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Characterization and biological studies of bivalent metal complexes of Schiff bases derived from aminothiazole and azosalicylaldehyde compound

Ritu Rani Chaudhary[1], Ravi Prakash[1], RB Singh[2*]
[1] Department of Chemistry, BSA College, Mathura, Uttar Pradesh, India
[2] Department of Zoology, School of Life Sciences, Dr. Bhimrao Ambedkar University, Khandari Campus, Agra, Uttar Pradesh, India

Abstract

Metal complexes of Co (II). Ni (II), Cu (II). Zn (II). Cd (II) and Hg (II) have been synthesised using 5- phenylazosalicylidene-4-phenyl-2-aminothiazole (PASPAT), 5-(chlorophenyl)-4-phenyl-2-aminothiazole (PCPASPAT) and 5- (*p*-tolulyl)-azosalicylidene-4-phenyl-2-aminothiazole (PTASPAT). The resulting complexes have been characterized on the basis of their elemental analysis, infrared spectra, electronic spectra, magnetic susceptibilities and molar conductance measurements. The ligands act as monobasic Iridentatu ligands and the complexes appear to be four co-ordinate. The antibacterial activities of the ligands and their metal complexes have been screened against *Escherichia coli. Bacillus substilis, Klebsiella pneumoniae, Pseudomonas aerogens, Salmonella paralyphi B., Staphylococcus aureus and Proteus vulgaris.*

Keywords: metal complexs, schiff base biological, physical and magnetic studies

Introduction

Hetrocyclic schiff base ligands containing an additional azo function find various applications. They have been of great importance due to their synthetic flexibilityselectivity and sensitivity towards the metal ions [1, 2]. Heterocyclic ring containing sulphur, nitrogen and oxygen impart special biological activity to these Schiff bases and their metal complexes [3, 4, 5]. In the present investigation showed the synthesis and structural studies of some metal complexes of Schiff bases derived from substituted azo salicylaldehyde and 4-phenyl-2-aminothiazole are described together with their antibacterial properties.

Matetials and Methods

All chemicals used were of analytical reagent grade. The compounds 5-phenylazosalicylaldehyde (PAS), 5(p)-chlorophenylazosalicylaldehyde (PCPAS and 50p)-tolulyl-azo-salicylaldehyde (PTAS)[6].

Preparation of Paspat

4-Phenyl 2-aminothiazole (0.176 g, I mmol) was dissolved in 50ml ethanol and was added dropwise to the ethanolic solution of PAS (0.226 g, I mmol) was dissolved in 50 ml ethanol with constant stirring. The resulting mixture was refluxed for 3 to 4 h on a water bath. After cooling, the separated precipitate was filtered, washed and recrystallized from ethanol. Other ligands PCPASPAT, PTASPAT were also synthesized in a similar manner.

Synthesis of nickel (II) complex

To a solution of PASPAT (0.769 g, 1 mmol in 30 ml ethanol), 10 ml aqueous solution of $NiCl_2.6H_2O$ (0.2377 g, 1 mmol) was added drop wise with constant stirring. The reaction mixture was refluxed on water bath for about 1 h and then cooled at room temperature. The pH was adjusted to 7.5 using 1:1 ammonia solution. Precipitate obtained was separated by filtration, washed with distilled water, followed by ethanol and then dried in *vacuo*. Other metal complexes were also synthesized using similar procedure.

Microbial activities

All metal complexes were screened against gram positive bacteria *(Bacillus substilis and Staphylacoccus aureus)* and gram negative bacteria *(Escherichia coli, Klebsiella pneumoniae, Pseudomonos aerogens, Salmonella paratyphi B and Proteus vulgaris)* at a concentration of 100 μg/ml by agar cup plate method and DMF system. A nutrient agar at 45°C was poured into petridishes (20-25 ml each) and allowed to solidify. To this 0.5-0.6 ml of 18-24 h old culture was added and the inoculum was spread evenly by using a spreader. Thereafter, filter paper disc (6 mm) were dipped into complex solution (10^{-3} M) and were placed on seeded medium. These plates were incubated at 37°C and extent of inhabitation was measured by the zone of inhibition produced after 24 hours. Elemental analysis was carried out in the microanalytical laboratory of Dr. Bhimrao Ambedkar University, Agra IR spectra was recorded on a Perkin-Elmer 783 Spectrophotometer, electronic spectra on a Schimadzu UV-160 using quartz cell, magnetic susceptibilities of complexes were measured by a Gouy balance method at room temperature using Hg[Co(CNS)4] as calibrant and molar conductance was measured in DMF (10- M) solution using a Elico conductivity bridge model EQ-660.

Results and Discussion

The analytical data of the metal complexes and their magnetic moment values are given in Table-1. All the complexes were found to be stable at room temperature and non-hygroscopic in nature. They decomposed on heating above 200°C and were found to be almost insoluble in water but soluble in aprotic solvents such as DMF, DMSO giving respective colour to the solutions. IR spectra of all three ligands show a broad to medium band at about 3000-2700 cm due to intramolecularly hydrogen bonded –OH group[7,8] In the spectra of metal complexes the broad band disappears indicating deprotonation of the ligands and involvement of the phenolic oxygen in bonding with metal ions. Another band observed in the range 1630-1610 cm^{-1} can be assigned to C=N- imino group. In aromatic Schiff bases [9, 10]. this band appears around 1637 cm^{-1} but in the present case due to hydrogen bonding of -C=N- and ortho hydroxyl group of aldehyde. This band is shifted to lower region by 15+5 cm^{-1} indicating the coordination through azomethyl nitrogen [11]. The spectral region1600-1400 cm^{-1} is a little complicated due to the presence of –C=C-and-N-N-stretching vibrations, the band appearing at 1555-1520 cm can be assigned to -N=N-frequency of azo group which is also observed to be lowered in complex due to involvement of azo nitrogen in bonding with metal [12] is in the spectra of the complexes, γ(M-N), γ(M-O) and γ(M-Cl) frequencies can be assigned in the region of 470-460 cm^{-1}, 320-305 cm^{-1} and 370- 350 cm^{-1} respectively [13, 14].

The UV spectra of cobalt complexes in DMF show two bands in the range of 15240 15950 and 5100-6000 cm^{-1} which are assigned to $^4A_2 \rightarrow {}^4T_1$ (P) and $^4A_2$ (F) → $^4T_1$ (F) transitions respectively[15]. B^1 (888 to 801) values calculated indicate about 70% reduction in free ion values which is attributed to considerable orbital overlap. Ni(II) complexes exhibit two bands at about 16000-16500 cm^{-1} and 7900-8200 cm^{-1} which are assigned to $^3T_{1g}$ (F)$\rightarrow {}^3A_{2g}$ (F) and $^3T_{2g}$(F) $\rightarrow$ $^3T_{1g}$ (P) transitions respectively. B values are found to be reduced (880, 891 & 862 for complexes ot PASPAT, PCPASPAT and PTASPAT respectively) compared to be free ion value (1041 cm^{-1}). β Values (0.84, 0.85 and 0.82) are in good agreement with the literature values for tetrahedral Ni (II) complexes [16]. Copper complexes shows a broad shoulder at about 19500 cm^{-1} which may be considered as *d-d* transition band. A band in region 25900-26400 cm^{-1} is of considerable controversy [17].

Table 1: Elemental analysis, physical properties and magnetic susceptibilities of the moral complexes.

Compound	Molecular formula (Molecular wt.)	Elemental analysis Found (Calcd)%			Colour	M.P.	μeff B.M. (R.T.)
		N	C	H			
Ligand (PASPAT)	$C_{22}H_{16}N_4OSCl_2$ (384.83)	--	68.66 (68.72)	4.09 (4.19)	Dark red	168^{0}C	--
Co_2 (PASPAT)$_2$ CI_2	$Co_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (955.61)	(12.15) (12.33)	55.19 (55.29)	3.09 (3.16)	Brown red	280^{0}C	3.66
Ni_2 (PASPAT)$_2$ CI_2	$Ni_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (964.83)	(12.24) (12.29)	55.29 (55.32)	3.07 (3.16)	Light brown	<300^{0}C	2.95
Cu_2 (PASPAT)$_2$ CI_2	$Cu_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (968.49)	13.03 (13.17)	55.70 (54.76)	3.04 (3.13)	Light green	175^{0}C	1.87
Zn_2 (PASPAT)$_2$ CI_2	$Zn_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1062.55)	13.41 (13.49)	54.51 (54.56)	3.07 (3.12)	Brown	220^{0}C	--
Cd_2 (PASPAT)$_2$ CI_2	$Cd_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1238..93)	21.02 (21.15)	49.64 (49.73)	2.72 (2.82)	Light brown	<300^{0}C	--
Hg_2 (PASPAT)$_2$ CI_2	$Hg_2(C_{44}H_{30}N_8O_2\ S)Cl_2$	32.28 (32.28)	42.59 (42.65)	2.37 (2.44)	Light black	<300^{0}C	--
Ligand (PCPASPAT)	$C_{22}H_{16}N_4OSCl_2$ (146.87)	--	62.99 (63.07)	3.09 (3.16)	Red brown	150^{0}C	--
Co_2 (PCPASPAT)$_2$ Cl_2	$Co_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1024.50)	11.38 (11.50)	51.51 (51.38)	2.66 (2.75)	Dark pink	220^{0}C	3.68
Ni_2 (PCPASPAT)$_2$ Cl_2	$Ni_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1024..6)	11.41 (11.46)	51.45 (51.60)	2.66 (2.75)	Dark red	275^{0}C	2.90
Cu_2 (PCPASPAT)$_2$ Cl_2	$Cu_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1033.72)	12.25 (12.29)	51.02 (51.12)	2.68 (2.73)	Olive green	195^{0}C	1.82
Zn_2 (PCPASPAT)$_2$ Cl_2	$Zn_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1036.38)	12.52 (12.60)	50.73 (50.93)	2.66 (2.72)	Light brown	167^{0}C	--
Cd_2 (PCPASPAT)$_2$ Cl_2	$Cd_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1131.44)	19.78 (19.86)	46.56 (46.70)	2.33 (2.40)	Light brown	260^{0}C	--
Hg_2 (PCPASPAT)$_2$ Cl_2	$Hg_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1307.82)	30.59 (30.67)	40.25 (40.40)	2.07 (2.15)	Dark black	200^{0}C	--
Ligand (PTASPAT)	$C_{22}H_{18}N_4OS$ (398.43)	---	69.12 (69.32)	4.45 (4.54)	Red Brown	120^{0}C	--
Co_2 (PTASPAT)$_2$ CI_2	$Co_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (983.66)	11.78 (11.98)	56.01 (56.11)	3.40 (3.48)	Dark brown	248^{0}C	3.63
Ni_2 (PTASPAT)$_2$ CI_2	$Ni_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (983.22)	11.78 (11.94)	56.10 (51.18)	3.39 (3.48)	Light red	215^{0}C	2.97
Cu_2 (PTASPAT)$_2$ CI_2	$Cu_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (992.88)	12.70 (12.79)	55.60 (55.64)	3.58 (3.45)	Olive green	140^{0}C	1.80
Zn_2 (PTASPAT)$_2$ CI_2	$Zn_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (996.54)	13.02 (13.11)	55.40 (55.43)	3.34 (3.43)	Light brown	270^{0}C	--
Cd_2 (PTASPAT)$_2$ CI_2	$Cd_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1090.60)	20.50 (20.55)	47.78 (47.90)	3.01 (2.58)	Dark brown	197^{0}C	--
Hg_2 (PTASPAT)$_2$ CI_2	$Hg_2(C_{44}H_{30}N_8O_2\ S)Cl_2$ (1265.98)	31.61 (31.68)	41.16 (41.26)	2.58 (2.70)	Dark black	<300^{0}C	--

It is seen that in many complexes this hand has been contemplated to be due to the Cu-Cu linkage. Keeping in view the observed magnetic moments, the band observed at about 26000 cm may be due to n-* transitions of diazo ligands. Thus, copper complexes under study appear to have a distorted tetrahedral geometry [18]. Zinc(II). cadmium(II) and mercury(II) complexes being d^{10} ions are diamagnetic do not show d-d-transitions and are isostructural while Co(II). Ni (II) and Cu(II) complexes, are tetrahedral[19].

Table 2: Bacteriological results of Schiff bases and their metal complexes.

Ligand/Complex	**Eschericha coli**	**Bacillus subtills**	**Klebsiella Pneumoniae**	**Pseudomonas aerogens**	**Salmonella Paratyphi B**	**Staphylococcus aureus**	**Proteus vulgaris**
Ligand (PASPAT)	-	+++	+	+	-	++	+
Co$_2$ (PASPAT)$_2$ CI$_2$	+	+	+	++	+	+	+
Ni$_2$ (PASPAT)$_2$ CI$_2$	++	++	++	+	+	+	+
Cu$_2$ (PASPAT)$_2$ CI$_2$		+	-	++	+	++	+
Zn$_2$ (PASPAT)$_2$ CI$_2$	-	+++	-	-	+	+	+
Cd$_2$ (PASPAT)$_2$ CI$_2$	++	+++	+	+	+	++	+
Hg$_2$ (PASPAT)$_2$ CI$_2$	-	++	++	+++	++	++	-
Ligand (PCPASPAT)	-	-	+	-	-	++	-
Co$_2$ (PCPASPAT)$_2$ Cl$_2$	+	++	+	-	+	+	++
Ni$_2$ (PCPASPAT)$_2$ Cl$_2$	++	-	++	-	++	-	++
Cu$_2$ (PCPASPAT)$_2$ Cl$_2$	++	++	-	+	+	+	+
Zn$_2$ (PCPASPAT)$_2$ Cl$_2$	+	++	+	+	+	-	++
Cd$_2$ (PCPASPAT)$_2$ Cl$_2$	+	+	+++	+	--	+	+
Hg$_2$ (PCPASPAT)$_2$ Cl$_2$	+	++	+++	+	++	++	+
Ligand (PTASPAT)	-	++	+	-	++	+	+
Co$_2$ (PTASPAT)$_2$ CI$_2$	++	+	+	-	++	+	+
Ni$_2$ (PTASPAT)$_2$ CI$_2$	++	+	++	+	+	++	-
Cu$_2$ (PTASPAT)$_2$ CI$_2$	+	-	-	+	++	+	+
Zn$_2$ (PTASPAT)$_2$ CI$_2$	+	-	-	+	++	-	++
Cd$_2$ (PTASPAT)$_2$ CI$_2$	+++	+	+	++	+	+	++
Hg$_2$ (PTASPAT)$_2$ CI$_2$	+++	+	+	+	++	+	++

Magnetic moments at room temperature for the complexes under study are given in Table 1. All the complexes μ_{eff} values were found to be lower than the normal values indicating a dimeric or polymeric structure. Considering structures of ligands, two metal centres are not so close to each other to have exchange interaction but there is an anti-ferromagnetic interaction due to the polarization of spins of the unpaired electrons of the metal atoms and the electrons of nitrogen atom, which is then transmitted via the π-electron system of the benzene ring to the second metal atom. Cu (II) and Ni (II) complexes with some Schiff bases are reported to have such type of interaction [20]. All the metal complexes were found to be insoluble in water but soluble in DMSO and DMF. The molar conductance values for all the metal complexes in DMF solutions fall in the range of 8.15 to 39, 69 ohm^{-1} cm^{-1} mol^{-1}, indicating them to be non- electrolytes. The slightly high conductivity value may be due to partial solvolysis of the chloride ions. On the basis of all our observations, it appears that complexes under present study may have a dimeric structure with four coordinated metal centre. All the ligands and their respective metal complexes were screened against selected fungi and bacteria to examine their antimicrobial properties. The results of Schiff base and their metal complexes are given in Table -2 reveal that the metal complexes are more potent than their parent ligands and hence may serve as vehicles for activation of the ligands as principle cytotoxic species [21].

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