial activity of benzil thiosemicarbazone and benzil semicarbazone and their dioxomolybdenum complexes has been evaluated in the vitro against *E. coli, S. aureus, Eutrobactor aerogenus, Citrobactor, P. pyocyancus and S. citrus* at 1000 ppm concentration using the inhibition zone technique[6]. A 5 mm diameter sterilized filter paper disc impregnated with the compound was placed on agar plate seeded with the test organism. The plates were incubated 24 hrs., at 37°C. The zone of inhibition of bacterial growth around the disc was observed. The screening data show moderate activity against *E. coli, S. aureus, Eutrobactor aerogenus,* while all the compounds are highly active against *P. pyocyancus* and *S. citrus.* The above ligands and complexes were also screened for their fungicidal activity at two different concentrations. The data recorded in Table-5 indicate that the compounds are capable of inhibiting the fungal growth to a considerable extent both at high and low dilutions.

TABLE 5
FUNGICIDAL DATA OF LIGANDS AND THEIR DIOXOMLYBDENUM COMPLEXES

| Compound | Average percentage inhibition after 96 hrs. | | | | | |
|---|---|---|---|---|---|---|
| | Aspergillus flaves | | Aspergillus niger | | Alternaria alternata | |
| | 50 ppm | 75 ppm | 50 ppm | 75 ppm | 50 ppm | 75 ppm |
| $C_{16}H_{16}N_6S_2$ | 42 | 49 | 35 | 445 | 68 | 79 |
| $[MoO_2(C_{16}H_{14}N_6S_2)]$ | 50 | 58 | 38 | 50 | 75 | 32 |
| $C_{16}H_{16}N_6O_2$ | 38 | 45 | 30 | 34 | 63 | 67 |
| $[MoO_2(C_{16}H_{14}N_6O_2)]$ | 40 | 55 | 35 | 41 | 69 | 75 |

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