http://dx.doi.org/10.5012/bkcs.2013.34.8.2381

Manganese(II) and Dioxomolybdenum(VI) Complexes with Monobasic Bidentate Schiff Bases : Synthesis, Characterization and Biological Investigation

Rekha Garg, Anita Kumari, S. C. Joshi,[†] and Nighat Fahmi[*]

Department of Chemistry, University of Rajasthan, Jaipur - 302 004, India
[*]E-mail: nighat.fahmi@gmail.com; anitasigger@yahoo.in
[†]Department of Zoology, University of Rajasthan, Jaipur - 302 004, India
Received March 8, 2013, Accepted May 16, 2013

A new series of Mn(II) and Mo(VI) complexes containing the Schiff bases hydrazinecarbothioamide and hydrazinecarboxamide of 5,6-dimethyl-1*H*-indol-2,3-dione have been synthesized.The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, molecular weight determinations and spectral studies *viz.* electronic IR, ESR, ^{1}H NMR and ^{13}C NMR and X-ray diffraction spectral studies. The magnetic moment values of the manganese(II) complexes are in the range of 5.80-6.15 B.M. suggesting a high spin state of manganese in these complexes. The spectral data are consistent with a tetrahedral geometry around Mn(II) and an octahedral geometry for Mo(VI), in which the ligands act as bidentate chelating agents, coordinated through the nitrogen and sulfur/oxygen atoms. The ligands and their metal complexes have been tested against a number of pathogenic fungi and bacteria at different concentrations and were found to possess sufficient fungicidal and bactericidal properties. Further, the complexes were also tested for their antifertility activity in male albino rats and the results were indeed positive.

Key Words : Metal Schiff base complexes, Spectroscopic studies, Antimicrobial activity and antifertility activity

Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups and it is multiplied manifold when the ligands have biological importance.[1] Schiff-base complexes of transition metals are of particular interest to inorganic chemists because their structural, spectral, and chemical properties are often strongly dependent on the nature of the ligand structure.[2] A large number of Schiff bases and their complexes have been studied for their interesting and important properties, *e.g.*, their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties and complexing ability towards some toxic metals.[3] Schiff bases are also superior reagents in biological, pharmacological, clinical, and analytical applications.[4] Thiosemicarbazones have considerable interest in the field of chemistry and biology due to their antibacterial, antifungal, antimalarial, antineoplastic and antiviral activities.[5-10] Interest in metal complexes of sulfur-nitrogen chelating agents, especially those formed from thiosemicarbazide[11] has been stimulated by their interesting physicochemical properties and potentially useful pharmacological properties.[12] Metal complexes of these ligands possess a wide spectrum of medicinal properties.[13] Sulfur containing ligands can show pronounced biological potency as antituberculosis[14] and anti-tumor agents.[15] Thiosemicarbazones are known as analytical reagents.[16-20] Metal chelates of these reagents inhibit tumor growth and increase the activity of some drugs.[21]

In the present work, we report the synthesis, spectral studies as well as antibacterial, antifungal and antifertility properties of manganese(II) and dioxomolybdenum(VI) complexes containing Schiff bases derived from 5,6-dimethyl-1*H*-indol-2,3-dione.

Experimental Section

All the reagents used were of AR grade and the solvents used were dried, distilled and purified by the standard methods. The starting material of the manganese and molybdenum were purchased from Lancaster. The molecular weights were determined by the Rast Camphor method and conductivity measurements were made with a Systronic Model 305 conductivity bridge. Nitrogen and sulfur were estimated by the Kjeldahl's and Messenger's methods, respectively.[22] Chlorine was determined by Volhard's method. Manganese was estimated complexometrically with EDTA using Erichrome Black T as an indicator. Molybdenum was determined gravimetrically as bis(8-hydroxyquinolato)dioxomolybdenum by the standard method.[23]

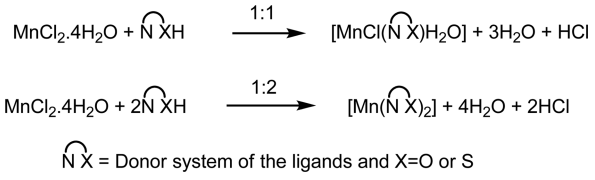
Electronic spectra of the complexes were recorded in methanol on a UV-160A, Shimadzu spectrophotometer in the range 200-600 nm. Infrared spectra were recorded on a FT-IR spectrophotometer using KBr pellets. ^{13}C and ^{1}H NMR spectra were recorded using a JEOL-AL-300 FTNMR spectrophotometer in DMSO-d_6 using TMS as the internal standard. ESR spectra were recorded at the IIT Madras, Chennai.

Synthesis of Ligand. The starting material 5,6-dimethyl-1*H*-indol-2,3-dione was synthesized by Sandmeyer isonitrosoacetanalide synthesis method.[24]

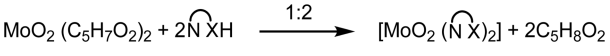
Preparation of L^1H. Ethanolic solution of 5,6-dimethyl-1*H*-indol-2,3-dione (4 g, 0.22 mol) was added to a ethanolic solution of thiosemicarbazide (2.08 g, 0.22 mol) in the 1:1 molar ratio. The reaction mixture was refluxed at 70-80 °C for 30-40 mins and allowed to stand overnight. The products were recrystallized from the ethanol and dried *in vacuo*. The resulting products were analysed before use. ^{1}H NMR Spectral data (δ, ppm) 11.90 [-NH(ring)], 11.26 [-NH(free)], 3.44 (-NH_2), 2.92 (-CH_3), 6.23-8.72 (Aromatic protons); ^{13}C NMR Spectral data (δ, ppm) 156.45 (Azomethine carbon), 167.92 (enolic carbon), 141.54, 127.33, 126.14, 128.45, 124.16, 129.17 (Aromatic carbon).

Preparation of L^2H. Ethanolic solution of 5,6-dimethyl-1*H*-indol-2,3-dione (4 g, 0.22 mol) was added to a ethanolic solution of semicarbazide hydrochloride (2.54 g, 0.22 mol) (in the presence of sodium acetate) in the 1:1 molar ratio. The reaction mixture was refluxed at 70-80 °C for 30-40 mins and allowed to stand overnight. The products were recrystallized from the ethanol and dried *in vacuo*. The resulting products were analysed before use. ^{1}H NMR Spectral data (δ, ppm) 11.99 [-NH(ring)], 11.28 [-NH(free)], 3.59 (-NH_2), 2.90 (-CH_3), 7.81-8.41 (Aromatic protons); ^{13}C NMR Spectral data (δ, ppm) 158.42 (Azomethine carbon), 165.91 (enolic carbon), 142.52, 126.31, 124.12, 129.43, 125.12, 128.16 (Aromatic carbon).

Sythesis of Compounds. The unimolar and bimolar reactions of hydrated manganese dichloride with the monobasic bidentate ligand have been carried out in methanol.



The bimolar reactions of dioxobis (2,4-pentanedinato) molybdenum(VI) with the ligand may be represented as follows.



Preparation of 1, [Mn(L^1)Cl H_2O]. Hydrated manganese dichloride (1.5 g, 0.07 mol) in methanol (25 mL) was added to a solution of L^1H (1.88 g, 0.007 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 254 °C. IR (KBr pellet): 1620, 3448-3310, 395, 350 cm^{-1}. Analysis % Found (Calculated) for [Mn(L^1)Cl H_2O]: Mn 15.12 (15.44), N 15.11 (15.75), S 8.94 (9.01), Cl 9.85 (9.97)% Yield 89% Molecular Weight Found (Calculated) 314 (355) Colour: Dim yellow.

Preparation of 2, [Mn(L^1)$_2$]. Hydrated manganese dichloride (1.3 g, 0.066 mol) in methanol (25 mL) was added to a solution of L^1H (3.26 g, 0.0131 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 272 °C. IR (KBr pellet): 1590, 3440-3305, 400, 290 cm^{-1}. Analysis % Found (Calculated) for [Mn(L^1)$_2$]: Mn 10.81 (10.95), N 22.02 (22.34), S 12.22 (12.78)% Yield 79% Molecular Weight Found (Calculated) 483 (501) Colour: Dim yellow.

Preparation of 3, [Mn(L^2)Cl H_2O]. Hydrated manganese dichloride (1.8 g, 0.09 mol) in methanol (25 mL) was added to a solution of L^1H (2.11 g, 0.009 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 214 °C. IR (KBr pellet): 1585, 3478-3305, 385, 440 cm^{-1}. Analysis % Found (Calculated) for [Mn(L^2)Cl H_2O]: Mn 16.05 (16.17), N 16.28 (16.49), Cl 10.18 (10.44)% Yield 78% Molecular Weight Found (Calculated) 321 (339) Colour: yellow.

Preparation of 4, [Mn(L^2)$_2$]. Hydrated manganese dichloride (1.9 g, 0.09 mol) in methanol (25 mL) was added to a solution of L^1H (4.45 g, 0.018 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 259 °C. IR (KBr pellet): 1580, 3475-3312, 387, 445 cm^{-1}. Analysis % Found (Calculated) for [Mn(L^2)$_2$]: Mn 11.16 (11.70), N 23.71 (23.87)% Yield 86% Molecular Weight Found (Calculated) 412 (469) Colour: yellow.

Preparation of 5, [MoO_2 (L^1)$_2$]. Dioxobis (2,4-pentanedinato) molybdenum(VI) (1.7 g, 0.05 mol) in methanol (25 mL) was added to a solution of L^1H (2.58 g, 0.010 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 232 °C. IR (KBr pellet): 1600, 3445-3320, 460, 350 cm^{-1}. ^{1}H NMR Spectral data (δ, ppm) 12.07 [-NH(ring)], 3.56 (-NH_2), 2.75 (-CH_3), 6.24-8.21 (Aromatic protons). ^{13}C NMR Spectral data (δ, ppm): 155.47 (Azomethine carbon), 172.76 (enolic carbon): 141.57, 127.22, 126.44, 128.94, 124.74, 129.41 (Aromatic carbon) Analysis % Found (Calculated) for [MoO_2 (L^1)$_2$]: Mo 15.07 (15.41), N 17.86 (17.99), S 10.12 (10.30)% Yield 78% Molecular Weight Found (Calculated) 612 (622) Colour: Brown.

Preparation of 6, [MoO_2 (L^2)$_2$]. Dioxobis (2,4-pentanedinato) molybdenum(VI) (2 g, 0.06 mol) in methanol (25 mL) was added to a solution of L^1H (2.84 g, 0.012 mol) in methanol (25 mL). The reaction mixture was heated under reflux for 10-15 h. The residue formed was separated out, filtered off, washed with *n*-hexane and ether and dried at 40-60/0.5 mm of Hg pressure for 3-4 h. mp 217 °C. IR (KBr pellet): 1588, 3438-3325, 440, 625 cm^{-1}. ^{1}H NMR Spectral data (δ, ppm) 11.97 [-NH(ring)], 3.44 (-NH_2), 2.80 (-CH_3), 7.01-8.59 (Aromatic protons). ^{13}C NMR Spectral data (δ, ppm): 154.42 (Azomethine carbon), 170.70 (enolic carbon) 142.51, 126.25, 124.01, 129.32, 124.94, 128.11 (Aromatic carbon) Analysis % Found (Calculated) for [MoO_2 (L^1)$_2$]:

Mo 16.15 (16.25), N 18.17 (18.98)% Yield 84% Molecular Weight Found (Calculated) 581(590) Colour: Brown.

Biological Activity.

Antifungal Activity: The biological screening effects of the investigated compounds (**1-6**) were tested against the fungal species *Fusarium oxysporum* and *Macrophomina phaseolina* using agar plate technique. The linear growth of the fungus was obtained by measuring the diameter of colony in a petri plate after 96h and the percentage inhibition(I) was calculated as 100(C-T)/C, where C and T are the diameters of the fungus colony in the control and the test plates, respectively.[25]

The medium used was potato dextrose agar (glucose 20 g, starch 20 g, agar-agar 20 g and distilled water 1000 cm^3). The compounds were directly mixed with the medium. Fungi were placed on the medium with the help of an inoculum needle. These petri plates were wrapped in polythene bags containing some drops of alcohol and were placed in an incubator at 28 ± 2 °C.

Antibacterial Activity: Antibacterial activity was evaluated against *Staphylococcus aureus* and *Escherichia coli* by the paper disc plate method. The agar medium having the composition peptone (5 g), beef extract (5 g), NaCl (5 g), agar-agar (20 g) and distilled water 1000 mL and 5 mm diameter paper discs of Whatman No. 1 were used.[26] The agar medium was poured in petri plates. The solution of the test compound (**1-6**) in methanol in 500 and 1000 ppm concentration were prepared, the discs were dipped in solution of the test sample and placed on seeded plates. The petri plates having these discs on the seeded agar were placed at low temperature for 2 h to allow for the diffusion of a chemical and then incubated at suitable optimum temperature 28 ± 2 °C for 20-30 h.

Antifertility Activity: Thirty male albino rats of Wistar strain, weighing 170 to 190 g (90-100 days old) were used for the experiments. They were housed in an air conditioned animal room at 24 ± 2 °C with 14 h light and water and food was given *ad libitum*. These were divided into five groups containing six animals each. The group A served as vehicle (olive oil) treated control. In the group B, the ligand, *i.e*., L^1H 50 mg/kg suspended in olive oil was given orally for a period of 60 days. The animals of groups C, D and E received same doses of **1**, **2** and **5** complexes, for the same period.[27]

The fertility test of individual rats was done before the experiment and after 55 days of the experiment. Each rat was cohabited with progesterone female in 1:2 ratios. Vaginal smear was examined every morning for positive mating and number of litters delivered was recorded.

The rats were sacrificed within 24 h after the last administration of the compounds, *i.e*. on 61th day of the experiment. The testes, epididymis, seminal vesicle and ventral prostate were removed, cleared off fat, blood vessels and connective tissue before weighing. Sperm motility and sperm density were assayed in cauda epididymis and testes. The parts of testes, epididymis, seminal vesicle and ventral prostate from each rat were kept at −20 °C until assayed for protein, sialic acid, cholesterol and fructose. Student't' test was used for the assessment of the significance of variation and the data are presented as mean ± 5 EM.

Result and Discussion

Electronic Spectra. The electronic spectra of the ligands display two maxima at ~270 and ~320 nm which are due to π-π* transitions which remain unchanged in the metal complexes. The band around 370 nm is due to the n-π* electronic transitions of the azomethine, chromophore and shows a bathochromic shift of 20 to 30 nm after the coordination of the azomethine nitrogen to the metal atom, indicating the delocalization of the electronic charge within the chelate ring and thereby stabilizing the resulting complexes.[28]

E.S.R Spectra. The electronic spin resonance spectra of the manganese(II) complexes were recorded at the room temperature. These consists of a single broad peak in each case, from which the lande splitting factor (g values) has been calculated. The g values for the complexes lie in the range 2.05-1.93 in the present complexes which are in accordance with the values reported for tetracoordinated manganese complexes.[29]

X-ray Diffaction. The X-ray diffraction analysis of the finely powdered complex **6** has been carried out in order to have an idea about the lattice dynamics of the compound. The results show that the compound belongs to the orthorhombic crystal system a = 33.5631, b = 14.7645, c = 19.4520 with $\alpha = \beta = \gamma = 90^o$ respectively and Miller indices h, k and l have been assigned to each d value and 2θ angles are reported in Table 1.

The synthesized complexes are soluble in methanol, DMF,

Table 1. X-Ray diffraction data of the complex **6**

Peak No.	2θ (deg.) (obs.)	h	k	l	d-spacing (obs.) (Å)
1	14.2	2	0	3	6.2461
2	16.5	5	1	0	5.1243
3	17.4	4	1	2	4.0341
4	21.6	5	2	1	3.9863
5	22.4	6	1	2	3.5452
6	23.5	1	1	2	3.3263
7	24.1	7	0	2	3.1047
8	25.7	7	1	2	3.0461
9	27.2	4	1	1	2.9862
10	28.3	7	1	3	2.7463
11	30.4	4	5	3	2.6223
12	31.8	7	3	2	2.5543
13	32.1	10	1	0	2.3345
14	34.4	8	3	2	2.1827
15	36.2	9	4	3	2.1825
16	37.8	7	4	2	2.1047
17	38.2	1	2	8	2.0183
18	42.1	5	2	1	2.0014

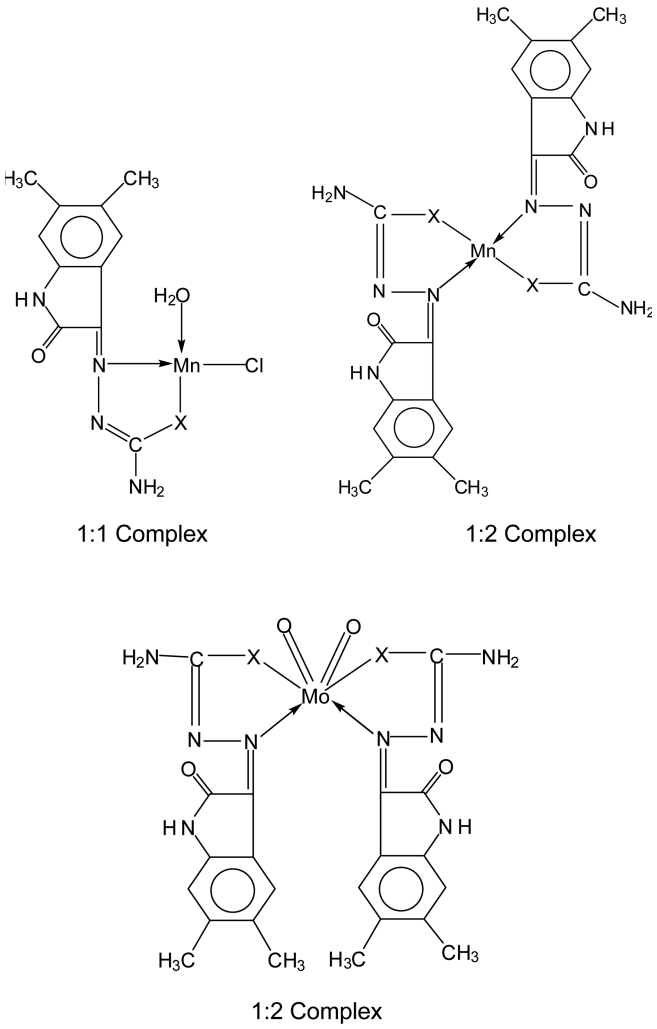


Figure 1. Proposed structure of the complexes.

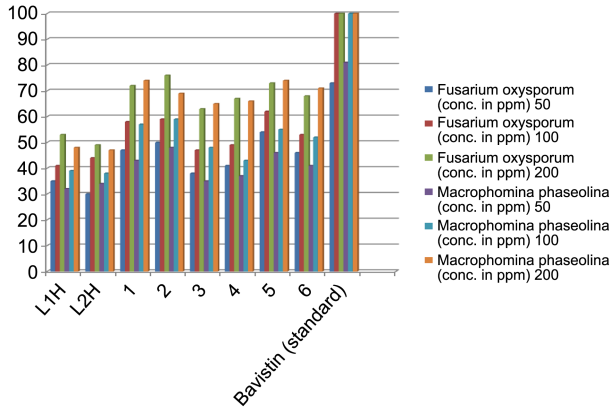


Figure 2. Antifungal screening data of the ligands and their metal complexes.

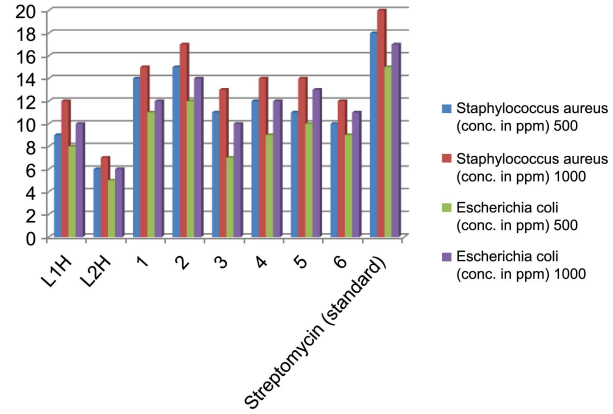


Figure 3. Antibacterial screening data of the ligands and their metal complexes.

DMSO and sparingly soluble in water. The molar conductance of 10^{-3} M solutions of the complexes in dry DMF lie in the 10-15 ohm^{-1} cm^2 mol^{-1} range, indicating that they are non-electrolytes. The magnetic moment values of the manganese(II) complexes are in the range of 5.80-6.15 B.M. suggesting a high spin state of manganese in these complexes. On the basis of these above studies for the manganese and dioxomolybdenum complexes, a tetrahedral and an octahedral geometry respectively have been suggested (Figure 1).

Antimicrobial Assay. The result reveals that there is a considerable increase in the activity of the complexes as compared to the ligands. The results achieved out of these studies have been enlisted in Figures 2 and 3.

The enhanced antimicrobial activity of the metal complexes over their corresponding chelating agents may conveniently be explained by the Tweedy's chelation theory.[30]

According to the chelation theory, the chelation reduces the polarity of the central metal atom mainly because of the partial sharing of its positive charge with the donor groups and possible π electron delocalisation over the whole chelate ring. This increases the lipophilic nature of the complex, which subsequently favours its permeation through the lipid layer of the cell membrane which interferes in the normal cellular processes and damages the cytoplasmic membrane leading to the cell death.[31]

Antifertility Activity. Experiments were conducted *in vivo* in male rats to check antifertility activity. The results reported are as follows.

Body and Organ Weights: Administration of Schiff base ligand L^{1}H and its **1**, **2** and **5** complexes did not cause any significant changes in the body weights of the treated rats. The weights of the testes, epididymis, seminal vesicle and ventral prostate were reduced significantly when compared with the vehicle treated control (Table 2).

Sperm Motility and Sperm Density: A sharp decline ($P \leq 0.001$) in the sperm motility was noticed in the rats treated with L^{1}H and its **1**, **2** and **5** complexes. Sperm density in the cauda epididymis was also reduced significantly ($P \leq 0.001$) in all treated groups (Table 3).

Tissue Biochemistry.

Protein and Sialic Acid: Protein and sialic acid contents in testes, epididymis, seminal vesicle and ventral prostate were significantly decreased after the treatment with the ligand L^{1}H and its **1**, **2** and **5** complexes (Table 3).

Testicular Cholesterol: Testicular cholesterol was increased significantly ($P \leq 0.001$) after the treatment with the

Table 2. Changes in the body weight and weights of the reproductive organs after the treatment with the ligand and its manganese and dioxomolybdenum complexes

Group	Treatment	Body weight (g)		Organ weights [mg/100 g body weight]			
		Initial	Final	Testes	Epididymis	Seminal vesicle	Ventral prostate
A	Control	176.0 ± 4.70	197.0 ± 5.2	1440.0 ± 21.4	482.0 ± 5.9	491.0 ± 10.6	397.0 ± 10.2
B	L^1H	186.0 ± 6.40	214.0 ± 6.2^c	1212.0 ± 12.6^b	426.0 ± 7.1^b	433.0 ± 5.9^b	284.0 ± 11.7^b
C	**1**	171.0 ± 6.30	201.0 ± 9.80^c	1006.0 ± 13.8^b	292.0 ± 5.7^b	307.0 ± 9.8^b	206.0 ± 11.5^b
D	**2**	181.0 ± 7.30	204.0 ± 8.50^c	982.0 ± 10.4^b	284.0 ± 7.3^b	314.0 ± 6.9^b	217.0 ± 10.8^b
E	**5**	177.0 ± 6.90	209.0 ± 6.0^c	914.0 ± 12.7^b	262.0 ± 6.4^b	292.0 ± 7.7^b	192.0 ± 7.9^b

Values means ± SEM of six determinations. Group B compared with Group A. Groups C, D and E compared with group B. a = P ≤ 0.05. b = P < 0.001. c = NS, non-significant

Table 3. Effects of the ligand and its manganese and dioxomolybdenum complexes on sperm motility concentration and fertility in rats

Group	Treatment	Sperm motility (%) Cauda epididymis	Sperm motility		Fertility (%)
			Testes	Cauda epididymis	
A	Control	77.0 ± 2.60	4.70 ± 0.26	48.80 ± 2.59	100 (+ve)
B	L^1H	52.0 ± 2.60^b	2.80 ± 0.22^b	21.0 ± 3.10^b	76 (−ve)
C	**1**	36.0 ± 2.80^b	1.70 ± 0.17^b	13.50 ± 2.10^b	91.8 (−ve)
D	**2**	39.0 ± 3.10^b	1.90 ± 0.16^b	12.50 ± 2.20^b	94.0 (−ve)
E	**5**	33.0 ± 5.70^b	1.50 ± 0.18^b	2.80 ± 2.10^b	93.0 (−ve)

Values means ± SEM of six determinations. Group B compared with Group A. Groups C, D and E compared with group B. a = P ≤ 0.05, b = P < 0.001

Table 4. Tissue biochemistry of the ligand and its manganese and dioxomolybdenum complexes

Group	Treatment	Protein (mg/g)				Sialic acid (mg/g)				Testicular Cholesterol (mg/g)	Seminarl Frustose (mg/g)
		Testes	Epididymis	Seminal vesicle	Ventral prostate	Testes	Epididymis	Seminal vesicle	Ventral prostate		
A	Control	234.0 ± 7.15	206.0 ± 6.80	196.0 ± 6.60	182.0 ± 3.60	4.80 ± 0.45	5.40 ± 0.49	5.43 ± 0.39	5.80 ± 0.46	7.66 ± 0.74	450.0 ± 30.0
B	L^1H	196.0 ± 6.70^b	172.0 ± 4.90^b	156.0 ± 4.70^a	146 ± 3.20^b	4.30 ± 0.45^a	4.34 ± 0.50^b	4.45 ± 0.42^b	4.62 ± 0.43^a	8.62 ± 0.47^b	390.0 ± 25.0^a
C	**1**	146.0 ± 6.80^b	126.0 ± 5.80^b	137.0 ± 4.40^a	106.0 ± 3.80^b	3.50 ± 0.44^b	3.24 ± 0.49^b	3.20 ± 0.42^b	3.92 ± 0.15^b	9.67 ± 0.40^b	310.0 ± 27.0^b
D	**2**	136.0 ± 6.80^b	132.0 ± 4.80^b	122.0 ± 3.80^b	111.0 ± 4.20^b	3.20 ± 0.45^b	3.25 ± 0.42^b	3.46 ± 0.41^b	3.56 ± 0.20^b	9.90 ± 0.34^b	305.0 ± 31.0^b
E	**5**	132.0 ± 4.90^b	139.0 ± 4.50^b	119.0 ± 3.80^b	109.0 ± 4.45^b	2.85 ± 0.50^b	3.10 ± 0.24^b	3.29 ± 0.50^b	3.31 ± 0.28^b	9.77 ± 0.18^b	280.0 ± 25.0^b

Values means ± SEM of six determinations. Group B compared with Group A. Groups C, D and E compared with group B. a = P ≤ 0.05, b = P < 0.001

ligand L^1H and its **1**, **2** and **5** complexes (Table 3).

Fructose: Fructose contents of seminal vesicle was decreased (P ≤ 0.001) in male albino rats treated with the ligand L^1H and its **1**, **2** and **5** complexes (Table 4).

In the present study a significant decrease was observed in the weight of testes, epididymis, seminal vesicle and ventral prostate after the treatment with the ligand L^1H and its **1**, **2** and **5** complexes. Significant decrease in testes weight may be due to the decrease in the number of spermatogenic elements,that is cell death which leads to regression of these organs.[32] Reductions in the weight of the accessory reproductive organs suggest the reduced availability of androgens. Treatment with the ligand L^1H and its **1**, **2** and **5** complexes resulted in the sharp decline in sperm motility of cauda epididymis. On the other hand the low caudal epididymal sperm density may be due to the alteration in the androgen metabolism.[33]

The low motility and negative fertility test may be attributed to the lack of the forward progression and reduction in the density of spermatozoa and altered biochemical milleu of cauda epididymis. Treatment with the various complexes also alters the biochemical parameters of the reproductive tract. Reduction in sialic acid contents in testes, epididymis, ventral prostate and seminal vesicle in treated rats may be correlated with the loss of the androgen. Reduced contents of the proteins in testes and sex accessory organs may be probably due to the absence of spermatogenic stages in the testes. A significant increase of testicular cholesterol indicates that pituitary gonadotropins may not be available for steroidogenesis. Our studies suggest that the addition of man-

ganese and molybdenum moiety to the ligand enhances its activity and the complex **5** is more effective in regulating the fertility in male rats.

Conclusion

We describe the synthesis, characterization and biological activity of Mn(II) and Mo(VI) complexes. On the basis of analytical and spectral data a tetrahedral geometry around Mn(II) and an octahedral geometry for Mo(VI) have been proposed. The antimicrobial activity results indicated that the complexes showed promising antibacterial and antifungal activities. The results suggested that the ligand (L^1H) is most effective in reducing fertility and addition of manganese(II) and dioxomolybdenum(VI) moiety to this ligand enhanced its activity.

Acknowledgments. One of the authors Anita Kumari is thankful to UGC, New Delhi for financial assistance through Grant No. 854/148 29/03/11. And the publication cost of this paper was supported by the Korean Chemical Society.

References

1. Kulkarni, A. K.; Avaji, P. G.; Bagihalli, G. B.; Badami, P. S.; Patil, S. A. *J. Coord. Chem*. **2009**, *62*, 481.
2. Nejo, A. A.; Kolawole, G. A.; Nejo, A. O. *J. of Coord. Chem.* **2010**, *63*, 4398.
3. Mohamed, G. G.; Omar, M. M.; Hindy, A. M. *Turk. J. Chem.* **2006**, *30*, 361.
4. Biyala, M. K.; Singh, R. V..; Phosphorus, Sulfur Silicon Relat. Elements **2006**, *181*, 1477.
5. Chandra, S.; Tyagi, M. *J. Serb. Chem. Soc.* **2008**, *73*, 727.
6. Abdullah, M. A.; Salman, A. K. *Molecules* **2010**, *15*, 4784.
7. Konstantinovic, S. S.; Randovanovic, B. C.; Sovilj, S. P.; Stanojevic, S. *J. Serb. Chem. Soc.* **2008**, *73*, 7.
8. Gaikwad, S.; Gaikwad, C. *J. Chem. Pharm. Res.* **2010**, *2*, 106.
9. Pingaew, R.; Prachayasittikul, S.; Ruchirawat, S. *Molecules* **2010**, *15*, 988.
10. Khan, S. A.; Yusuf, M. *European Journal of Medicinal Chemistry* **2009**, *44*, 2270.
11. Yadav, S.; Singh, R. V. *Spectrochimica Acta Part A* **2011**, *78*, 298.
12. Akbar, A. M.; Mirza A. H.; Voo, C. W.; Tan, A. L.; Bernhardt, P. V. *Polyhedron* **2003**, *22*, 3433.
13. Biyala, M. K.; Fahmi, N.; Singh, R. V. *Main Group Met. Chem.* **2004**, *27*, 181.
14. Sireesha, B.; Devi, S.; Refeez, M.; Ram Reddy, M. G. *J. Indian Chem. Soc.* **1999**, *76*, 498.
15. Yadav, L. D. S.; Singh, S. *Indian J. Chem.* **2001**, *40 B*, 440.
16. Riopedre, G. G.; Garcıa, M. I. F.; Noya, A. M. G.; Fernandez, M. A. V.; Bermejo, M. R.; Maneiro, M. *Phys. Chem. Chem. Phys*. **2011**, *13*, 18069.
17. Nigam, S.; Patel, M. M.; Ray, A. *Journal of Physics and Chemistry of Solids* **2000**, *61*, 1389.
18. Kasuga, N. C.; Sekino, K.; Koumo, C. *J. Inog. Biochem.* **2001**, *84*, 55.
19. Reddy, D. N.; Reddy, K. V. *Momona Ethiopian Journal of Science* **2012**, *4*, 70.
20. Karthikeyan, J.; Parameshwara, P.; Shetty, A. N. *Environ. Monit. Assess* **2011**, *173*, 569.
21. Nanda, K. K.; Das, R.; Venkatsubramanian, K. *Dalton. Trans.* **1993**, 2515.
22. Biyala, M. K.; Fahmi, N.; Singh, R. V. *Main Group Met. Chem.* **2004**, *27*, 3.
23. Jadon, S. C. S.; Fahmi, N.; Singh, R. V. *Synth. React. Inorg. Met. Chem.* **1995**, *25*, 1345.
24. Garg, R.; Saini, M. K.; Fahmi, N.; Singh, R. V. *Indian J. Chem.* **2005**, *44A*, 2433.
25. Biyala, M. K.; Fahmi, N.; Singh, R. V. *Indian J. Chem* **2004**, *43A*, 1662.
26. Sharma, K.; Joshi, S. C.; Singh, R. V. *Metal Based Drug* **2000**, *7*, 105.
27. Garg, R.; Fahmi, N.; Singh, R. V. *Russian J. Coord. Chem.* **2008**, *34*, 198.
28. Garg, R.; Saini, M. K.; Fahmi, N.; Singh, R. V. *Trans. Met. Chem.* **2006**, *31*, 362.
29. Saxena, C.; Bhardwaj, N. C.; Singh, D.; Singh, R. V. *Synth. React. Inorg. Met. Org. Chem.* **1993**, *23*, 1391.
30. Tweedy, B. G. *Phytopathology* **1964**, *55*, 910.
31. Mohamad, G. G.; Omar, M. M.; Hindy, A. M. M. *Spectrochimica Acta Part A* **2005**, *62*, 1140.
32. Cooper, R. L.; Goldman, J. M.; Stoper, T. E. *Toxicol. Indus. Health* **1999**, *15*, 25.
33. Dave, S.; Chaudhary, A.; Agarwal, M.; Joshi, S. C.; Singh, R. V. *Indian J. Chem.* **2003**, *42A*, 268.