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SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF Cr(III), Co(II), Ni(II) AND Cd(II) COMPLEXES WITH 4-AMINOANTIPYRINE AND THIOCYANATE ION AS LIGANDS

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ABSTRACT

The complexes of Cr(III), Co(II), Ni(II) and Cd(II) were synthesized with the ligands 4-aminoantipyrine (4-AAP) and thiocynate ion. The complexes were characterized by elemental analysis, electrical conductivity measurement, IR, ^{1}H-NMR and ^{13}C-NMR spectra. The antimicrobial, antifungal activities of 4-aminoantipyrine and its complexes were tested against the microorganisms such as *staphylococcus aurous, E.coli, Pseudomonas aeruginosa* and *Candida albicance* by disc diffusion method. The antimicrobial studies of the ligand 4-aminoantipyrine and its metal complexes indicate that the metal complexes showed greater antimicrobial activity than the free ligand.

KEYWORDS: 4-aminoantipyrine, thiocynate ion, antimicrobial, antifungal, metal complexes.

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INTRODUCTION

Heterocyclic compounds are important classes of compounds in Organic Chemistry. Many of them have biological activities like antimicrobial, antifungal, anti-inflammatory and anticancereous etc., One of the important pyrazole derivatives is 4-aminoantipyrine. The structural units of 4-aminoantipyrine play a vital role in Medicinal and Agricultural Chemistry[1-2]. 4-aminoantipyrine and its complexes have a variety of applications in analytical, biological and pharmacological areas[3-8]. 4-aminoantipyrine derivatives are also used as hair colour additives[9]. The present study aims at synthesizing and characterizing the complexes of 4-aminoantipyrine with Cr(III), Co(II), Ni(II) and Cd(II) ions.

MATERIALS AND METHODS

4-aminoantipyrine was purchased from Alfa Aesar Company and the solvents viz., DMSO, DMF, methanol, ethanol and metal nitrates used were of analar grade. Elemental analysis of the metal complexes was carried out by using a CHNS (O) analyzer (Flash EA1112 series model instruments). The molar conductance measurements were conducted by using 10^{-3} M solution of the metal complexes in acetonitrile solution on Systronic Conductivity Bridge 304 at 30°C. The IR spectra of the ligand (4-AAP) and its complexes were obtained on KBr pellets with a Shimadzu FT IR-8400S spectrometer. ^{1}H-NMR and ^{13}C -NMR spectra of 4-AAP and its cadmium complex were recorded on a 500MHz FT NMR spectrometer in DMSO-d6 using tetramethylsilane as internal reference. The antimicrobial and anti fungal studies were carried out by disc diffusion method.

Synthesis of metal complexes

The complexes were prepared by mixing proper proportions of each metal nitrate with 4-aminoantipyrine and potassium thiocyanate under microwave condition in methanol/ethanol medium.

Table 1
Preparation of metal complexes

S.No	Weight of metal nitrates $[M(NO_3)_x.yH_2O]$ in 20ml methanol	Weight of 4-AAP in 20 ml methanol	Condition	Colour of Solution	Weight of potassium thiocyanate in 10 ml ethanol	condition	Complex
1.	1g (2.5mmol) $[Cr(NO_3)_3.9H_2O]$	1.54g (7.53 mmol)	Microwave irradiation for 10 seconds	Dark green solution	0.75g (7.5mmol)	Microwave irradiation for 10 seconds	Green precipitate
2.	1g (3.4mmol) $[Co(NO_3)_2.6H_2O]$	2.83g (13.80mmol)		Dark red solution	0.70g (7.0mmol)		Brownish red precipitate
3.	1g (3.4mmol) $[Ni(NO_3)_2.6H_2O]$	2.83g (13.82mmol)		Dark green solution	0.70g (7.0mmol)		Pale green precipitate
4.	1g (3.22mmol) $[Cd(NO_3)_2.4H_2O]$	1.32g (6.45 mmol)		Yellow solution	0.65g (6.5mmol)		Colourless precipitate

RESULTS AND DISCUSSION

The prepared complexes, except that of cadmium were coloured. All are soluble in DMSO and DMF. The low values of molar conductance indicate the nonelectrolyte behavior of complexes, (i.e.) they are (1:0) type complexes[9-14]. Based on the elemental analysis data, the composition of metal complexes are assigned. The analytical data for the complexes are summarized in table-2. The IR Spectral data of 4-AAP and its metal complexes have been presented in table-2. In the spectrum, the strong band at 3425 to 3431 cm^{-1} indicates the presence of amino group in it, which gets shifted to 3425 to 3510 cm^{-1} in metal complexes, ensuring the complexation. The value at 1650 cm^{-1} indicates v C=O in 4-aminoantipyrine which is shifted to 1608--1633 cm^{-1} in complexes[13]. The values at 2083cm^{-1} to 2108cm^{-1} show v SCN[15-16] which are present in the metal complexes. The weak band at 530-560 cm^{-1} and 420-450 cm^{-1} corresponds to the v M-O and v M-N bonds respectively[10-17].

Table 2
Analytical data of metal complexes

S.No	Compound	C%	H%	O%	N%	Conductivity ($ohm^{-1}cm^2\ mol^{-1}$)	colour	Yield %
1.	$[Cr\ L_3(SCN)_3]$	51.67 (51.70)	4.62 (4.66)	5.72 (5.79)	20.60 (20.20)	49.30	Green	45.40
2.	$[CoL_4(SCN)_2]$	55.81 (55.87)	5.22 (5.26)	6.43 (6.47)	19.80 (19.84)	43.50	Brownish red	69.80
3.	$[NiL_4(SCN)_2]$	55.91 (55.85)	5.24 (5.19)	6.45 (6.49)	19.89 (19.92)	48.80	Pale green	69.00
4.	$[Cd\ L_2(SCN)_2]$	45.35 (45.31)	4.03 (3.98)	5.04 (5.01)	17.60 (17.55)	61.20	Colourless	43.54

L= 4-Aminoantipyrine (Theoretical values are given in parenthesis)

Table 3
IR spectral data of 4-aminoantipyrine and its metal complexes (cm^{-1})

S.No	ligand/complex	v (NH_2)	v (Ar-H)	v (C=O)	v (C=C)	v (M-N)	v (M-O)	v (SCN)
1.	L	3431	2914	1650	1587	-	-	-
2.	$[Cr\ L_3(SCN)_3]$	3429	2925	1608	1560	553	450	2073
3.	$[Co\ L_4(SCN)_2]$	3429	2926	1627	1575	509	447	2073
4.	$[Ni\ L_4(SCN)_2]$	3441	2926	1633	1579	547	451	2092
5.	$[Cd\ L_2(SCN)_2]$	3506	2925	1630	1575	501	460	2083

L= 4-aminoantipyrine

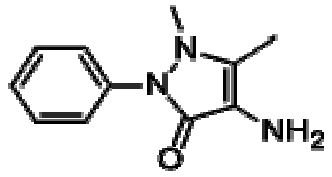

Figure 1
Structure of the 4-aminoantipyrine

^{1}H-NMR spectra

The ^{1}H-NMR spectrum of 4-aminoantipyrine shows three signals between δ 7.50-7.25 corresponds to aromatic protons of phenyl ring get Shifted to down field in the complex. The δ $C\text{-}CH_3$ proton is observed at 2.10ppm and δ $N\text{-}CH_3$ is observed at 2.80ppm.

^{13}C-NMR spectra

In the ^{13}C-NMR spectrum the expected chemical shift values are 11. But in spectrum there are nine chemical shift values which are corresponds to the nine carbon atoms in the ligand. The δ values at 120ppm indicate the carbon atom of thiocynate ion in the complex.

Table 3
^{1}H-NMR spectral data of 4-aminoantipyrine and its cadmium complex (ppm)

S.No	ligand/complex	δ Ar-H	δ NH_2	δ N-CH_3	δ C-CH_3
1.	L	7.30-7.50	3.90	2.80	2.10
2.	[Cd $L_2(SCN)_2$]	7.30-7.50	3.90	2.80	2.10

L= 4-aminoantipyrine

Table 4
^{13}C- NMR- spectral data of 4-aminoantipyrine and cadmium complex (ppm)

S No	ligand/ Complex	C1	C2	C3	C4	C5	C6	C7	C8	C9
1.	L	136	122	129	125	161	136	136	10.3	40.0
2.	[Cd $L_2(SCN)_2$]	136	122	129	125	162	136	133	10.4	40.0

L= 4-aminoantipyrine

Antimicrobial activity

Many Schiff bases derived from 4-aminoantipyrine shows bacteristatic and bactericidal activites[17] .These are active against various microorganisms[18-20]. The antimicrobial and antifungal activities of 4-aminoantipyrine and its metal complexes were tested against the following microorganisms: *E.coli, P.aurginosa, S.aureus and C.albicance*. The test solution was prepared in DMSO. Ketokonazole and amiokacin were used as standards for the tested microorganisms. The zone inhibition was measured in mm and it is presented in table-5**.** The Cd(II) complex is more active against *S.aureous* and *C.albicance* when compared with the Cr(III) and Ni(II) complexes.

CONCLUSION

The data obtained from elemental analysis, electrical conductivity, IR, ^{1}H-NMR and ^{13}C-NMR spectral studies proved by the formulae of the metal complexes. The antimicrobial and antifungal activities of the ligand and its metal complexes were tested against various microorganisms. The values indicate that the complexes have higher activity against the bacteria and fungus than the free ligand.

Table 5
Antibacterial and antifungal activities data for the 4-AAP and its metal complex

S.No	ligand/Complex	*E.coli* (G-)	*P.aurginosa* (G-)	*S.aureus* (G+)	*S.cocei* (G+)	*C.albicance* (*Fungus*)
1.	L	10	16	03	04	14
2.	[Cr $L_3(SCN)_3$]	02	11	11	05	10
3.	[Co $L_4(SCN)_2$]	02	05	08	11	11
4.	[Ni $L_4(SCN)_2$]	08	05	06	10	09
5.	[Cd $L_2(SCN)_2$]	10	09	16	10	19

L=4-AMINOANTIPYRINE

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