

Synthesis, Characterization and Biocidal Studies of Co(II), Ni(II) and Cu(II) Complexes with O, O and N- Donor Ligand

Vinod Kumar
Department of chemistry, Agra College, Agra
Email: vinodkchem@gmail.com

Co(II), Ni(II) and Cu(II) complexes of phenylglyoxal anil of 4-aminoantipyrine have been prepared and characterized by elemental analysis, infrared, magnetic measurements and electronic spectral studies. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1:2 (metal: ligand). All the complexes have octahedral structures. The Schiff base and the metal complexes have been screened for their antifungal activity against Aspergillus sydowi and Curvularia tetrasperma.

Keywords: Phenylglyoxal, Aminoantipyrine, Tridentate Schiff bases, Metal Complexes, Biocidal studies.

1. INTRODUCTION

Oxygen and nitrogen heterocyclic Schiff base has a variety of pharmaceutical activities and many of these gained wide acceptances in clinical activities. They are an important class of ligands in coordination chemistry [1]. 4-Aminoantipyrine is known for various clinical applications such as anti-inflammatory, analgesic, antipyretic [2,3] and several chemotherapeutic agents [4].

It is evident from the reported literature that compounds possessing pyrazole nuclei showed significant anthelmintic as well as antimicrobial activities [5,6,7]

Because of biological importance, it was thought worthwhile to synthesize and characterize metal complexes of Schiff base phenylglyoxal anil of 4-aminoantipyrine.

2. EXPERIMENTAL

The entire chemicals were used of AR or BDH grade without any further purification.

3. PREPARATION OF LIGAND

Phenylglyoxal anil of 4-aminoantipyrine was prepared by the condensation of phenylglyoxal and 4-aminoantipyrine as reported earlier [8].

4. SYNTHESIS OF COMPLEXES

The complexes were prepared by respective metal halides in ethanol with ligand phenylglyoxal anil of 4-aminoantipyrine in molar ratio 1:2. The contents were refluxed on a water bath for 3.5-5 hours. Excess solvent was removed under vacuum and the remaining residue was dissolved in the minimum quantity of ethanol. Coloured solid complexes precipitated out by adding ether with vigorous shaking. The precipitated complexes were filtered and washed with ether and dried under vacuum. Yield - 65-70%.

5. PHYSICAL MEASUREMENTS

Elemental analysis was carried out with Perkin Elmer CHN micro analyzer. The IR spectra ($4000-200\text{ cm}^{-1}$) were recorded on Perkin Elmer-577 spectrophotometer using KBr pellets. The electronic spectra of the complexes in DMF were recorded on Hitachi U-200 spectrophotometer. Magnetic susceptibility measurements were made at room temperature on Gouy's balance using copper sulphate pentahydrate as the calibrating reagent. Halogen and sulphur were estimated by standard methods [9].

6. RESULTS AND DISCUSSIONS

All the metal complexes are colored, stable at room temperature and are non-hygroscopic. The complexes are partially soluble in common organic solvents but are soluble in dimethylformamide and DMSO.

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	S	M	
1	$\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$	Yellow Turmeric	319.15	71.60 (71.47)	12.92 (13.17)	5.42 (5.33)	- -	- -	- -	-
2	$[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2](\text{ClO}_4)_2$	Brown	896.13	51.00 (50.90)	9.50 (9.40)	3.90 (3.79)	7.80 (7.91)	- -	6.70 (6.58)	5.12
3	$[\text{Ni}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2]\text{SO}_4$	Greenish Yellow	793.05	57.00 (57.50)	10.50 (10.63)	4.50 (4.29)	- -	3.9 (4.04)	7.5 (7.4)	3.10

4	$[\text{Ni}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2](\text{NO}_3)_2$	Greenish Yellow	821.09	55.50 (55.54)	13.30 (13.69)	4.25 (4.14)	-	-	7.00 (7.15)	3.17
5	$[\text{Cu}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2]\text{SO}_4$	Brownish Blue	797.90	57.00 (57.15)	10.40 (10.56)	4.40 (4.26)	-	4.20 (4.01)	7.50 (7.96)	1.90

The metal complexes decompose above 160°C. Elemental analysis suggests a 1:2 (metal:ligand) stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1.

The infrared spectra of the ligand as well as complexes have been recorded in the frequency region 4000-200 cm^{-1} (Table 2) and structurally important vibrational bands are C=O(ring) stretch, C=O (open chain) stretch and C=N stretch provide unequivocal evidences relating to the structure of the complexes.

TABLE 2: Selected important infrared bands and electronic transition (in cm^{-1}) of the ligand and its complexes.

S. No.	Ligand/Complexes	$\nu_{\text{C=O}}$ (ring)	$\nu_{\text{C=O}}$ (open chain)	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	Electronic Transition
1	$\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$	1620 m	1660 m	1520 s	-	-	-
2	$[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2](\text{ClO}_4)_2$	1575 m	1600 m	1480 m	450 sh	540 m	16510, 20617
3	$[\text{Ni}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2]\text{SO}_4$	1580 m	1610 s	1485 m	410 m	500 s	10410, 16320, 22410
4	$[\text{Ni}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)_2](\text{NO}_3)_2$	1590 m,b	1620 m	1490 m, b	405 m	480 m	12630, 18860, 21400
5	$[\text{Cu}(\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2)]\text{SO}_4$	1590 m	1630 m	1495 m	420 sh	520 m, b	14900, 20890

s=Strong, sh= Short, m= Medium, b=Broad

The IR spectra of the ligand exhibited a medium band at 1620 cm^{-1} ascribed to the $\nu_{\text{C=O}}$ of the pyrazolone ring. A medium band at 1660 cm^{-1} is assigned to the $\nu_{\text{C=O}}$ of the glyoxal. Upon complexation, the $\nu_{\text{C=O}}$ of the pyrazolone ring has shifted to a lower frequency region, suggesting that the carbonyl

group is coordinated to the metal ion. The carbonyl stretching frequency of the Phenylglyoxal moiety at 1660 cm^{-1} has been lowered by $30\text{-}60\text{ cm}^{-1}$ in the spectra of the complexes. This indicates the linkage of the carbonyl group to the metal ion. The IR spectrum of the ligand showed the characteristic $\nu\text{C=N}$ band at 1520 cm^{-1} . In the spectra of the complexes, this band appeared at a lower frequency region indicating the coordination of the azomethine nitrogen atom to the metal ion [10]. IR spectra showed that the ligand acts as a tridentate-chelating agent coordinated to the metal ion through the nitrogen $\nu(\text{C=N})$ and two oxygen atoms.

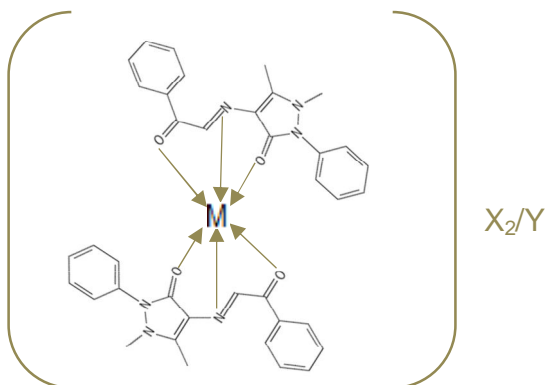
The coordination through nitrogen and oxygen atoms are supported by the appearance of bands in the far IR region at $405\text{-}450\text{ cm}^{-1}$ and $480\text{-}540\text{ cm}^{-1}$ which are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ respectively [11].

7. ELECTRONIC SPECTRA AND MAGNETIC MOMENT

Electronic spectra of the Co(II) complex displayed two bands at 16510 cm^{-1} and 20617 cm^{-1} . These bands are assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$ transitions respectively. These transitions of the Co(II) complex indicates octahedral environment [12] which is further supported [13,14] by magnetic moment value 5.12 BM.

The Ni(II) complexes exhibited three absorption bands at $10410\text{-}12630\text{ cm}^{-1}$, $16320\text{-}18860\text{ cm}^{-1}$ and $21400\text{-}22410\text{ cm}^{-1}$ which can be assigned to the transitions ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_3)$ respectively indicating octahedral geometry [14] which is further supported [15] by magnetic moment values (3.10 and 3.17 BM) for both the Ni(II) complexes. The spectrum of Cu(II) complex displayed two ligand field bands at 14900 cm^{-1} and 20890 cm^{-1} which may be assigned to the transitions ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ and charge transfer band respectively. The electronic spectra of the Cu(II) complex proposed an octahedral geometry [13] around the copper metal ion. The magnetic moment value for the Cu(II) complex was found 1.90 BM [10,11]

Based on the above discussion, the following structure may be assigned to the complexes.



Where $\text{M}=\text{Co(II)/Ni(II)/Cu(II)}$, $\text{X}_2=\text{ClO}_4^-/\text{NO}_3^-$ and $\text{Y}=\text{SO}_4^{2-}$

8. ANTIFUNGAL ACTIVITY

The antifungal activity was estimated against *C. tetrasperma* and *A. sydowi* by the radial growth method [16] using Czapek's agar medium. The compounds were dissolved in 50, 100 and 150 PPM concentrations in DMF and then mixed with medium. The linear growth of the fungus was determined by measuring the diameter of the colony after 5 days. The percentage inhibition was calculated as $(C-T)100 C^{-1}$ where C and T are the diameters of the fungus colony in the control and test plate respectively. The ligand as well as their complexes were screened for antifungal activities and mentioned in Table 3. The data indicates that ligand as well as complexes of Co(II), Ni(II) and Cu(II) shows antifungal activities.

TABLE 3: Fungicidal Screening data of ligand and their complexes.

Compounds	% inhibition after 5 days (conc. in PPM)					
	<i>Curvularia tetrasperma</i>			<i>Aspergillus sydowi</i>		
	50	100	150	50	100	150
$C_{19}H_{17}N_3O_2$	22	32	36	20	27	33
$[Co(C_{19}H_{17}N_3O_2)_2](ClO_4)_2$	62	72	80	55	70	73
$[Ni(C_{19}H_{17}N_3O_2)]SO_4$	68	77	88	60	69	77
$[Ni(C_{19}H_{17}N_3O_2)](NO_3)_2$	62	70	79	70	78	85
$[Cu(C_{19}H_{17}N_3O_2)]SO_4$	80	88	92	77	85	91

REFERENCES

- [1] P. Pattanayak, D. Patra, J.L. Pratihari, A. Burrows, M.F. Mahon and S. Chattopadhyay; "Osmium and Cobalt Complexes Incorporating Facially Coordinated N, N, O-Donor Azo-imine Ligands: Redox and Catalytic Properties", J. Chem. Sci., Vol. 125(1), pp. 51-62, 2013.
- [2] D. Burdulene, A. Palaima, Z. Stumbryavichyute and Z. Talaikite; "Synthesis and Anti-inflammatory Activity of 4-Aminoantipyrine Derivatives of Succinamides", Pharmaceutical Chemistry Journal, Vol. 33(4), pp. 191-193, 1999.
- [3] G. Turan-Zitouni, M. Sivaci, F.S. Kiliç and K. Erol; "Synthesis of Some Triazolyl-antipyrine Derivatives and Investigation of Analgesic Activity", European Journal of Medicinal Chemistry, Vol. 36,(7-8), pp. 685-689, 2001.
- [4] M.S. Alama, J.H. Choi and D.U. Lee; "Synthesis of Novel Schiff Base Analogues of 4-Amino-1,5-dimethyl-2-phenylpyrazol-3-one and Their Evaluation for Antioxidant and Anti-inflammatory Activity", Bioorganic Medicinal Chemistry, Vol. 20(13), pp. 4103-4108, 2012.

- [5] M. Himaja, K. Rai, K.V. Anish, M.V. Ramana, and A.A. Karigar; "Synthesis and Evaluation of Anthelmintic and Insecticidal Activities of 4-Amino-antipyrine Derivatives of Amino Acids and Peptides," *Journal of Pharmaceutical and Scientific Innovation*, Vol. 1, pp. 67-70, 2012.
- [6] S. Sigroha, B. Narasimhan, P. Kumar, A. Khatkar, K. Ramasamy, V. Mani, R.K. Mishra and A.B. Abdul Majeed; "Design, Synthesis, Antimicrobial, Anticancer Evaluation, and QSAR Studies of 4-(substituted benzylidene-amino)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-ones", *Medicinal Chemistry Research*, Vol. 21, pp. 3863-3875, 2012.
- [7] Y. K. Vaghasiya, R. Nair, M. Soni, S. Baluja and S. Shanda; "Synthesis, Structural Determination and Antibacterial Activity of Compounds Derived from Vanillin and 4-Aminoantipyrine", *Journal of the Serbian Chemical Society*, Vol. 69(12), pp. 991–998, 2004.
- [8] V. Kumar and R. Dhakarey; "Synthesis and Studies of Some Metal Chelates with Phenylglyoxal-4-iminoantipyrine (PGIA) and 4-N-(m-phenoxybenzylidene) aminoantipyrine [4-N-(MPB)AAP]", *Journal Indian Council of Chemists*, Vol. 20(1), pp. 61-68, 2003.
- [9] A.I. Vogel; "A Text Book of Quantitative Inorganic Analysis", (Longmans, London), 3rd Ed., 1961.
- [10] G.S. Kurdekar, M.P. Sathisha, S. Budagumpi, N.V. Kulkarni, V.K. Revankar and D.K. Suresh; "4-Aminoantipyrine-based Schiff-base Transition metal Complexes as Potent Anticonvulsant Agents", *Med. Chem. Res.*, Vol. 21, pp. 2273-2279, 2012.
- [11] S. Lakshmi, K. Geetha, P. Mahadevi et. al.; "Tridentate Schiff Base (ONO) Transition Metal Complexes: Synthesis, Crystal Structure, Spectroscopic and Larvicidal Studies", *J. Chem. Sci.*, Vol. 128(7), pp. 1113-1118, 2016.
- [12] A.B.P. Lever; "Inorganic Electronic Spectroscopy", Elsevier, New York, 1994.
- [13] R.L. Carlin and A.J. Van Dyneveledt; "Magnetic Properties of Transition Metal Compounds", Springer-Verlag, New York, 1997.
- [14] P.S. Mane, S.G. Shirodkar, B.R. Arbad and T.K. Chondhekar; "Synthesis and Characterization of Manganese(II), Cobalt(II), Nickel(II), and Copper(II) Complexes of Schiff Base Derivatives Dehydroacetic Acid", *Indian Journal of Chemistry*, Vol. 40A(6), pp. 648-651, 2001.
- [15] B.K. Rai; "Synthesis and Structural Investigation of Co(II), Ni(II) and Cu(II) Complexes of Tridentate Ligand Derived from 3-Amino-2-phenyl-4(3H) Quinazoline One", *J. Ind. Council Chem.*, Vol. 27(1), pp. 68-71, 2010.
- [16] K. Sharma, S.C. Joshi and R.V. Singh; "Fertility Inhibitor Heterobimetallic Complexes of Platinum(II) and Paladium(II): Synthetic, Spectroscopic and Antimicrobial Aspects", *Metal Based Drugs*, Vol. 7(2), pp. 105-133, 2000.