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Structural studies on Co(II), Ni(II), Cu(II) and Cr(III) complexes with phenylglyoxal-4-iminoantipyrine and their antifungal screening

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Abstract : Some new complex compounds of Co(II), Ni(II), Cu(II) and Cr(III) with Phenylglyoxal -4-iminoantipyrine have been isolated. All the complexes are colored solids. They have been characterized by elemental analysis, UV-vis, infrared and magnetic studies. On the basis of elemental analysis and spectral studies, six coordinated geometry may be assigned for these complexes. The ligand is tridentate and coordination takes place through ONO. The Schiff base and its complexes have been tested for their antifungal activity against various organisms.

(Keywords : Metals, Schiff base, Complexes, Antifungal Activities)

Introduction

Metal complexes of heterocyclic ligand have been studied extensively due to synthetic flexibility and their selectivity as well as sensitivity towards the central metal ions. A large number of heterocyclic compounds have been studied for their interesting and important biological activities[1,2,3]. Heterocyclic compounds are very widely distributed in nature and are essential to many fields of medicine as drugs for varied diseases[4,5,6].

From the survey of existing literature, it appears that heterocyclic Schiff base and their metal complexes have a variety of applications in biological, industrial and pharmacological fields. Keeping the above facts in the mind and in the continuation of our research program on transition metal complexes with Schiff base, in this paper we report some new Schiff base metal complexes of Co(II), Ni(II), Cu(II) and Cr(III) derived from phenylglyoxal-4-iminoantipyrine.

Experimental

All reagents, solvents were of good quality and used directly. IR spectra were recorded on Perkin Elmer-577 spectrophotometer using KBr pellet method. The elemental analysis (C, H, N) were performed on a Perkin-Elmer CHN microanalyzer. The magnetic measurements were made on a Gouy's balance and the diamagnetic corrections for the ligand molecules were applied. The instrument was calibrated using a copper sulphate pentahydrate. The UV and visible spectra of the complexes were recorded on Hitachi U-200 spectrophotometer in DMF medium at room temperature. The metal and halide estimations were done by standard procedures[7].

Preparation of ligand

Phenylglyoxal-4-iminoantipyrine was prepared as reported earlier[8].

Synthesis of Schiff base metal complexes

The Co(II), Ni(II), Cu(II) and Cr(III) complexes were prepared by mixing of methanolic/ /ethanolic solution (50ml) of $CoBr_2.6H_2O$/ $NiCl_2.6H_2O$/$CuCl_2.2H_2O$/$Cr(CH_3COO)_3.6H_2O$ with the methanolic/ethanolic solution (50 ml) of Schiff base (PGIA) in 1:2 (metal:ligand) ratio. The resulting content was refluxed on water bath for 3.5 to 5 hours. Excess of solvent was removed under vacuum and remaining residue was dissolved in the minimum quantity of alcohol. A colored complex was precipitated out by adding ether with vigorous shaking. It was filtered and

washed with ether thoroughly and dried under vacuum.

Results and Discussion

The complexes prepared are stable at room temperature and a non-hygroscopic. The complexes are soluble in DMF and DMSO. The analytical data and colors of the complexes have been presented in Table 1. The analytical data of all the new complexes agree very well with the proposed molecular formulae.

Table - 1
Physical and analytical data of the synthesized Schiff base and its complexes

S. No	Compounds	Color	Molecular Weight	Percentage Composition F(C)					Magnetic moment in BM
				C	N	H	Cl/Br	M	
1	$C_{19}H_{17}N_3O_2$	Yellow Turmeric	319.15	71.52 (71.49)	13.17 (13.20)	5.36 (5.33)	- -	- -	-
2	$[Co(C_{19}H_{17}N_3O_2)_2]Br_2$	Dark Brown	896.13	53.40 (53.21)	9.70 (9.84)	3.90 (3.96)	18.70 (18.65)	6.75 (6.88)	4.95
3	$[Ni(C_{19}H_{17}N_3O_2)_2]Cl_2$	Greenish Yellow	793.05	59.30 (59.23)	10.90 (10.95)	4.50 (4.42)	9.15 (9.21)	7.45 (7.50)	3.20
4	$[Cu(C_{19}H_{17}N_3O_2)_2]Cl_2$	Brown	821.09	59.50 (59.01)	10.83 (10.90)	4.35 (4.40)	9.10 (9.18)	8.10 (8.22)	1.90
5	$[Cr(C_{19}H_{17}N_3O_2)_2](CH_3COO)_3$	Buff	797.90	60.98 (60.88)	9.78 (9.72)	4.86 (4.96)	- -	5.95 (6.00)	3.75

The six coordinated Co(II) complex exhibits magnetic moment of 4.95 B.M. which supports an octahedral geometry for the Co(II) complex[9]. The Ni(II) complex shows magnetic moment of 3.20 B.M. which is slightly higher than the spin only value (2.83B.M.) and indicates the octahedral geometry around the Ni(II) ions[10]. The observed magnetic moment value for the Cu(II) complex is 1.90 B.M. suggesting a distorted octahedral environment[11] of the ligand around the central Cu(II) ion. Magnetic moment value of Cr(III) complex is 3.75 B.M. corresponding to three unpaired electrons indicating the distorted octahedral environment.

The electronic spectra of the metal complexes were taken in DMF (10^{-3}M) solution. Electronic spectra of Co(II) complex shows three absorption bands at 9700 cm^{-1}, 16330 cm^{-1} and 22610 cm^{-1}.These are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively which indicate octahedral geometry of the Co(II) complex. The calculated ligand field parameters 10 Dq (6630cm^{-1}), B (656cm^{-1}) and β (0.68) value support the six coordination geometry around Co(II) ion. The reduction in Racah parameter value B from the free ion value (971cm^{-1}) testifies the presence of metal-ligand covalent bond. The electronic spectra of Ni(II) complex shows three transitions at 10400 cm^{-1} 16300 cm^{-1} 22400 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$ transitions respectively. The transitions reveal its octahedral environment [12,13]. The ligand field parameters such as Dq (1040 cm^{-1}) B (793 cm^{-1}) and β (0.77) were calculated and these values support the proposed octahedral geometry for Ni(II) complex. The β nephelauxetic parameter value (0.77) indicates the covalent character of metal-ligand bond[14]. The spectrum of Cu(II) complex displays two absorption bands at 11400 cm^{-1} and 18400cm^{-1} which may be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer band

respectively. The electronic spectra of the Cu(II) complex suggests octahedral geometry around central metal ion[15]. The spectrum of Cr(III) complex has three spin allowed transitions at 17350 cm^{-1}, 23820 cm^{-1} and 38717 cm^{-1} which are assignable to $^4A_{2g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_2)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions respectively. These favors the distorted octahedral geometry of Cr(III) complex. The ligand field parameters Dq, Dq/B, B, and β have been found 1735 cm^{-1}, 2.60, 665 cm^{-1} and 0.72 respectively. These values are in good agreement with the reported values for distorted octahedral Cr(III) complexes[16].

The data of IR spectra of the ligand and its metal complexes are listed in Table-2. IR spectra of the complexes compared with the free ligand in order to determine the involvement of coordination sites in chelation.

Table - 2
Selected important infrared bands (cm^{-1}) of the Schiff base and their metal complexes

Ligand/Complexes	$\nu_{C=O}$ (ring)	$\nu_{C=O}$ (open chain)	$\nu_{C=N}$	ν_{M-O} (ring)	ν_{M-N}	ν_{M-O} (open chain)
$C_{19}H_{17}N_3O_2$	1620 m	1660 m	1520 s	-	-	-
$[Co(C_{19}H_{17}N_3O_2)_2]Br_2$	1580 m	1620 s	1505w	460 sh	560 m	475m
$[Ni(C_{19}H_{17}N_3O_2)_2]Cl_2$	1590 m	1600 s	1490 m	405 m	505 s	440s
$[Cu(C_{19}H_{17}N_3O_2)_2]Cl_2$	1600 s	1620sh	1505 m	480sh	525vw	500m
$[Cr(C_{19}H_{17}N_3O_2)](CH_3COO)_3$	1585 m	1610 s	1500 sh	450 w	555 s	480s

s = Strong, sh = Short, m = Medium, b = Broad, vw = very weak

The IR spectrum of the ligand exhibited the most characteristic absorption bands at 1620 cm^{-1} 1660 cm^{-1} and 1520 cm^{-1} which were assigned [8] to νC=O (ring), νC=O (open chain) and νC=N respectively. In the IR spectra of all the metal complexes, the band due to νC=O (ring), νC=O (open chain) and νC=N were shifted towards lower frequency side after complexation. These shifts are suggesting coordination of metal through oxygen of ring, oxygen of open chain and nitrogen of azomethine group. The coordination through ONO atoms may be supported by the appearance of non ligand new bands in the far IR region at 505-560 cm^{-1}, 405-460cm^{-1} and 440-500 cm^{-1} which are assigned to νM-N, νM-O (ring), νM-O (open chain) stretching vibrations[17,18, 19].

Hence on the basis of elemental analysis, IR spectra, electronic spectra, and magnetic moment measurement data the geometry of the complexes of Co(II), Ni(II), Cu(II) and Cr(III) can be presumed to have octahedral geometry as shown in figure-1 and the coordination number of the central metal is found to be six satisfied by ONO of ligand PGIA.

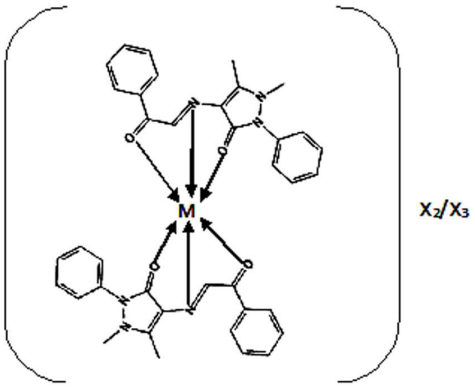

Figure-1 Where M = Co(II), Ni(II), Cu(II) and Cr(III) and X = Cl^-/CH_3COO^-

Antifungal activity studies

Schiff base and all the complexes were screened for their antifungal activity against *A. Sydowi* and *C. tetrasperma* at 50, 100 and 150 ppm concentration in DMF solvent by the radial growth method[20] using Czapek's agar medium. The fungi were grown at 25±1° C and the average of three replications was recorded in each case. After five days the individual fungus was measured. The amount of growth inhibition was calculated as (C-T)X100/C Where C = diameter of fungus colony in control plate, T= diameter of fungus colony in test plate. The Schiff base and complexes were found highly active against both fungi tested in Table-3.

Table - 3
Fungicidal screening data of ligand and their complexes

Compounds	% inhibition after 5 days (conc. in PPM)					
	Curvularia tetrasperma			*Aspergillus sydowi*		
	50	100	150	50	100	150
$C_{19}H_{17}N_3O_2$	22	32	36	20	27	33
$[Co(C_{19}H_{17}N_3O_2)_2]Br_2$	55	65	72	50	60	75
$[Ni(C_{19}H_{17}N_3O_2)]Cl_2$	70	80	84	65	75	83
$[Cu(C_{19}H_{17}N_3O_2)]Cl_2$	60	67	74	74	80	88
$[Cu(C_{19}H_{17}N_3O_2)](CH_3COO)_3$	55	60	70	50	58	68

References

1. M. Gupta, *Int. J. Physical Chem. Mat. Sci.*, **4(1),** 21 (2015).
2. M.S. Saini, A. Kumar, J. Dwivedi and R. Singh, *Int. J. Pharma. Sci. Res.,* **4(3),** 66 (2013).
3. Y. Deng, et al., *J. Med. Chem*., **60(6)**, 2498 (2017).
4. B. Eftekhari-Sis, M. Zirak and A. Akhari, *Chem. Rev*., **113**, 2958 (2013).
5. Y. Ju and R.S. Varma, *J. Org. Chem*., **71**, 135 (2006).
6. D. Z. Zarate, R. Aguilar, R. I. Hernandez-Benitez, E.M. Labarrios, F. Delgado and J. Tamariz, *Tetrahedron*, **71**, 6961 (2015).
7. A.I. Vogel, "*A Text Book of Quantitative Inorganic Analysis*", Longmans Green, London (1971)
8. V. Kumar and R. Dhakarey, *J. Ind. Council Chem*. **20(1)**, 61, (2003).
9. Dr P. Sasidharan, *International Journal of Chemical and Physical Sciences*, **3(5)**, 35 (2014).
10. K. Siddappa *et al.*, *Proc. Indian Natn. Sci. Acad.,* **72(4)**, 163 (2010).
11. Abdou Saad El-Tabl, *Trantition Metal Chemistry*, **27**, 166 (2002).
12. A.P. Mishra and K. Krishna, *J. Indian Chem. Soc*., **86**, 1150 (2009).
13. G. Chitra, *J. Indian Council Chem*., **24(1)**, 16 (2007).
14. M.B. Halli, P. Vithal Reddy, K. Shivkumar, A. Basavaraja, B.A. Jumnal and V.B. Patil, *J. Ind. Council Chem*. **27(1)**, 58 (2010).
15. C.H. Krisha, C.M. Mahapatra and A.K. Dash, *J. Inorg. Nucl. Chem*., **39**, 1253 (1977).
16. R.L.Datta and A.Shyamal, *Element of Magneto chemistry*, 2nd Ed.,New Age(press) (1992).
17. S. Shaygan, H. Pasdar et al., *Appl. Sci*., **8**, 85 (2018).
18. D.C. Dash, A.K. Paridesh and D. Jeana, *J. Indian Chem. Soc*., **79**, 48 (2002).
19. C.N.R. Rao, *Chemical Applications of Infrared Spectroscopy,* Academic Press, New York, (1963).
20. K. Sharma, S.C. Joshi and R.V. Singh, *Metal Based Drugs*, **7(2)**, 105, (2000).