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ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (1): Pg. 221-225

Studies on the Complexes of 2-Hydroxy-4-Methoxy Acetophenone oxime

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(Received: January 04, 2011; Accepted: February 17, 2011)

ABSTRACT

Cu(II), Ni(II), Co(II), Mn (II) & VO (II) complexes of 2-Hydroxy-Methoxy Acetophenone oxime (HMAOX) have been isolated and characterized by elemental analysis, thermogravimetric analysis, magnetic susceptibility measurements, spectral studies and the biological studies of ligand and their complexes.

Key words: Acetophenone oxime, Thermogravimetric analysis, Biological Study.

INTRODUCTION

The oximes of o-hydroxy phenones have aroused considerable interest as regards to their chelating ability with the transition metal ions¹⁻⁵. The present communication deals with the isolation and characterization of Cu(II), Ni(II), Co(II), Mn (II) & VO (II) complexes with HMAOX their biological behaviours and relation between stability.

EXPERIMENTAL

The ligand was synthesized by standard methods. The micro analysis and estimation of metal ions were done by the usual methods. Magnetic measurements were made by 'Gouy's technique using Hg [Co(CNS)₄] as calibrant. Systronic Digital-pH Meter (Type 335) was used for the pH measurements. The electronic spectra of the

complexes were recorded on spectrophotometer. The IR spectra were recorded on Perkin Elmer Infra red spectrophotometer in KBr. All the chemicals used were of Analar grade.

The biological activity of different concentrations of test compounds were measured by determining the growth of test fungus and bacteria by dry weight increased method and by agar diffusion method. The test organism was *Aspergillus Flavus* which was screened in vitro on Richard's liquid medium to calculate the percentage of inhibition (Table 2) while antibacterial activity was calculated against *Streptoproteus* (Table 3).

Isolation of the complexes

Isolation of Cu(II), Ni(II) & Co (II) complexes of HMAOX

The metal ion solution was treated with

an ethanolic solution of HMAOX and the mixture digested on water-bath for about half an hour. Cu (II), Ni (II) & Co (II) formed buff, green and brown coloured complexes in the range 3.0-3.5, 5.0-9.0 & 6.0-9.0 respectively, which were filtered, washed with hot water and then with 25% ethanol and finally dried at 105-110°C in an air oven.

Isolation of Mn(II) and V (IV) complexes of HMAOX

The metal ion solution was treated with an ethanolic of HMAOX and the mixture stirred for about two hours at room temperature. Mn (II) and V (IV) formed brownish black and grey coloured complexes in the pH range 8.0-9.0 and 2.5-4.0 respectively. The product was isolated as in (i) above.

RESULTS AND DISCUSSION

The complexes were analysed for C, H, N and the metals (table 1). The results revealed at 1:2 (metal:ligand) stoichiometry in all the complexes. Thermodynamic analysis indicated that the chelates were not in the hydrated form. The electronic spectra were recorded in solution and the results interpreted in terms of appropriate d-d transitions. Some ligand field parameters were also calculated. The structures of the complexes were assigned on the basis of their IR spectral data.

Thermogravimetric analysis

The chelates of Cu(II) and Ni(II) were stable upto 282 & 285°C respectively whereas the chelates of Co(II) and Mn(II) were stable even above 300°C. This indicates that the chelates are not in the hydrated form. The initial decomposition temperature from the TGA curve is taken as measure of the thermal stability of the chelates.

In the case of Cu(II), Ni(II), Co(II), and Mn(II) chelates, the weight after decomposition decreases continuously upto 640, 650, 645 and 530°C respectively. On further heating the weight of the residue remains constant and corresponds to their oxide-CuO, NiO, CoO and MnO₂.

Magnetic moments and electronic spectra

The observed magnetic moment (1.82 B.M.) of Cu(II) HMAOX complex is very close to the spin only value for one unpaired electron (1.73 B.M.).

Thus, the orbital contribution is almost quenched by the crystalline field. The electronic spectra of the complex show three bands at 16020, 20000 and 22550 cm⁻¹ due to transitions ²B_{1g}→³A_{1g}, ²B_{1g}→³E_g and charge transfer respectively, which suggest a square-planar arrangement for the complex.

The observed magnetic moment of Ni(II) - HMAOX complex suggests it to be diamagnetic and square-planar. The three well defined bands at 17040, 19000 and 29660 cm⁻¹ are observed corresponding to the transition ¹A_{1g}→³A_{1g}, ¹A_{1g}→³B_{1g} and ¹A_{1g}→³E_g respectively. The values of Δ₁, Δ₂ and Δ₃ are found to be 22540, 10460 and 4160 cm⁻¹ respectively.

The observed magnetic moment (4.31 B.M.) of Co (II)-HMAOX complex suggests it to be tetrahedral⁷. In the field of tetrahedral symmetry, three spin allowed bands are expected corresponding to the following transition in the increasing order to energies¹. ⁴A_{2g}(F)→⁴T_{2g}(F) (ν_{L1}), ⁴A_{2g}(F)→⁴T_{2g}(F) (ν₂), ⁴A_{2g}(F)→⁴T_{1g}(F) (ν₃).

In tetrahedral complexes the ν₁ occurs in the region 3000-5000 cm⁻¹ and is equivalent to 10Dq. However, this band has not been observed as it is inherently weak due to an orbital selection rule. In the present case, only two bands were observed at 7310 and 18770 cm⁻¹ which corresponding to ν₂ and ν₃ respectively. The values of B, β and λ were calculated using the equations suggested by Figgis⁶. The value of β is comparable to that reported in the literature for a tetrahedral complex.

The observed magnetic moment (1.72 B.M.) of VO(II) - HMAOX complex is quite close to the spin only value for unpaired electron (1.73 B.M.). Hence orbital contribution is completely quenched. The electronic spectra of the complex shows three bands at 13600, 18100 and 26050 cm⁻¹. The first is assigned to an unresolved band resulting from ²B₂→³E₁ transition, the second to the transition, ²B₂→²B₁ and the third may either be assigned to ²B₂→³A₁ transition or to the low energy charge transfer and inter-ligand transition. This complex appears to be five co-ordinate with 'O' of the vanadyl group lying at the apex of a square based pyramid N and O of the ligand forming the basal plane.

Table 1: Analytical and physical data of ligand and complexes

Compound	Decomposition Temp. °C	Analysis % Found (Caled)			
		C	H	N	M
C ₉ H ₁₀ NO ₃	101°C	59.85 (59.66)	6.30 (6.08)	6.54 (7.73)	
Cu (C ₉ N ₉ NO ₃) ₂	282.85	51.05 (50.98)	4.91 (4.72)	6.58 (6.70)	14.16 (14.08)
Co (C ₉ N ₉ NO ₃) ₂	>300	51.42 (51.36)	4.76 (4.68)	6.67 (6.74)	13.98 (13.96)
Ni (C ₉ N ₉ NO ₃) ₂	285	46.94 (46.80)	4.97 (4.78)	6.49 (6.68)	14.06 (14.19)
Mn (C ₉ N ₉ NO ₃) ₂	>300	53.21 (53.00)	4.93 (4.82)	7.26 (7.48)	12.75 (12.99)
VO (C ₉ N ₉ NO ₃) ₂	>300	52.54 (52.38)	4.98 (4.86)	6.78 (6.92)	12.49 (12.39)

Table 2: Fungicidal screening data of HMAOX and their metal chelates against *Aspergillus flavus* at varying concentration

Test Solution	0.10 % Conc.		0.20 % Conc.		0.30 % Conc.		0.40 % Conc.	
	W.t.	% inhibition	W.t.	% inhibition	W.t.	% inhibition	W.t.	% inhibition
Control	1.082	-	1.072	-	1.060	-	1.047	-
HMAOX	1.049	3.0	1.001	6.56	.955	9.92	.915	12.65
HMAOX-Mn(II)	.977	9.75	.889	17.10	.838	20.90	.789	24.65
HMAOX-Co(II)	.975	9.90	.885	17.50	.831	21.40	.784	25.10
HMAOX-Ni(II)	.972	10.20	.883	17.70	.830	21.70	.780	25.50
HMAOX-VO(II)	.955	11.80	.783	18.60	.815	23.15	.750	28.40
HMAOX-Cu(II)	.952	12.10	.825	23.00	.768	27.60	.704	32.70

Table 3: Antibacterial activity data of HMAOX and their metal chelates against streptococcus at varying concentrations

Test Solution	Inhibition zone (mm)			
	0.10 % Conc.	0.20 % Conc.	0.30 % Conc	0.40 % Conc.
Control	-	-	-	-
HMAOX	-	-	6.0	8.5
HMAOX-Mn(II)	-	6.0	8.5	12.0
HMAOX-Co(II)	-	7.0	9.8	14.0
HMAOX-Ni(II)	-	7.5	10.5	15.0
HMAOX-VO(II)	-	9.5	12.0	17.0
HMAOX-Cu(II)	5.4	15.0	15.4	35.0

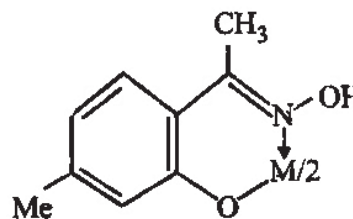
The observed magnetic moment of (5.92 B.M.) of Mn(II) - HMAOX indicates five unpaired electron. The d^5 configuration being spherically, the ground state suffers no change in the stereochemistry. Both the octahedral and the tetrahedral d^5 ions have been the same order of energy levels. The bands occurring at 17100, 18750, 20050, 21200, 22450 and 27500 cm^{-1} in the complex correspond to the ${}^6A_1 \rightarrow {}^4T_1(G)$, ${}^6A_1(G) \rightarrow {}^4A_2$, ${}^6A_1 \rightarrow {}^4E(G)$ and ${}^6A_1 \rightarrow {}^4E(P)$ transitions respectively. The tetrahedral nature of the complex has been confirmed on the basis of its molar absorbance value⁸.

Infrared Spectra

The IR spectra of the ligands show strong bands at 3280 cm^{-1} (ν_{OH} chelated), 3200 cm^{-1} (ν_{OH} for N-OH), 2900 cm^{-1} ($\nu_{\text{C-H}}$ of methylene group) and 1600 cm^{-1} ($\nu_{\text{C-N}}$). The bands at 1260 cm^{-1} and 1070 cm^{-1} are due to the presence of OCH_3 group in the benzene ring. The band at 1150 cm^{-1} further confirms benzene ring substitution. The band at 1000 cm^{-1} is due to N-O stretching.

The IR spectra of the chelates show that the phenolic hydrogen is replaced by the metals as the band 3280 cm^{-1} (ν OH chelated) disappears in the complexes. The strong band at 1600 cm^{-1} ($\nu_{\text{C-N}}$) shifts from 10-20 cm^{-1} to lower frequency in the metal chelates indicating that 'N' of the N-OH group co-ordinates with the metal ion. The ν N-O band at 1000 cm^{-1} in the ligand HMAOX shifts 1020 cm^{-1} in the chelates, a position recommended by various workers⁹⁻¹¹. The bands at 970, correspond to V=O . The bands in the ranges 490-460 cm^{-1} and 610-570 cm^{-1} indicate M-O and M-N bands respectively¹², which may also be coupled with ligands bands.

Taking into account the above observations, the following structure may be assigned to the complex.

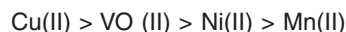


Where, M=Cu. Ni. Co. Mn and VO.

Biological activities

The screening result indicates the fungal & bacterial growth was inhibited on addition of the chemicals at varying concentrations. However, the ligand as well as the metal complexes showed increased activity at higher concentrations than at lower concentrations for a given fungus and bacteria.

The activity showed a gradual change with change of metal ion in the complexes and observed the following order.



Thus, Mn(II) complexes is least toxic while Cu(II) complex has the maximum activity. This may be attributed to the fact that copper itself is a toxic element and the increase in toxicity in the metal chelates is probably either due to the diffusion of the chelates as a whole through the cell membrane¹³ which may block enzymic activity of the cell or else it may catalyse toxic reactions among cellular constituents.

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