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Synthesis and Characterization of Dioxotungsten(VI) Complexes of Azodyes Derived from 1-Phenyl-2,3-dimethyl-4-Amino-5-Pyrazolone

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Some novel dioxotungsten(VI) complexes of general formula [WO_2LXCl] (X = Cl, NO_3, NCS or ClO_4 and L = 1-phenyl-2,3-dimethyl-4-(2-hydroxy naphthylazo)-5-pyrazolone or 1-phenyl-2,3-dimethyl-4-(2,4-dihydroxy phenylazo)-5-pyrazolone have been synthesized and characterized by elemental analysis, IR and NMR spectral studies. The thermal behaviour of one of the complexes has also been examined. Ligands and thier few metal complexes were screened for their antibacterial activities against gram positive and gram negative bacteria. The molar conductance values of the complexes indicate that the complexes are non-electrolytes.

Key Words: Dioxotungsten(VI), Complexes, Azo dyes.

INTRODUCTION

Tungsten is the only element in the third transition series known to have biological functions[1]. Not only does it sometimes occur in enzymes that usually contain molybdenum, but also there are some enzymes that are known only with tungsten. Only a few reports are available on metalloenzyme models of tungsten. Dioxotungsten(VI) complexes with Schiff bases are limited. They are mostly organometallics and a few studies dealing with dioxotungsten(VI) complexes of chelating molecules have been reported[2]. The main reason for the lack of dioxotungsten(VI) is the non-availability of a suitable starting material. Yamanouchi *et al.*[3, 4] have used WO_2Cl_2 or WO_2Cl_4 as a starting material, while Syamal *et al.*[5] have tried the reactivity of Schiff bases in aqueous medium with limited success. Recently, Yu and Holm[6] have successfully used [$WO_2(acac)_2$], (where acac = H-acetyl acetone) to prepare dioxotungsten(VI) complexes. In view of the above, some ligands derived from 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone (4-aminoantipyrine) have been chosen and attempts made to synthesize and charcterize their dioxotungsten(VI) complexes such as 1-phenyl-2,3-dimethyl 4-(2-hydroxy naphthylazo)-5-pyrazolone (NAAP) and 1-phenyl-2,3-dimethyl-4-(2,4-dihydroxy phenylazo)-5-pyrazolone (RAAP).

EXPERIMENTAL

WCl_6 (Acros Organics, Belgium) and 4-aminoantipyrine (Fluka, Switzerland) were used as such. All other chemicals were of AR grade.

Preparation of ligands NAAP and RAAP: The ligand 1-phenyl-2,3-dimethyl-4-(2-hydroxy naphthylazo)-5-pyrazolone (naphthyl azoantipyrine, NAAP) was synthesized from 4-amino antiyprine and β-naphthol and the ligand 1-phenyl-2,3-dimethyl-4-(2,4-dihydroxy phenylazo)-5-pyrazolone (Resorcinol azoantipyrine, RAAP) was synthesized from 4-amino antipyrine and resorcinol by diazotization and coupling as described in literature[7] [Fig. 1 (1) and 1 (2)].

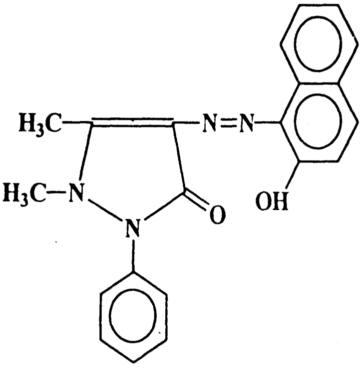

Fig. 1 (1). 1-Phenyl-2,3-dimethyl-4-(2-hydroxy naphthylazo)-5-pyrazolone (NAAP)

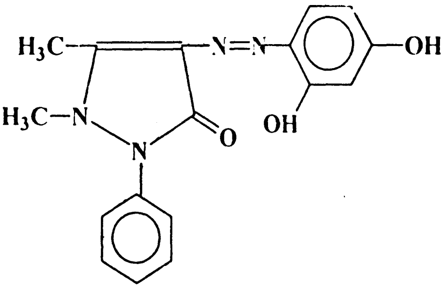

Fig. 1 (2). 1-Phenyl-2,3-dimethyl-4-(2,4-dihydroxy naphthylazo)-5-pyrazolone (RAAP)

Preparation of the Complexes

A methanolic solution of WCl_6 (2 mmol) was mixed with ligand (2 mmol) in 1 : 1 methanol-chloroform mixture and refluxed for *ca.* 4–5 h. The solid separated on concentrating the solution, 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.

Methanolic solutions of WCl_6 (2 mmol), containing 2–3 drops of $HClO_4$/ *ca.* 0.5 g of $LiNO_3$/ *ca.* 0.5 g of NH_4NCS as the case may be were mixed with the ligand (2 mmol) solution in 1 : 1 mixture of methanol : chloroform and refluxed for *ca.* 4 h. The solid separated on concentrating the solution, was suction filtered, washed with aqueous methanol and dried over P_4O_{10} *in vacuo.*

The tungsten content[8] of the complexes was determined by treating the complex with conc. HNO_3 and then igniting to WO_2 at 500°C while chlorine was determined by Volhard's method[9]. Perchlorate in the complexes was determined by Kurz's method[10] and sulphur present in the thiocyanate complexes was estimated as barium sulphate[9].

RESULTS AND DISCUSSION

The reaction of WCl_6 with NAAP and RAAP gave complexes of the general composition $[WO_2LXCl]$ (X = Cl, NO_3, NCS or ClO_4 and L = NAAP or RAAP). The ligands and their metal complexes were characterized by elemental analysis, conductivity measurements, infrared and NMR spectra, thermal and biological studies. The analytical data of these complexes are given in Table-1. The electrical conductivity (Table-1) of these complexes in nitrobenzene, methnaol and acetonitrile indicate that the complexes are essentially non-electrolytes.

In the IR spectrum, the free ligands exhibit a broad medium intensity band *ca.* 2900 cm^{-1}, assignable to the hydrogen bonded OH group[11, 12]. This band disappears on complexation in all the cases. A new band *ca.* 3400 cm^{-1} appears in all the complexes, suggesting the non-participation of the OH group in coordination. Evidently, the hydrogen bond is broken during complexation. In all the complexes, the ligands NAAP and RAAP act as neutral chelating agents[11, 12].

The $\nu(C{=}O)$ observed at 1675 cm^{-1} in the ligand spectra are shifted to *ca.* 1629 and 1608 cm^{-1} in the spectra of the complexes of NAAP and RAAP, respectively showing the participation of the (C=O) group in coordination. The azo group vibration $\nu(N{=}N)$ in the ligands NAAP and RAAP at 1490 and 1500 respectively show slight downward shift by *ca.* 20 cm^{-1} in all the complexes, suggesting the participation of this group in complexation. Thus, the ligands NAAP and RAAP behave as neutral bidentate chelating agents in these complexes. In the spectra of $[WO_2(NAAP)(ClO_4)Cl]$ and $[WO_2(RAAP)$- $(ClO_4)Cl]$, two bands (split bands) observed at *ca.* 1114 and *ca.* 1094 cm^{-1} assigned to ν_4 and ν_1 and another set of split bands *ca.* 621 and *ca.* 619 cm^{-1} assigned to ν_3 and ν_5 vibrations are characteristic of monodentately coordinated perchlorate group. This is supported by the molar conductance data[13] (Table-1). The N-coordinated nature[14] of the thiocyanate group is indicated by $\nu(C{-}N)$ (*ca.* 2039), $\nu(C{-}S)$ (*ca.* 767) and $\delta(NCS)$ (*ca.* 509 cm^{-1}). The IR spectra of the nitrate complexes[15] are suggestive of monodentately coordinated nitrate group ($\nu_4 \sim 1529$, $\nu_1 \sim 1384$ cm^{-1}). Strong bands exhibited by the dioxotungsten(VI) complexes in the region 958–935 and 880–860 cm^{-1} are attributed to ν_{sym} (O=W=O) and ν_{asym} (O=W=O) respectively of *cis*-WO_2 configuration[4, 16].

In the ^1H NMR spectra of the ligands NAAP and RAAP, the signal of $>C{-}CH_3$ group of pyrazolone ring appears as a sharp singlet (3H) in the region $\delta(2.50–2.75)$. The $N{-}CH_3$ signal is observed as another singlet in the region $\delta(3.4–3.7)$. The aromatic protons of the compound appear as multiplet in the region $\delta(7.4–7.8)$ (comprising eleven protons). A detailed assignment of the aromatic proton signals are not attempted. The OH proton signal appears as doublet between $\delta(8.58–8.61)$.

TABLE-1
ANALYTICAL AND CONDUCTIVITY DATA OF COMPLEXES

Complex	Analysis %: Found (Calcd.)					Molar conductance (Ω^{-1} cm^2 mol^{-1})					
						$C_6H_5NO_2$		CH_3CN		CH_3OH	
	C	H	N	S	W	Conc. × 10^{-3}	Cond.	Conc. × 10^{-3}	Cond.	Conc. × 10^{-3}	Cond.
[WO_2(NAAP)Cl_2]	39.01 (39.08)	2.79 (2.87)	8.80 (8.85)	—	28.1 (28.5)	0.992	6.010	1.100	1.44	1.180	12.20
[WO_2(NAAP)NCSCl]	39.48 (39.59)	2.67 (2.72)	10.40 (10.49)	4.75 (4.80)	27.49 (27.55)	0.995	4.800	0.959	5.15	0.995	12.81
[WO_2(NAAP)ClO_4Cl]	35.51 (35.58)	2.50 (2.56)	7.81 (7.90)	—	25.88 (25.93)	0.999	5.330	0.897	9.99	0.980	14.04
[WO_2(NAAP)NO_3Cl]	37.48 (37.57)	2.65 (2.70)	10.30 (10.43)	--	27.30 (27.38)	1.010	3.450	0.889	4.11	0.899	10.61
WO_2(RAAP)Cl_2]	33.38 (33.43)	2.50 (2.64)	9.08 (9.17)	—	30.01 (30.09)	1.198	1.179	1.260	4.49	1.000	9.46
[WO_2(RAAP)NCSCl]	34.10 (34.14)	2.45 (2.55)	11.01 (11.06)	5.01 (5.05)	29.01 (29.03)	0.998	1.618	1.020	6.38	0.998	12.21
[WO_2(RAAP)ClO_4Cl]	30.21 (30.26)	2.30 (2.39)	8.25 (8.30)	—	27.20 (27.24)	1.010	1.535	0.948	7.03	0.996	11.52
[WO_2(RAAP)NO_3Cl]	32.01 (32.04)	2.49 (2.53)	10.91 (10.99)	—	28.78 (28.84)	1.000	1.541	0.992	6.35	1.000	9.21

TABLE-2

KEY INFRARED BANDS (cm^{-1}) OF DIOXOTUNGSTEN(VI) COMPLEXES OF NAAP AND RAAP

NAAP	[WO_2(NAAP)-Cl_2]	[WO_2(NAAP)-NCSCl]	[WO_2(NAAP)-ClO_4Cl]	[WO_2(NAAP)-NO_3Cl]	RAAP	[WO_2(RAAP) Cl_2]	[WO_2(RAAP)-NCSCl]	[WO_2(RAAP)-ClO_4Cl]	[WO_2(RAAP)-NO_3Cl]	Assignment
—	3440	3440	3420	3440	—	3400	3420	3440	3400	ν(OH) Free
2900	—	—	—	—	2904	—	—	—	—	ν(OH) hydrogen bonded
—	—	2039	—	—	—	—	2040	—	—	ν(C—N) of thiocynate group
1675	1629	1632	1600	1600	1674	1630	1640	1630	1632	ν(C=O)
1490	1470	1472	1470	1470	1490	1472	1470	1470	1470	ν(N=N)
—	—	—	1114	—	—	—	—	1115	—	$\nu_4(ClO_4)$ coordinated
—	—	—	1094	—	—	—	—	1095	—	$\nu_1(ClO_4)$ coordinated
—	947	952	950	940	—	950	950	942	940	ν_{sym}(O=W=O)
—	870	878	870	868	—	868	870	870	876	ν_{asym}(O=W=O)
—	—	767	—	—	—	—	760	—	—	ν(C—S) of thiocyanate group
—	—	—	621	—	—	—	—	620	—	$\nu_3(ClO_4)$ (coordinated)
—	—	—	619	—	—	—	—	618	—	$\nu_5(ClO_4)$ (coordinated)

On analyzing the spectra of the complexes [WO_2(NAAP)(ClO_4)Cl] and [WO_2(RAAP)Cl_2], no appreciable change of signals is observed. A signal observed in the region *ca.* 8.59 in the complexes are due to the proton of —OH group. Thus it can be concluded that the —OH group coordinates to the metal without deprotonation. IR spectral data are also in conformity with these observations.

Thermogravimetric curves of the complex [WO_2(NAAP)Cl_2] was recorded in the temperature range from room temperature–1000°C. The complex shows first a weight loss of 5.36% around 225°C. This corresponds to the elimination of one chlorine atom. The second weight loss of 20.82% at 446°C was observed corresponding to the loss of β-naphthol. Finally, a weight loss of 30.94% at 559°C has been ascribed to the oxidative decomposition to give WO_2 as the ultimate residue.

The ligands NAAP and RAAP and the complexes [WO_2(NAAP)Cl_2], [WO_2(NAAP)(NCS)Cl] and [WO_2(RAAP)(NCS)Cl] were screened for their possible antibacterial activities against the gram positive bacteria staphylococcus aureus ATCC25923 and gram negative bacteria *Escherichia coli* ATCC 25922 at concentrations 10, 20, 40, 80 and 100 μg/disc tested. But they do not exhibite any antibacterial activities.

On the basis of the above evidences, an octahedral geometry is suggested for the complexes.

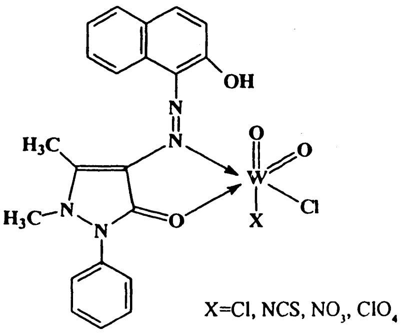

Fig. 2 (1). [WO_2(NAAP)XCl]

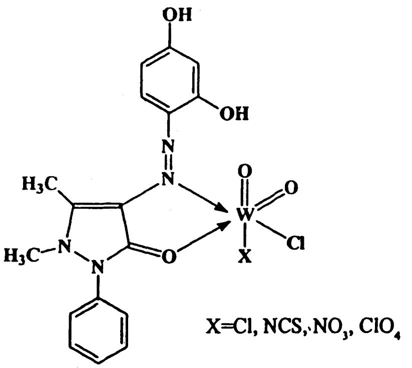

Fig. 2 (2). [WO_2(RAAP)XCl]

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REFERENCES

1. F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, Advanced Inorganic Chemistry, 6th Edn., John Wiley & Sons, New York (1999).
2. M.G.B. Drew, G.W.A. Fowles, D.A. Rice and K.J. Stanton, *J. Chem. Commun.*, 1125 (1974); C.A. Rice, P.M.H. Kroneck and J.K. Spence, *Inorg. Chem.*, **20,** 1996 (1981).
3. K. Yamanauchi and S. Yamada, *Inorg. Chim. Acta,* **11,** 223 (1974).
4. ———, *Inorg. Chim. Acta,* **12,** 9 (1975).
5. A. Syamal and M.R. Maurya, *Indian J. Chem.*, **25A,** 934 (1986).
6. S.B. Yu and R.H. Holm, *Inorg. Chem.*, **28,** 4385 (1989).
7. A.I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Edn., ELBS, London (1973).
8. S.C. Chaudhry, R. Sharma and N. Sharma, *Indian J. Chem.*, **33A,** 952 (1994).
9. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis,3rd Edn., Longmanns, London (1962).
10. E. Kurz, G. Kober and M. Beri, *Anal. Chem.*, **30,** 1983 (1958).
11. C.P. Prabhakaran and M.L. Harikumaran Nair, *Indian J. Chem.*, **35A,** 771 (1996); C.P. Prabhakaran and M.R. Gopalakrishnan Nair, *Indian J. Chem.*, **24A,** 345 (1985).
12. M.R. Gopalakrishnan Nair and S. Rawther, *J. Indian Chem. Soc.*, **69,** 157 (1992).
13. M.R. Rosenthal, *J. Chem. Educ.*, **50,** 331 (1973).
14. A. Sabatini and I. Bertini, *Inorg. Chem.*, **5,** 204 (1960)
15. C.C. Addison and G. House, *J. Chem. Soc.*, 613 (1960).
16. A.O. Rajan, S. Adhikari and A. Chakravorty, *Indian J. Chem.*, **15A,** 377 (1977).

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