Structural Features and Biological Studies of Dioxomolybdenum(VI) Complexes of Thiosemicarbazones

Neeta KANOONGO, Ranvir SINGH, and Jagdish Prasad TANDON*
Department of Chemistry, University of Rajasthan, Jaipur 302004, India
(Received August 22, 1988)

Synopsis. Synthesis, characterization, and spectral features of six-coordinated dioxomolybdenum(VI) complexes of the type, $[MoO_2(tscz)_2]$ (where Htscz represents the thiosemicarbazone moiety) are reported. These have been characterized by elemental analysis, conductance measurements, molecular weight determinations, and magnetic studies. Based on IR, ^1H NMR, ^{13}C NMR, and electronic spectral studies, an octahedral geometry with *cis*-MoO_2 structure has been proposed. The antibacterial and fungicidal activities of two representative ligands and their dioxomolybdenum complexes have also been evaluated and discussed.

Molybdenum exhibits a large number of stable and accessible oxidation states as well as varying coordination numbers from four to eight.[1] A large number of important chemical reactions catalyzed by molybdenum compounds, e.g. industrial process such as hydrodesulfurization[2] and olefin epoxidation[3] are carried out in presence of molybdenum catalyst. Nature has also incorporated molybdenum into a number of important[4] redox enzymes.

In view of industrial and biological importance of molybdenum complexes,[5,6] it was considered of interest to synthesize some molybdenum(VI) complexes of bidentate Schiff bases and study their structural features as well as biological activity. The ligands used are biologically active thiosemicarbazones and the results of these investigations are being presented in this paper.

Experimental

All the chemicals of analytical grade were used and the solvents were dried by the standard methods. Thiosemicarbazones[7] and $MoO_2(acac)_2$[8] were prepared according to the literature methods and analyzed before use. The ligands derived from 2-furancarbaldehyde, 2-pyridinecarbaldehyde, 2-thiophenecarbaldehyde, 3-indolecarbaldehyde, cinnamaldehyde 2-propanone, 1-phenylethanone and 4-methyl-2-pentanone are abbrevied as $Htscz_1$, $Htscz_2$, $Htscz_3$, $Htscz_4$, $Htscz_5$, $Htscz_6$, $Htscz_7$ and $Htscz_8$, respectively.

Synthesis of $[MoO_2(tscz)_2]$. To a calculated amount (1 mol) of $MoO_2(acac)_2$ in dry MeOH (ca. 40 cm^3) the requisite amount (2 mol) of thiosemicarbazone was added. The resulting mixture was refluxed for 4 h. After the completion of the reaction the solvent was removed and the residue dried in vacuo for 3 h. The analytical data (C, H, N, S, and Mo) of the complexes are within the limit of experimental errors. Molybdenum was determined gravimetrically as bis(8-quinolinalato) dioxomolybdenum(VI). Other methods of analyses and physical measurements are same as reported earlier.[7]

Results and Discussion

The reactions between $MoO_2(acac)_2$ and monobasic bidentate, thiosemicarbazones were carried out in 1 : 2 molar ratio in methanol. The replacement of acetylacetonato group by the ligands resulted in the formation of the products of the type $[MoO_2(acac)_2]$. The resulting derivatives were recrystallized by adding solvent ether to the methanolic solution of the complexes and their purity was further checked by TLC on silica gel G using anhydrous methanol as the solvent. These are soluble in methanol, DMSO, and DMF.

The low values of molar conductance in DMF (10—14 $ohm^{-1}\,cm^2\,mol^{-1}$) show these complexes to be non-electrolytes and the molecular weight determinations by the Rast camphor method correspond to the formula weight indicating their monomeric nature. All the derivatives are diamagnetic as expected for $4d^0$ configuration for Mo(VI) species.

The IR spectra of thiosemicarbazones[7] show a strong band at ca. 3280 cm^{-1} due to ν_{NH} vibrations and which disappears in the metal complexes suggesting its deprotonation on complexation with the metal ion. In the IR spectra of ligands in solution, bands due to ν(C=S) and ν_{NH}, which are observed in the IR spectra in KBr optics do not appear. This may be attributed to the existence of two tautomeric forms, viz, an thioamide form in the solid state and iminothiol form in solution.[9] On complex formation, these bands disappear indicating the coordination of the ligand through the thiolic sulfur. A strong band in the ligands in the region, 1610—1620 cm^{-1} due to the azomethine (>C=N) group shifted to the lower frequency region in the molybdenum complexes.[10]

In the spectra of the complexes, two bands in the regions, 900—920 and 890—900 cm^{-1} can be ascribed to ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O) vibrations[11] respectively. The presence of these bands is indicative of *cis*-MoO_2 structure as the *trans*-MoO_2 structure would show only one ν_{asym}(O=Mo=O) band in this region. Further, medium to weak intensity bands in the regions, 450—430 and 370—300 cm^{-1} which do not appear in the ligands, may be attributed to νMo-N and νMo-S, respectively.[12,13]

The electronic spectrum of $Htscz_1$ shows one band of weak intensity at 245 nm and a broad band at 340 nm attributable to π-π^* (double bond) and n-π^* (azomethine) electronic transitions, respectively. In $[MoO_2(tscz_1)_2]$ the first band remains almost unchanged whereas, the second band shows a blue shift due to the donation of nitrogen lone pair of the azomethine group to molybdenum atom. The spectrum of complex also exhibits a strong band at 380—450 nm due to the ligand to metal charge transfer transitions between the lowest empty molybdenum d orbital and the highest occupied ligand molecular orbital as reported earlier.[1]

The proton magnetic resonance spectra of $Htscz_1$

Table 1. ^{1}H NMR Data (δ/ppm) of Ligands and Dioxomolybdenum(VI) Complexes

S. No.	Compound	-NH	Aromatic	Azomethine	$-NH_2$
1	$Htscz_1$[a)]	11.40bs	6.60—7.68m	8.00s	2.40bs
2	$[MoO_2(tscz_1)_2]$[a)]	—	7.35—8.16m	8.20s	2.66bs
3	$Htscz_2$	11.08bs	6.32—6.80m	8.40s	2.55bs
4	$[MoO_2(tscz_2)_2]$	—	7.00—7.72m	8.50s	2.60bs
5	$Htscz_4$	11.78bs	6.00—7.60m	8.32s	2.40bs
6	$[MoO_2(tscz_4)_2]$	—	7.46—8.00m	8.48s	2.80bs

s=singlet, bs=broad singlet, and m=complex multiplets.
a) ^{13}C NMR data: Ligand; C_1 (179.48), C_2 (150.79), C_3 (134.77), C_4 (114.75), C_5 (146.14), C_6 (199.9).
Complex; C_1 (176.77), C_2 (148.49), C_3 (131.78), C_4 (111.87), C_5 (144.00), C_6 (188.69).

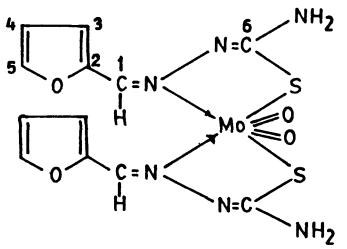
Table 2. Fungicidal Data of Ligands and Their Dioxomolybdenum Complexes

Compound	Average percentage inhibition after 96 h					
	Aspergillus Flaves		Aspergillus niger		Alternaria alternata	
	50 ppm	75 ppm	50 ppm	75 ppm	50 ppm	75 ppm
$Htscz_1$	40	48	32	45	65	70
$[MoO_2(tscz_1)_2]$	52	61	38	50	68	75
$Htscz_3$	44	55	37	47	70	79
$[MoO_2(tscz_3)_2]$	60	67	48	59	77	85

(**1**), $Htscz_2$ (**3**), $Htscz_4$ (**5**), and their corresponding dioxomolybdenum complexes **2**, **4**, and **6** respectively have been recorded in DMSO-d_6 using TMS as the internal standard. The chemical shifts value (δ/ppm) of the different protons have been recorded in Table 1. The broad signals due to NH protons at δ 11.40 (**1**), δ 11.08 (**3**), and δ 11.78 (**5**) in the ligands disappear in the case of molybdenum complexes showing ligation of molybdenum to nitrogen as well as sulfur atoms. The azomethine proton signals (-C(H)=N) appearing at δ 8.00 (**1**), δ 8.40 (**3**), and δ 8.32 (**5**) in the ligands undergo deshielding and appear at δ 8.20 (**2**), δ 8.50 (**4**), and δ 8.48 respectively in the molybdenum complexes indicating the coordination of the azomethine nitrogen to the molybdenum atom. The positions and assignment of other protons are recorded in Table 1.

^{13}C NMR spectra of $Htscz_1$ and its molybdenum complex have also been recorded in Table 1 (foot note). The shifts of the carbons attached to the donor S and N atoms further substantiate the bonding pattern discussed earlier.

Thus on the basis of above evidences the following cis-octahedral structure can be proposed for the molybdenum(VI) complexes with $Htscz_1$ as the ligand:



The antibacterial activity of $Htscz_1$ and $Htscz_3$ and their dioxomolybdenum complexes has been evaluated in vitro against *E. Coli, S. aureus, Eutrobactor aerogenus, Citrobactor, P. Pyocyancus,* and *S. Citrus* at 1000 ppm concentration using the inhibition zone technique.[14] 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 for 24 h 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 by determining the percentage inhibition of colonial growth in comparison to the growth in control. From the data recorded in Table 2, it is evident that the compounds are capable of inhibiting the fungal growth to a considerable extent both at high and low dilutions.

One of us (N.K.) is thankful to the U.G.C. New Delhi, India for financial assistance.

References

1) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
2) B. C. Gates, J. R. Katzer, and G. C. Aschuit "Chemistry of Catalytic Process," McGraw Hill, New York (1979), p. 390.
3) M. L. H. Green, Proc. 3rd Int. Conf. on the Chemistry and Uses of Molybdenum Climax, Molybdenum Co., Ann. Arbor MI, p. 34 (1979).
4) R. C. Bray, *Enzyme,* **12**, 299 (1975).
5) T. D. Tullius, D. M. Kurtz, Jr., S. D. Conradson, and K. O. Hodgson, *J. Am. Chem. Soc.*, **101**, 2776 (1969).
6) S. P. Cramer, H. B. Gray, and K. V. Rajagopalan, *J. Am. Chem. Soc.*, **101**, 2772 (1979).
7) N. Kanoongo, R. V. Singh, and J. P. Tandon, *Transition Met. Chem.*, **12**, 271 (1987).
8) G. J.-J. Chen, W. J. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
9) S. P. Mital, R. V. Singh, and J. P. Tandon, *Synth. React.*

Inorg. Met.-Org. Chem., **11**, 547 (1981).
10) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Prog. Inorg. Chem.*, **7**, 83 (1966).
11) P. W. Moore and M. L. Larsen, *Inorg. Chem.*, **6**, 998 (1967).
12) K. Nakamoto, "The Infrared Spectra of Inorganic and Coordination Compounds," Wiley Eastern, New Delhi (1967).
13) S. K. Sengupta and S. Kumar, *Indian J. Chem.*, **22A**, 257 (1983).
14) R. S. Verma and S. A. Imam, *Indian J. Microbiol.*, **13**, 45 (1973).