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Synthesis, Spectral and Antibacterial Studies of Dioxotungsten(VI) Complexes of 2,3-Dimethyl-1-phenyl-4-(2-hydroxy-4-methoxyphenylazo)pyrazol-5-one

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Some novel dioxotungsten(VI) complexes of the ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-4-methoxy-phenylazo)pyrazol-5-one (methoxyphenolazoanti-pyrine, MOPAAP) having the compositions $[WO_2LXCl]$ (X = Cl, NO_3, NCS or ClO_4 and L = MOPAAP) have been synthesized and characterized by elemental analysis, molar conductance, IR and ^1H NMR spectral studies. The thermal behaviour of one of the complexes has also been examined. The ligand and one of its complexes were screened for their possible antibacterial activity against gram positive and gram negative bacteria. The X-ray powder diffraction patterns of one of the complexes has also been examined. The complex was found to be orthorhombic with the unit cell dimensions such as a = 5.4467 Å, b = 12.1792 Å and c = 17.2240 Å and the lattice constants A = 0.02195, B = 0.004 and C = 0.00204. The ligand behaves as neutral bidentate. The complexes are found to be non-electrolytes with octahedral geometry.

Key Words: Synthesis, Dioxotungsten(VI), Complexes, Methoxy-phenolazoantipyrine.

INTRODUCTION

High - valent oxotungsten complexes have attracted attention owing to their roles in various catalytic processes such as alcohol oxidation[1], olefin epoxidation[2] and olefin metathesis[3]. It is believed that most of these organic transformations and biological processes involve oxygen atom transfer (OAT) reactions as one of the crucial steps[4]. Numerous dioxomolybdenum (VI) complexes with a variety of supporting ligands have been prepared and studied[5], whereas the chemistry of analogous dioxotungsten (VI) complexes is still inadequately studied[6,7]. One reason for the relatively low number of known dioxotungsten (VI) complexes is the poor availability of suitable starting materials[8], since typical synthetic routes start from soluble derivatives of WO_2Cl_2.

In view of the importance of dioxotungsten (VI) complexes, we have isolated and characterized some new complexes of potential multidentate

ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-4-methoxyphenylazo)pyrazol-5-one [methoxyphenolazoantipyrine (MOPAAP)] derived from biologically active molecule, 4-aminoantipyrine.

EXPERIMENTAL

Tungsten (VI) chloride (Acros Organics, Belgium), 4-aminoantipyrine (Fluka, Switzerland) and 3-methoxy phenol (Alfa Aesar - Lancaster) were used as supplied. All other chemicals used were of AR grade.

The ligand 2,3-dimethyl-1-phenyl-4-(2-hydroxy-4-methoxyphenylazo)-pyrazol -5-one (methoxyphenolazoantipyrine, MOPAAP) was synthesized from 4-aminoantipyrine and 3-methoxy phenol by diazotization and coupling as described in literature[9] (Fig.1).

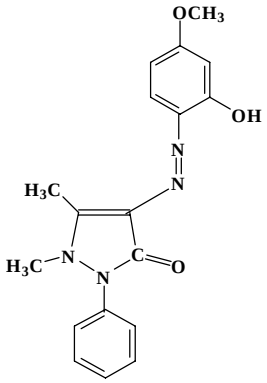


Fig.1 Methoxy phenolazoantipyrine (MOPAAP)

Complexes were prepared by refluxing methanolic solutions of WCl_6 and the ligand in 1 : 1 molar ratio for 5-6 h. The solid complex obtained by volume reduction was suction filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*. The following general method was adopted for the preparation of other complexes.

By refluxing methanolic solutions of WCl_6 containing 2-3 drops of $HClO_4$/*ca.* 0.5 g of $LiNO_3$/*ca.* 0.5 g NH_4NCS as the case may be and the ligand in 1 : 1 molar ratio for 5-6 h. The solid complex obtained by volume reduction was suction filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo*.

The tungsten contents of the complex was determined gravimetrically as *bis*(8-hydroxy quinolinato) dioxotungsten (VI) after decomposing the complex with conc.nitric acid and precipitating with 8-hydroxyquinoline[10]. The chloride contents was estimated by Volhard's method[11]. The perchlorate content was estimated by Kurz's method[12] and sulphur present in the thiocyanate was estimated as barium sulphate[11]. Molar conductance of the complexes were determined by Elico conductivity bridge type CM 82T

with a dip type conductivity cell by using 10^{-3} M solutions in methanol, acetonitrile and nitrobenzene. The infrared spectra of the ligand and the complexes were recorded in the range of 4000-400 cm^{-1} on a Perkin-Elmer 347 spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded in $CDCl_3$ on a 300 MHz FT NMR instrument using TMS as reference. X-ray powder diffraction patterns of the complexes were recorded using Philips PW 1710 diffractometer. TG and DTG curves of the complex was recorded on Mettler thermal analyzer model TA 3000 at a heating rate of 10°C/min from ambient to 750°C. The antibacterial activity of the ligand and one of its complexes were tested by disc diffusion method using two bacteria, *viz.*, *Staphylococcus aureus* and *Escherichia coli*.

RESULTS AND DISCUSSION

The complexes are non-hygroscopic, stable and crystalline solids. They are soluble in methanol and ethanol but insoluble in benzene and ether. Analytical data (Table-1) are in agreement with the composition proposed or the complexes. The electrical conductivity of the complexes in nitrobenzene, acetonitrile and methanol indicate that the complexes are non-electrolytes[13].

TABLE-1
ANALYTICAL AND CONDUCTIVITY DATA OF COMPLEXES

Complex	Analysis : Found (Calculated) %					Molar conductance ($\Omega^{-1}cm^2$ mol)		
	C	H	N	S	W	$C_6H_5NO_2$	CH_3CN	CH_3OH
$[WO_2(MOPAAP)Cl_2]$	34.25 (34.57)	2.53 (2.88)	8.75 (8.96)	-	29.05 (29.43)	5.8	33.7	44.1
$[WO_2(MOPAAP)NCSCl]$	35.01 (35.22)	2.65 (2.78)	10.95 (10.81)	5.05 (4.94)	27.50 (28.40)	4.2	20.5	41.2
$[WO_2(MOPAAP)NO_3Cl]$	33.53 (33.66)	2.73 (2.76)	10.52 (10.75)	-	27.97 (28.20)	3.4	39.2	27.4
$[WO_2(MOPAAP)ClO_4Cl]$	31.45 (31.36)	2.75 (2.60)	8.75 (8.13)	-	27.05 (26.69)	9.0	53.9	32.3

The ^1H NMR spectrum[14] of the ligand shows three singlets which corresponds to the methyl protons. >C - CH_3 group of pyrazolone ring appears as a sharp singlet in the region δ 2.62. N-CH_3 signal is observed as another singlet in the region δ(3.31- 3.34) and O-CH_3 signal is observed at δ(3.84 - 4.00). The signal due to the five aromatic protons of the antipyrine phenyl ring appeared as multiplet between δ 7.5 - 7.8 and that due to the protons of the phenol ring is observed as a multiplet between δ 6.9 - 7.3. The signal due to the phenolic -OH proton appeared at δ(9.72- 9.83).

The infrared spectra of the ligand exhibits a broad medium intensity band *ca.* 2900 cm^{-1} assignable to hydrogen bonded OH group[15]. This band is absent in the spectra of all the complexes. Instead a new broad band of medium intensity appears *ca.* 3400 cm^{-1} indicating the presence of free OH

group and its non involvement in complexation. The ν(C = O) occurring at 1639 cm^{-1} in the ligand spectrum is shifted to a lower frequency *ca.* 1580 cm^{-1} in the spectra of the complex, showing the participation of the C=O group in coordination. The azo group vibration (N=N) in the free ligand at 1490 cm^{-1} is also red shifted to 1444 cm^{-1} in all complexes, confirming the coordination through one of the azo group nitrogens. Thus the ligand exhibits neutral bidentate behaviour in all the complexes, coordinating through the >C = O and the - N = N - groups only[16]. For the perchlorate complex, ν_3 and ν_4 appear as strong and medium intensity bands *ca.* 630 and 1113 cm^{-1}, respectively indicating a monodentately coordinated perchlorate group[17]. IR spectra of the nitrate complex[18] are suggestive of monodentately coordinated nitrate group ν_4 *ca.* 1527, ν_1 *ca.* 1381 cm^{-1}. The N-coordinated[19,20] nature of the thiocyanate group is indicated by the ν(C-N) (*ca.* 2056 cm^{-1}), ν(C-S) (*ca.* 763 cm^{-1}) and ν(NCS) (*ca.* 509 cm^{-1}). The infrared spectra of all the complexes exhibit bands in the region 880-860 and 958-935 cm^{-1} due to the ν_{as}(O = W = O) and ν_s(O = W = O) modes respectively, indicating the presence of *cis* WO_2 structure[21].

The complex $[WO_2(MOPAAP)Cl_2]$ was found to be orthorhombic by X-ray powder diffraction method and was indexed using Hesse and Lipson's procedure[22]. The lattice constants were found to be A = 0.02195, B = 0.004 and C = 0.00204 and unit cell dimensions a = 5.4467 Å, b = 12.1792 Å and c = 17.2240 Å.

The ligand MOPAAP and $[WO_2(MOPAAP)Cl_2]$ were screened for their possible antibacterial activity against the gram positive bacteria *Staphylococcus aureus* ATCC 25923 and the gram negative bacteria *Escherichia coli* ATCC 25922 by disc diffusion method[23] at different concentrations using gentamicin as positive control and absolute methanol as negative control. The test results (Table- 2 and 3) show that the ligand MOPAAP exhibited antimicrobial activity against gram positive *S. aureus* ATCC 25923 from 50 μg/disc onwards and as the concentration of the sample per disc increased, the zone of inhibition also increased. At 1 mg/disc, the zone of inhibition was 4 mm diameter. But the ligand MOPAAP did not exhibit any antimicrobial property against gram negative *E-coli* ATCC 25922 under test conditions. The complex $[WO_2(MOPAAP)Cl_2]$ did not exhibit any antimicrobial activity against gram negative *E-coli* ATCC 25922 and gram positive *S. aureus* ATCC 25923 under the test conditions.

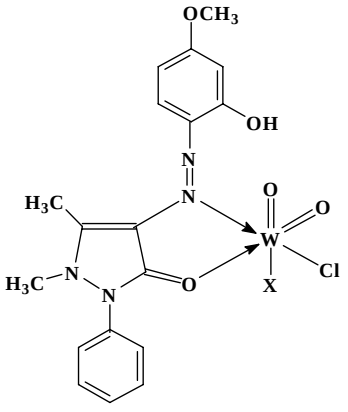
Thermogravimetric curves of the complex $[WO_2(MOPAAP)Cl_2]$ was recorded in air at a heating rate of 10°C/min from room temperature to 750°C. The complex undergoes a two stage decomposition as indicated by the DTG peaks at 221 and 424°C. A plateau up to 213°C in the TG curve indicates that the complex is stable up to this temperature and the absence of coordinated water or other solvent molecules. The first stage decompo-

sition begins at 213°C and gets completed at 225°C. The complex shows a weight loss of 11.8% at 225°C due to the elimination of two chlorine atoms. In the second stage decomposition a plateau upto 406°C and after that a mass loss occurs up to 424°C, which corresponds to the formation of metal oxide (WO_3)[24,25].

TABLE-2
TEST RESULTS OF ANTIBACTERIAL ACTIVITY OF MOPAAP

Test Sample		Zone of inhibition	
		E. coli ATCC 25922	*S. aureus* ATCC 25923
50 µg	Unit 01	Nil	<1 mm
	Unit 02	Nil	<1 mm
	Unit 03	Nil	<1 mm
100 µg	Unit 01	Nil	<1 mm
	Unit 02	Nil	<1 mm
	Unit 03	Nil	<1 mm
200 µg	Unit 01	Nil	1 mm
	Unit 02	Nil	1 mm
	Unit 03	Nil	1 mm
400 µg	Unit 01	Nil	2 mm
	Unit 02	Nil	2 mm
	Unit 03	Nil	2 mm
1 mg	Unit 01	Nil	4 mm
	Unit 02	Nil	4 mm
	Unit 03	Nil	3 mm

On the basis of the above physico-chemical studies, an octahedral geometry is suggested for all the complexes (Fig. 2).



(X = Cl, NCS, NO_3, ClO_3)

Fig. 2

TABLE-3
TEST RESULTS OF ANTIBACTERIAL ACTIVITY OF $[WO_2(MOPAAP)Cl_2]$

Test Sample		Zone of inhibition	
		E. coli ATCC 25922	*S. aureus* ATCC 25923
50 μg	Unit 01	Nil	Nil
	Unit 02	Nil	Nil
	Unit 03	Nil	Nil
100 μg	Unit 01	Nil	Nil
	Unit 02	Nil	Nil
	Unit 03	Nil	Nil
200 μg	Unit 01	Nil	Nil
	Unit 02	Nil	Nil
	Unit 03	Nil	Nil
400 μg	Unit 01	Nil	Nil
	Unit 02	Nil	Nil
	Unit 03	Nil	Nil
1 mg	Unit 01	Nil	Nil
	Unit 02	Nil	Nil
	Unit 03	Nil	Nil
Negative control		Nil	Nil
Gentamicin 10 mcg		19 mm	24 mm

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