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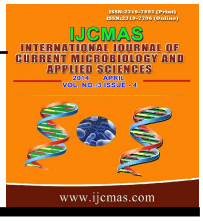

Original Research Article

Iron(II), Nickel(II), Copper(II) and Zinc(II) Complexes of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate : Synthesis, characterization and Antimicrobial Activities

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Keywords

2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate, Thiocyanate IonTransition Metal ions,

A B S T R A C T

An ethanolic solution of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate was added to an aqueous solution of metal nitrate and followed by adding ethanolic solution of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate and aqueous solution of potassium thiocyanate to give complexes with general formula [M L X_2] where M= Co(II), Ni(II), Cu(II) and Zn(II), L = 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate and X = thiocyanate ion. The resulting products were characterized using UV-visible and infrared spectroscopy. Elemental analyses were performed using C, H, N analysis and atomic absorption techniques. The magnetic susceptibility and the conductivity were also measured. The results suggested that the complexes have octahedral geometry. The relative antimicrobial studies of different metal complexes shows that Cu(II) complex is more effective towards gram positive bacteria like *S. aureus*. The molar conductance of metal complexes suggests their non electrolytic nature.

Introduction

The preparation of a new mixed ligand was aperhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies (Gehad G. Mohamed, biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing O and N donor atoms show pronounced biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions (Hung, and Lin, 2009). A number of mixed ligand complexes of substituted salicylaldehyde with various transition metals ions have been synthesized[3-10].

These complexes often possess remarkable and unique spectroscopic, photophysical and electrochemical properties which may be exploited in sensory and diagnostic applications an d there have been a number of reviews(Beer, 1994; Van Vegg et al., 1994; Nabeshima, 1996; Canary and B. C. Gibb, 1997; Gray, 1995; . Pecoraro et al., 1997) on the utilisation of transition metal complexes as ion and molecular sensors. In contrast to most metals from the left and center of the transition metal row, which are mostly six coordinate and more or less octahedral, complexes of metals such as Cu, Ni, Co and Mn show a much richer structural diversity. For the Cu(II) ion the d9 configuration is Jahn–Teller active: a single unpaired d-electron occupies one of the d-orbitals which gives rise to structural flexibility with coordination numbers varying between 4 and 6 with often severely distorted coordination geometries (Kaabi et al., 2012).

Copper is an attractive prospect, being an essential trace element which is required for normal cellular activity as a cofactor for many enzymes However, role of copper is much more complex because it can also promote nucleic acid cleavage and therefore has been utilized as metallodrug to cause DNA damage (Sartaj Tabassum et al., 2012). In Ni(II) no odd unpaired electron is present and its metal complexes are less likely to be distorted, but they still show a diversity of coordination geometries rarely found for other transition metal complexes, with square planar and octahedral being the most common (Sengottuvelan, et al., 2002). Thus, the aim of this paper is to synthesize and characterize mixed ligand complexes as we attempted to throw light on the coordination position for 2,4-dinitro- 6 (pyridine-2-ylmethylamino) methylphenolate with the transition ions. The structure of ligand is -

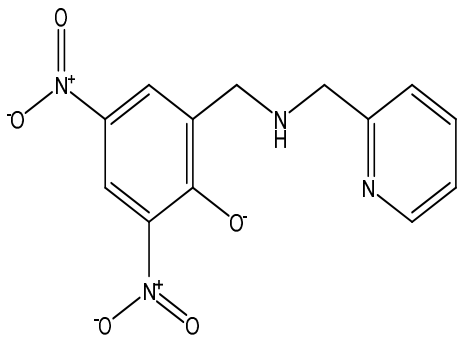

Fig. 1-2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate

Experimental

Materials and spectral measurements

All the chemicals used were of analytical grade and procured from standard firm like Merk and Aldrich. All the solvents used were purified by using standard procedure (Manuel et al., 2005). The molar conductivities in DMSO (10^{-3}M) at room temperature were measured using an Equiptronics digital conductivity meter. The magnetic susceptibility measurements of the complexes were made on Goy balance using $Hg[Co(SCN)_4]$ as standard. Electronic spectra of complexes were recorded on Elico SL-171 spectrophotometer at 25°C using ethanol/acetone as solvent. Thermo gravimetric analysis of mixed ligand metal complexes were done at a constant heating rate of 10°C /min up to 1000°C temperature on a TGA instrument model Perkins Elmer (Pyris Diamond) and FTIR spectra of metal complexes were recorded on Perkin Elmer–842 spectrophotometer. Metal content and water percentage were determined by thermogravimetric techniques (Vogel, 1964).

Synthesis of Metal Complexes of Co(II), Ni(II), Cu(II) and Zn(II)

All the mixed ligand metal complexes were prepared by the same general procedure with stoichiometric amount of ligands and metal nitrate in a 1:1:1 mole ratio. Mixed ligand metal complexes were prepared by refluxing the equimolar solutions of 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate, metal nitrate solutions and potassium thiocyanate solution at 50-60°C for 3hrs. The pH of the reaction mixture was maintained between 6.5 to 7.0. The colored precipitates obtained were filtered washed several times with hot water followed by ethanol to remove the soluble impurities. The washed colored solids were dried in an oven at 100 °C for 1hr and finally kept in desiccators over anhydrous $CaCl_2$. The dried solid were recrystalized with benzene : methanol (9.5:0.5) solution.

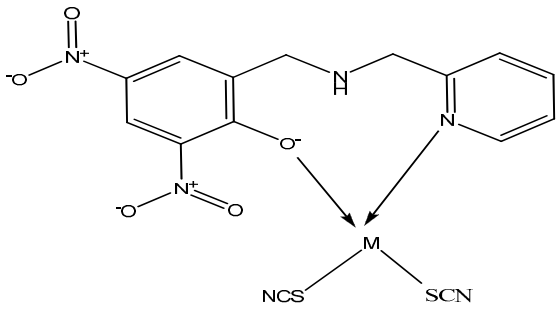

Fig. 2- Structure of Metal Complexes

Pharmacological Evaluation of Antimicrobial Activity

The ligand and their metal complexes were evaluated for their in-vitro antibacterial activity against *Bacillus subtilis, Staphylococcus aureus, Escherichia coli and Salmonella typhi* and antifungal activity against *Aspergillus flavous, Aspergillus niger, Penicillium triticena and Fusarium species* by the agar-well diffusion method (Greenwood, 1983)**,** disc-diffusion method (Bennett et al., 1999; Nishiyama et al., 2002; Suthakaran et al., 2005) and the serial dilution method (Quasted, 1996) using Mueller-Hinton agar (MHA) medium and Sabouraud's dextrose agar (SDA) medium, for bacteria and fungi respectively. The dilution plate method was used to enumerate microorganisms (105 CellsmL_1) for 24 hours (Collins et al., 1989; Kannan, et al., 2008). The discs (9mm in diameter), impregnated with the test compounds (250µg/ml/disc for bacteria and 1000 µ g/ml/disc for fungi). Ligands or complexes dissolved in DMSO were added (100 µmolmL^{-1}) to these wells. Negative controls were prepared using the DMSO solvent. Streptomycin and Penicillin were used as positive reference standards for determining the sensitivity of each microbial species tested. The inoculated plates were incubated at 37°C for 24 hours and 27°C for 72 hours for bacterial and fungal strains respectively. At the end of the period, inhibition zones formed on the medium were evaluated as millimeters (mm) diameter.

Determination of minimal inhibitory concentration (MIC)

Mueller-Hinton agar (MHA) medium and Sabouraud's dextrose agar (SDA) medium are employed as basal medium for the growth of bacteria and fungi, respectively, during the test of 250, 500, 750 ana 1000 ppm. The culture medium (20 mL) was poured into Petri dishes (9mm in diameter) and maintained at 45^0C until the samples were incorporated into the agar. The samples were added as 1mL using an automatic micropipette while constantly stirring to assure a uniform distribution. Each sample was tested at 250, 500, 750 and 1000 µmolmL^{-1} in DMSO.

Table.1 Analytical & physical data of Metal Complexes

S. No.	Metal Complexes	Mol. wt.	Yield %	Molar Conductivity mhos cm^2 mol^{-}	Magnetic moment Calc (Found)	Elemental analysis (Found)/ Cal %				
						C	H	N	M	S
1.	$C_{13}H_{11}N_4O_5Ni(SCN)_2$	477.7	74	2.86	3.872(4.090)	35.16 (32.49)	2.30 (2.89)	17.58 (16.33)	12.28 (10.59)	13.39 (11.98)
2.	$C_{13}H_{11}N_4O_5Fe(SCN)_2$	474.9	69	4.40	2.828(2.898)	35.37 (33.85)	2.31 (2.93)	17.68 (16.20)	11.77 (11.51)	13.47 (11.89)
3.	$C_{13}H_{11}N_4O_5Zn(SCN)_2$	484.4	68	5.71	zero	34.68 (33.09)	2.27 (2.96)	17.34 (15.96)	13.50 (12.27)	13.21 (12.10)
4.	$C_{13}H_{11}N_4O_5Cu(SCN)_2$	482.5	78	5.93	1.732(1.707)	34.81 (32.02)	2.27 (1.94)	17.40 (15.97)	13.16 (13.05)	13.26 (11.79)

Table.2 The characteristic infrared absorptions of the prepared complexes

Compound	ν(NH)	ν(CN)	ν(C=O)	ν(-C-N)	ν(CS)	ν(M-N)	δ(M-SCN)
$C_{13}H_{11}N_4O_5Ni(SCN)_2$	3340	2060	1690	1350	730	560 505	430
$C_{13}H_{11}N_4O_5Fe(SCN)_2$	3330	2110	1700	1345	650	585 520	420
$C_{13}H_{11}N_4O_5Cu(SCN)_2$	3320	2160	1690	1350	660	540 475	415
$C_{13}H_{11}N_4O_5Zn(SCN)_2$	3340	2120	1680	1350	670	545 490	450

Table.3 Electronic Spectral data of ligand metal complexes

Compounds	Electronic spectra (nm) π→π* n→π* L→M	d-d	Geometry of the complex
Ligand	265, 355		
$C_{13}H_{11}N_4O_5Ni(SCN)_2$	275, 385, 465	635	Octahedral
$C_{13}H_{11}N_4O_5Fe(SCN)_2$	255, 370, 470	500, 605	Octahedral
$C_{13}H_{11}N_4O_5Cu(SCN)_2$	285, 360, 435	625	Octahedral
$C_{13}H_{11}N_4O_5Zn(SCN)_2$	270, 365, 450	650, 620	Octahedral

Table.5 Zone of inhibition of Metal Complexes against Bacteria

Compounds	E. coli				S. typhi				S. aureus				B. subtilis			
	% Conc. In ppm				% Conc. In ppm				% Conc. In ppm				% Conc. In ppm			
	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000
Standard	**0.3**	**0.7**	**0.7**	**0.8**	**0.3**	**0.6**	**0.7**	**0.8**	**0.3**	**0.5**	**0.7**	**0.8**	**0.3**	**0.6**	**0.7**	**0.8**
Ligand	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$C_{13}H_{11}N_4O_5$ $Ni(SCN)_2$	**0.6**	**1.6**	**1.8**	**1.9**	**0.7**	**1.8**	**2.0**	**2.3**	**0.3**	**1.7**	**1.9**	**2.1**	**0.4**	**2.0**	**2.3**	**2.5**
$C_{13}H_{11}N_4O_5$ $Fe(SCN)_2$	**0.7**	**1.3**	**1.5**	**1.6**	**0.9**	**1.2**	**1.7**	**1.8**	**0.3**	**1.7**	**1.9**	**2.1**	**0.3**	**0.8**	**1.0**	**1.3**
$C_{13}H_{11}N_4O_5$ $Cu(SCN)_2$	**1.1**	**2.1**	**2.4**	**2.6**	**0.3**	**2.7**	**2.9**	**3.1**	**0.8**	**1.9**	**2.1**	**2.3**	**0.9**	**2.0**	**2.4**	**2.5**
$C_{13}H_{11}N_4O_5$ $Zn(SCN)_2$	**0.7**	**1.1**	**1.4**	**1.7**	**0.3**	**1.1**	**1.6**	**2.0**	**0.7**	**1.5**	**1.7**	**1.8**	**0.5**	**0.8**	**0.9**	**1.8**

Table.6 Zone of inhibition of Metal Complexes against Fungi

Compounds	A. flavous				A. niger				P. triticena				F. species			
	% Conc. In ppm				% Conc. In ppm				% Conc. In ppm				% Conc. In ppm			
	250	500	750	1000	250	500	750	1000	250	500	750	1000	250	500	750	1000
Standard	0.5	0.8	0.9	0.9	0.4	0.6	0.8	0.8	0.3	0.4	0.7	0.8	0.4	0.6	0.7	0.8
Ligand	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$C_{13}H_{11}N_4O_5Ni(SCN)_2$	0.8	1.8	2.0	2.3	0.5	1.9	2.0	2.3	0.5	1.7	1.9	2.1	0.6	1.5	1.7	1.9
$C_{13}H_{11}N_4O_5Fe(SCN)_2$	0.7	1.0	1.4	1.6	0.9	1.5	1.7	1.8	0.4	0.9	1.1	1.3	0.5	1.2	1.4	1.6
$C_{13}H_{11}N_4O_5Cu(SCN)_2$	0.9	2.2	2.4	2.5	1.0	2.0	2.3	2.5	0.9	1.9	2.1	2.3	0.9	1.8	2.0	2.0
$C_{13}H_{11}N_4O_5Zn(SCN)_2$	0.6	1.1	1.3	1.3	0.7	1.2	1.4	1.5	0.5	0.9	1.3	1.5	0.7	0.8	0.9	1.2

The different bacterial strains were layered to place 30 mL over the surface of the solidified culture medium containing a sample. After the bacteria were absorbed into the agar, the plates were incubated at 30^0C for 24–48 hours. Bacterial growth was monitored visually and the MIC was determined (Sato et al., 2008; Refaat MS and Ibrahim , 2008)**.**

The growth of inhibition was calculated by measuring the diameter of the microbial colony in the control and test plates.

Results and Discussion

The coloured microcrystalline mixed ligand metal complexes were found to be stable at room temperature. The complexes were soluble in methanol and DMSO but insoluble in water, carbon tetrachloride and chloroform. On elemental analyses and mass estimation by Fenger's method (Job, 1928), it was concluded that in mixed ligand metal complexes, ligands and metal are in 1:1:1 molar ratio possessing general formula [M L X_2] where M= Co(II), Ni(II), Cu(II) and Zn(II), L = 2,4-dinitro-6(pyridine-2-ylmethylamino) methylphenolate and X = thiocyanate ion. The molar conductivities (∧m) in DMSO at 25_C are in the range 2.86–5.93Ohm_1 cm2 mol_1, indicating the presence of non-electrolytes (Bhattacharjee et al., 2010; Geary. Coord, 1971). All analytical and physical data of mixed ligand metal complexes were shown in Table-1.

Infrared Spectra

The important infrared data of the free ligands and complexes are presented in Table.2. The infrared spectra of 2,4-dinitro- 6 (pyridine-2- ylmethylamino) methylphenolate exhibited a strong band at 1658 cm-1 and 1356 cm-1 which is attributed to ν(C=N) and C-N stretching frequencies respectively. This band shifted to lower wave numbers in all the complexes by 23-3 cm-1 and 11-6 cm-1, indicating that the (C=N) and (C-N) group is involved in complex formation respectively. The coordination through the nitrogen atom in (C=N) and (C-N) groups are further supported by the occurrences of new bands at 475-585 cm-1 in the spectra of the complexes which, may be assigned to ν(M-N) (Cramer Roger et al., 1981). The potassium thiocyanate spectrum showed a very strong band at 2048 cm-1 which is caused by the ν(C≡N). However, on complex formation this band is shifted to higher frequencies by 12-112 cm-1 (Kazuo Nakamoto 1997; Socrates, G. 1980) . Another indication for S-bonded SCN- is the weak bands appearing at 415-450 cm-1, which could be due to the bending of the absorbed thiocyanate δ(M-SCN). The bending of N-bonded NCS would be expected at higher frequencies (Michael Bron & Rudolf Holze. 1995; Nicholls, D. 1984). The presence of new weak bands around the region at 568 cm^{-1} and 497 cm^{-1} in all the complexes were attributed to υ (M-O) linkage (Belaid et al., 2008; Nakamoto et al., 1958).

Magnetic susceptibility

The magnetic moment for Ni^{+2} complex should be around 3.872 B.M while the measured value of μeff were shown to be higher than the expected value. This could be related to orbital-spin coupling. However, the values of μeff of all Fe^{+2} and Cu^{+2} complexes were found to be closer to that of spinning only models. The complexes of Zn^{+2} diamagnetic as expected from their electron configuration.

Magnetic susceptibility data are presented in Table 1

Electronic Spectral Study

The electronic spectra for free ligand and SCN^- ion showed that the absorption bands in the UV region can be annotated as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectrum of the dark brown Fe(II) complex exhibits weak broad bands at 279, 408 and 981nmwhich is attributed to the electronic transitions of 4T1g(F) →4A2g(F), 4T1g(F) →4T1g(P) and 4T1g(F) →4T2g(F) respectively. These transitions correspond for Fe(II) as a distorted octahedral complex.

The tetrahedral complexes of the Ni(II) ion are generally blue or green, unless the ligands also have absorptions in the visible region.The electronic spectra of Ni(II) complex shows an absorption band at 278 nm, which is attributed to the electronic transition 3A2g(F) →3T1g(P) while its bands exhibited at 429 and 480 nm is caused by the electronic transition of 3A2g(F)→3T1g(F). The electronic transition of 3A2g(F) →3T2g(F) appeared at 778, 906 and 992 nm. These assignments correspond for Ni(II) as an octahedral complex.

The spectrum of Cu(II) complex show that its bands in the visible region which is attributed to the electronic transitions of 2a1g(D) →2b1g(D) and 2eg(D) →2b1g(D) appeared at 496 and 730 nm respectively. Therefore, these transitions confirmed that the Cu(II) complex has a distorted octahedral geometry(Lever, 1968).

Finally Zn(II) complexe with an electronic configuration of *d10* did not show any (d-d) transitions. Instead the absorption bands in the spectra were due to charge transfer transitions which suffered from blue shift with hyper chromic effect (Lever, 1968). These absorptions have been fully assigned in Table 3.

Antimicrobial Studies

The antibacterial and antifungal activities of synthesized mixed ligand metal complexes were screened in vitro, against various bacteria and fungi. The results were recorded in **Table 5 and 6.** The percentage of growth of inhibition capacities of metal complexes follows the order given below against different bacteria and fungi.

Bactericidal activities of metal complexes

E. coli: Cu (II) > Ni (II) > Fe (II) > Zn (II)
S. typhi: Cu (II) > Ni (II) > Fe (II) > Zn (II)
S. aureus: Cu (II) > Ni (II) ≈ Fe (II) > Zn (II)
B. subtilis: Cu (II) ≈ Ni (II) > Fe (II) ≈ Zn (II)

Fungicidal activities of metal complexes

A. flavous: Cu (II) > Ni (II) > Zn (II) > Fe (II)
A. niger: Cu (II) > Ni (II) > Fe (II) > Zn (II)
P. triticena: Cu (II) > Ni (II) > Zn (II) ≈ Fe (II)
F. species: Cu (II) > Ni (II) > Fe (II) > Zn (II)

The results indicate that the Cu (II) complex is more toxic compared to other complexes, as well as Cu (II) complex is more effective towards bacteria *S. typhi*

compared to other microbes. The overall results obtained from the above studies confirm that with increase in the concentration of the complexes above 500 ppm the activity almost remains unchanged or is slightly increased.

From the above study we conclude that the decomposition of newly synthesized metal ligand complexes were nonelectrolytic in nature. The mixed ligand metal complexes of Fe(II), Ni(II), Cu(II) and Zn(II) were found to have octahedral geometry. All Cu (II) metal ligand complexes show the best antimicrobial activity at 500ppm as compared to other metal complexes.

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