Novel 8-Coordinate *cis*-MoO_2(VI) Complexes with Some 4-Aminoantipyrine Schiff Base Derivatives

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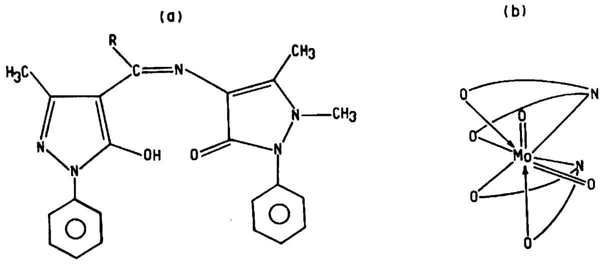
The synthesis and characterisation of some 8-coordinate *cis*-dioxomolybdenum(VI) complexes of Schiff bases derived from 4-aminoantipyrine and 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one, 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one, and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one are reported. Spectroscopic and other analytical data reveal that these Schiff bases behave as monobasic tridentate ligands and react with $[MoO_2(acac)_2]$ in 2 : 1 ratio to give diamagnetic molybdenum(VI) mononuclear complexes having the general formula *cis*-$MoO_2(L)_2$ (L=Schiff base). These complexes were characterised by elemental analysis, molar conductance, IR, UV-vis, ^{1}H NMR, and cyclic voltammetry.

In continuation of our work to synthesise some *cis*-dioxomolybdenum(VI) Schiff base complexes,[1,2] we report here the synthesis and characterisation of some 8-coordinate *cis*-dioxomolybdenum(VI) Schiff base complexes derived from 4-aminoantipyrine. It has been reported that the Schiff base ligands derived from 4-aminoantipyrine and certain carbonyl compounds behave either as[3] didentate or tridentate ligands,[4—6] coordinating with the metal center in two ways depending upon the nature of the metal ion and the type of substituent.[3] Several metal complexes of the Schiff bases derived from 4-aminoantipyrine are reported[3—7] but so far no work has been reported on 8-coordinate *cis*-dioxomolybdenum(VI) complexes with Schiff bases derived from 4-aminoantipyrine. In this paper we report the synthesis and characterisation of some *cis*-dioxomolybdenum(VI) Schiff base complexes derived from 4-aminoantipyrine and 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (AMPHP=Hamphp), 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one (MPHPP=Hmphpp), and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPHP=Hbmphp). These Schiff bases form mononuclear molybdenum(VI) complexes having the general formula *cis*-$MoO_2(L)_2$, where L=Schiff base namely *N*-[1-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-4-pyrazolyl)ethylidene]aminoantipyrine (AAMPHP=Haamphp), *N*-[1-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-4-pyrazolyl)propylidene]-aminoantipyrine) (PAMPHP=Hpamphp), and *N*-[1-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-4-pyrazolyl)-benzylidene]aminoantipyrine (BAMPHP=Hbamphp) (Chart 1). Elemental analysis, molar conductance, spectroscopic (IR, UV-vis and ^{1}H NMR), and cyclic voltammetry data are given for all the complexes.



LIGAND	R
AAMPHP	$-CH_3$
PAMPHP	$-C_2H_5$
BAMPHP	$-C_6H_5$

Chart 1.

Experimental

Materials. All reagents required for compound preparation were of analytical grade. 3-Methyl-1-phenyl-2-pyrazolin-5-one was procured from Johnsons Chemical Company, Bombay, India. Ammonium molybdate, acetylacetone, 4-aminoantipyrine, acetyl chloride, propionyl chloride, and benzoyl chloride were procured from BDH, UK.

Synthesis of the Ligands. 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPHP=Hbmphp) was prepared according to the reported method[8] using 3-methyl-1-phenyl-2-pyrazolin-5-one and benzoyl chloride. Following the same procedure, 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (AMPHP=Hamphp) and 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one (MPHPP=Hmphpp) were prepared using acetyl chloride and propionyl chloride, respectively.

The Schiff base ligand BAMPHP (Hbamphp) was prepared by taking 1:1 ethanolic solution of BMPHP and 4-aminoantipyrine and refluxing the resulting solution for 5—6 h. The reaction mixture was then poured into distilled water (250 ml) when a yellow precipitate was obtained which was filtered, washed several times with water and then dried in vacuo. Yield: 70—75%. The ligands AAMPHP and PAMPHP could not be isolated from their respective reaction solutions. Hence their ligand solutions were used directly for metal complex synthesis.

Synthesis of the Complexes. [MoO$_2$(acac)$_2$] was prepared according to the reported method.[9] The *cis*-dioxomolybdenum(VI) Schiff base complexes [MoO$_2$(aamphp)$_2$] (**1**) and [MoO$_2$(pamphp)$_2$] (**2**) were prepared by taking ethanolic solutions of 0.02 mol of AMPHP and MPHPP each respectively and adding it to the hot ethanolic solution of 0.02 mol of 4-aminoantipyrine and the resulting solution was refluxed for 5—6 h. Then, to it was added 0.01 mol [MoO$_2$(acac)$_2$] in ethanol and the reaction mixture was refluxed for 8—10 h when the color of the solution changes to dark green. Some insoluble material was obtained which was filtered off. The volume of the filtrate was reduced (10 ml) by concentrating on a water bath. Then excess of diethyl ether was added and again some material was obtained which was filtered off and the filtrate was left overnight when yellowish-green complexes *cis*-[MoO$_2$(aamphp)$_2$] and [MoO$_2$(pamphp)$_2$] were obtained. *cis*-[MoO$_2$(bamphp)$_2$] (**3**) was obtained by refluxing 2:1 ethanolic solutions of BAMPHP ligand and [MoO$_2$(acac)$_2$] for 8—10 h. The procedure for obtaining this complex is similar to that described above for [MoO$_2$(aamphp)$_2$] and [MoO$_2$(pamphp)$_2$]. Yield 60—65%. The analysis of the insoluble material was done but it could not be identified.

Physical Measurements. Microanalyses (C,H,N) of the complexes were done on a Carlo Erba 1106 elemental analyser. Solution electrical conductivity was measured at 298 K using Digisun Electronics Conductivity Bridge. IR spectra were recorded at 298 K on a FT-IR (Bio-Rad) Spectrometer as Nujol mulls/KBr pellets. Electronic spectra were recorded on a Shimadzu model UV-160 Spectrophotometer. The ^{1}H NMR spectra were recorded at 298 K on JEOL FX-100 FT-NMR spectrometer. Cyclic voltammetry traces of the complexes were recorded on a Princeton Applied Research Model 384 B Polarographic Analyser.

Results and Discussion

The analytical data (Table 1) show that the reaction of [MoO$_2$(acac)$_2$] with the Schiff base ligands aamphp, pamphp, and bamphp gave 2:1 (ligand: metal) 8-coordinate metal complexes. These complexes are soluble in ethanol, methanol, acetone, DMF, and dimethylsulfoxide. The conductance data (Table 1) of the complexes **1**—**3**, indicate that they are non-electrolytes.

IR Spectra. In the IR spectrum of the ligand BAMPHP (Table 1), bands were observed at 3500, 1645, 1625, and 1155 cm^{-1} due to ν(OH), ν(C=O), ν(C=N), and ν(C–O), respectively. The IR spectra of the complexes **1**—**3** (Table 1) exhibited bands in the region 892—907 and 915—951 cm^{-1} due to ν_{as} (O=Mo=O) and ν_s (O=Mo=O) respectively[1,2,10,11] indicating the O=Mo=O species to be in the cis-form. In complexes [MoO$_2$(aamphp)$_2$] **1** and [MoO$_2$(pamphp)$_2$] **2**, the absence of band at 3500 cm^{-1} and the presence of a band at 1174 cm^{-1} due to ν(C–O) indicate deprotonation and coordination of enolic oxygen to the metal center.[1] The presence of bands at 1635 and 1615 cm^{-1} due to ν(C=O) of pyrazolone ring of antipyrine and ν(C=N), respectively, suggest the coordination of carbonyl oxygen of pyrazolone ring and azomethine nitrogen to the metal center. In the IR spectrum of complex [MoO$_2$(bamphp)$_2$], **3**, no band was observed at 3500 cm^{-1} indicating the deprotonation of OH in the ligand BAMPHP. The bands observed at 1634 and 1614 cm^{-1} due to ν(C=O) and ν(C=N), respectively, showed lowering in frequency as compared to free ligand, indicating the coordination of carbonyl oxygen of pyrazolone ring of antipyrine and azomethine nitrogen to the metal center.[3,5,6] The coordination of enolic oxygen to the metal center is indicated by the increase in ν(C–O) (1174 cm^{-1}) as compared to that of free ligand.[1,2,12]

Electronic Spectra. The electronic spectra of the complexes **1**—**3** (Table 2) were studied in the concentration range 1×10^{-4}—1×10^{-3} M in ethanol (1 M=1 mol dm^{-3}). In addition to the ligand based peaks, a broad band was observed in the region 448—484 nm in the complexes which may be due to ligand to metal charge transfer transition (LMCT). As is evident from Table 2, the λ_{max} and for this LMCT band varied with change in substituent on the azomethine carbon, the LMCT requires more energy in the order **3**>**2**>**1**. This may be due to more electron donating ability of –CH$_3$ group (in complex **1**) as compared to –C$_2$H$_5$ group (in complex **2**) and –C$_6$H$_5$ group (in complex **3**) on azomethine carbon, thus making this LMCT easier in the case of complexes **1** and **2** as compared to **3**. An additional broad band of low intensity was also observed in the region 580—676 nm. Although the band appearing at such a low energy is unexpected for 4d^0 molybdenum(VI) complexes but it was also observed in our earlier reported *cis*-MoO$_2$ Schiff base complexes[1,2] and also in the case of Schiff base complex *cis*-MoO$_2$ (3-OCH$_3$-Saltrien).[13]

Proton NMR Spectra. The mononuclear *cis*-MoO$_2$(VI) complexes were found to be diamagnetic by ^{1}H NMR spectroscopy. The chemical shifts observed in the ^{1}H NMR spectra of the Schiff base ligand BAMPHP and the complexes **1**—**3** are listed in Table 2. In the spectrum of the ligand BAMPHP a peak was observed at $\delta=12.4$ which may be due to –OH proton, indicating its existence in enolic form. In the spectrum of the complex **3** of Schiff base ligand BAMPHP the peak corresponding to –OH proton disappears, indicating deprotonation and coordination through enolic oxygen to the metal center. Further, in the spectra of the complexes **1** and **2** of Schiff base ligands AAMPHP and PAMPHP the absence of peaks corresponding to –OH proton and –CH proton suggest coordination through enolic oxygen to the metal center in complexes **1** and **2**

Table 1. Melting Point, Molar Conductance, Elemental Analysis and IR Data for Ligand BAMPHP and *cis*-MoO_2 Complexes **1**—**3**

Ligand/complex	MP	Ω^{-1} a)	Elemental analysis (%) b)			IR (cm^{-1}) c)			
	°C		C	H	N	Mo=O	C=N	C–O	C=O d)
BAMPHP	180	—	72.30	5.35	14.90	—	1625	1155	1645
($C_{28}H_{25}N_5O_2$)			(72.57)	(5.39)	(15.11)				
1. [MoO_2(aamphp)$_2$]	135	6	59.40	4.72	15.10	890,915	1617	1174	1636
($MoC_{46}H_{44}N_{10}O_6$)			(59.48)	(4.74)	(15.08)				
2. [MoO_2(pamphp)$_2$]	130	5	59.98	5.00	14.60	892,915	1615	1174	1635
($MoC_{48}H_{48}N_{10}O_6$)			(60.25)	(5.02)	(15.08)				
3. [MoO_2(bamphp)$_2$]	120	6	64.00	4.61	13.25	907,951	1614	1174	1634
($MoC_{56}H_{48}N_{10}O_6$)			(63.80)	(4.56)	(13.30)				

a) Molar conductance in ethanol. b) Found (Calcd). c) In KBr pellets at 298 K. d) Carbonyl on pyrazolone ring of antipyrine.

Table 2. UV-vis, ^{1}H NMR and Cyclic Voltammetric Data for the Ligand BAMPHP and Complexes **1**—**3**

Ligand/complex	λ_{max} (nm) e)	^{1}H NMR f)	E_{pc} g)	E_{pa}
	(ε, M cm^{-1})	(δ/ppm)	V	
BAMPHP	397	12.4 (s, 1H, -OH)	—	—
		7.12—8.18 (m, 15H, aromatic)		
		3.30 (s, 3H, N-CH_3)		
		2.96 (s, 3H, =C-CH_3)		
		1.49 (s, 3H, -CH_3)		
1. [MoO_2(aamphp)$_2$]	484 (2600)	7.20—7.95 (m, 20H, aromatic)	−1.34	—
	600 (470)	3.58 (s, 6H, -N-CH_3)		
		2.70 (s, 6H, =C-CH_3)		
2. [MoO_2(pamphp)$_2$]	470 (2400)	7.40—8.02 (m, 20H, aromatic)	−1.26	—
	580 (400)	3.59 (s, 6H, -N-CH_3)		
		2.44—2.70 (q, 4H, -CH_2)		
		2.37 (s, 6H, =C-CH_3)		
		1.48 (s, 6H, -CH_3)		
		1.09—1.15 (t, 6H, -CH_3)		
3. [MoO_2(bamphp)$_2$]	448 (1220)	6.88—8.02 (m, 30H, aromatic)	−1.16	−0.82
	676 (100)	3.33 (s, 6H, -N-CH_3)		
		2.70 (s, 6H, =C-CH_3)		
		1.49 (s, 6H, -CH_3)		

e) Electronic spectral data in ethanol. f) The solvent is acetone-d_6. g) Pt working electrode, Ag/AgCl reference electrode, Bu_4NPF_6 supporting electrolyte in DMF solvent.

also.

Cyclic Voltammetry. The cyclic voltammograms (scan range +1.2 to −1.5 V vs. Ag/AgCl) for the *cis*-MoO_2 complexes **1**—**3** in DMF (Table 2) consists of one reduction wave in the region −1.16 to −1.34 V, which is attributed to Mo^{VI}/Mo^{V} reduction.[1,2,14,15] This reduction was irreversible for complexes **1** and **2** and quasireversible in the case of complex **3** (CV of **3** exhibited scan rate dependent reduction potential, $E_{pc}=-1.16$ V and $E_{pa}=-0.82$ V). Further in the case of complexes **1** and **2**, a reoxidation wave was seen at anodic potentials, −0.68 and −0.55 V, respectively. However, when the scan was reversed at a potential relatively positive to the reduction waves at −1.34 and −1.26 V these oxidation waves at −0.68 and −0.55 V were not seen, indicating that they appear as a consequence of the observed reduction waves. In complex **3** this particular reoxidation wave was absent.

As is evident from Table 2, the E_{pc} increased in the order **1**>**2**>**3**. The reduction of Mo^{VI}/Mo^{V} is more facile in the complex **3**. This may be due to the effect of substituent on azomethine carbon. In case of complex **3**, the phenyl ring attached to azomethine carbon appears to delocalize the electron density effectively from the metal center causing its easier reduction[16] and also quasireversibility. In the complexes **1** and **2**, it appears that the added electron during $Mo^{VI}\rightarrow Mo^{V}$ reduction is located on one of the Mo=O bonds (due to absence of delocalizing groups on azomethine carbon) and thus the reduced species participates in some side reaction for which the oxidation waves were seen at −0.68 and −0.55 V.

Thus on the basis of the above data, it is evident that these Schiff base ligands behave as monobasic tridentate, coordinating to the metal center through carbonyl oxygen of pyrazolone ring of antipyrine, azomethine nitrogen and enolic oxygen. Two molecules of ligand coordinate to the single metal center, forming 8-coordinate *cis*-dioxomolybdenum(VI) complexes. In general, the structure of the tridentate Schiff base ligands and their *cis*-dioxomolybdenum(VI) complexes (**1**—**3**) can be represented as shown in Chart 1 (**a**) and (**b**) respectively.

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