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MICROWAVE IRRADIATED SYNTHESIS, SPECTRAL, ANTIBACTERIAL AND ANTIFUNGAL CHARACTERIZATION OF Zn(II) and Cd(II) COMPLEXES WITH 2,4-THIAZOLIDINEDIONE AND BENZOATE ION

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ABSTRACT

Transition metal complexes of Zn(II) and Cd(II) with 2,4-thiazolidinedione (TZD)and benzoate ion(BEN) have been synthesized under microwave irradiation and characterized by elemental analysis, metal estimation, molar conductance, UV-Visible, IR, Far-IR and NMR spectral studies. Composition and non-electrolytic nature (1:0 type) of the complexes were confirmed by the elemental analysis, metal estimation and molar conductance values. The probable geometry of the complexes was arrived from the UV spectral data. IR and Far-IR spectra of the complexes confirmed the TZD coordination through nitrogen atom whereas benzoate ion can coordinate through the oxygen atom. The NMR spectra of the complexes are confirmed the entry of the ligand into the coordination sphere of the metal ions. The antibacterial and antifungal activities of various microorganisms viz., *Chromo Burcol, salmonella, S.aures, seratia, C.albicans, Aspergilus* were studied at various concentrations (30 & 50 ml) by disc diffusion method. All the complexes show the higher activity than the free ligand.

KEYWORDS: 2,4-thiazolidinedione, Benzoate ion, Metal complexes Microwave, Microorganisms.

INTRODUCTION

2,4-thiazolidinedione (TZD) belongs to a pharmacologically important class of heterocyclic compounds used for the treatment of type-2 diabetes.[1-3] TZD derivatives lower the plasma glucose levels by acting as ligands for γ-peroxyzome proliferators-activated receptors.[4-5]In addition, this class of heterocyclic compounds possesses various other biological activities such as antihyperglycemic, antimicrobial, anti-inflammatory, anticonvulsant and insecticidal, etc., [6-8] TZDs are also known for lowering the blood pressure and thereby reducing chances of heart failure and micro-albuminuria in patients with type-2 diabetes.[9-10] A survey of literature reveals that metal complexes of many drugs have been found to be more effective than the drug alone.[11-13]Therefore much attention is given to the use of TZD due to its high complexing nature with essential metals. On the other hand, microwave irradiation now a day is an accepted tool for accelerating the organic and inorganic reactions. It leads to high reaction selectivity and utilization of minimum amount of solvents. It is an eco-friendly technique.[14-17] This paper deals with the microwave assisted preparation and spectral characterization of Cr(III) using TZD and benzoate ion (BEN) as ligands.

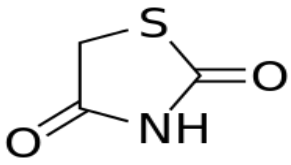


Figure -1

Structure of 2, 4-thiazolidinedione

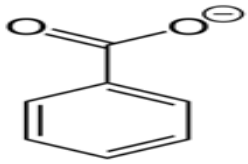


Figure- 2

Structure of benzoate ion

EXPERIMENTAL

1. MATERIALS

2,4-thiazolidinedione (Merck), Zinc nitrate, Cadmium nitrate, DMSO, DMF, methanol and ethanol were of AnalaR grade and used as such without further purification.

2. METHOD

1. Preparation of Zn(II) complex

Zinc nitrate 1.00g (2.50 mmol) dissolved in methanol, 2,4-thiazolidinedione 0.90 g (7.47 mmol) in methanol was added in drops with constant stirring; The mixture was irradiated in a microwave oven for about 10 sec. Then sodium benzoate 1.08 g (7.50 mmol) in ethanol was added to the above solution and the whole mixture was irradiated in a microwave oven for about 10 sec. The precipitated complexes was filtered, washed with ethanol and dried.

2. Preparation of Cd(II)complex

Cadmium nitrate 1.00g (2.50 mmol) dissolved in methanol, 2,4-thiazolidinedione 0.90 g (7.47 mmol) in methanol was added in drops with constant stirring; The mixture was irradiated in a microwave oven for about 10 sec. Then sodium benzoate 1.08 g (7.50 mmol) in ethanol was added to the above solution and the whole mixture was irradiated in a microwave oven for about 10 sec. The precipitated complexes was filtered, washed with ethanol and dried.

C) Instrumental techniques

The elemental analysis of the complexes was carried out by using (Thermo Finnegan make, Flash EA1112 Series Instrument) CHNS (O) analyzer. The molar conductance measurements were conducted using 10^{-3} M solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge 304 at 30°C. The UV spectra of Zn(II) and Cd(II) complexes were recorded on a Varian make, Cary 5000 model, UV-visible Spectrophotometer. The IR spectra of the ligands and their complexes were recorded on a Perkin Elmer, Spectrum RX-I, FT- IR spectrometer in 4000-400 cm^{-1} range with KBr pellet technique. The Far-IR Spectra of the complexes was recorded by Bruker 3000, FT- IR Spectrometer. The ^{1}H NMR and $^{[13]}C$ NMR spectra of the ligand and its complexes were recorded by 500MHz, FT-NMR Spectrometer in DMSO-d6 using TMS as internal standard. The antibacterial and antifungal activities of the TZD and its complexes were recorded by Kirby Bauer disc diffusion method at various concentration (50 and 100 ml) using Amikacin and Ketoconazole as standards and DMSO as solvent.

RESULTS AND DISCUSSION

Analytical data

The elemental analytical data were in good agreement with the calculated values. From the results of elemental analysis and metal estimation, the formulae of the complexes is given as $[Zn(BEN)_2(TZD)_2]$ and $[Cd(BEN)_2(TZD)_2]$. The molar conductance value (91.2 and 76.6$ohm^{-1}cm^2mol^{-1}$) indicate the non electrolyte (1:0 type) of the complexes.

UV spectra of Zn(II) and Cd(II) complexes

The Zn(II) and Cd(II) ions completely filled 3d orbitals in the absence of unpaired electrons in the d orbital. The absence of d-d transition in the complex the UV spectra of Zn(II) and Cd(II) complex exhibit λmax value at 288nm and indicating the CT spectra of the complexes.

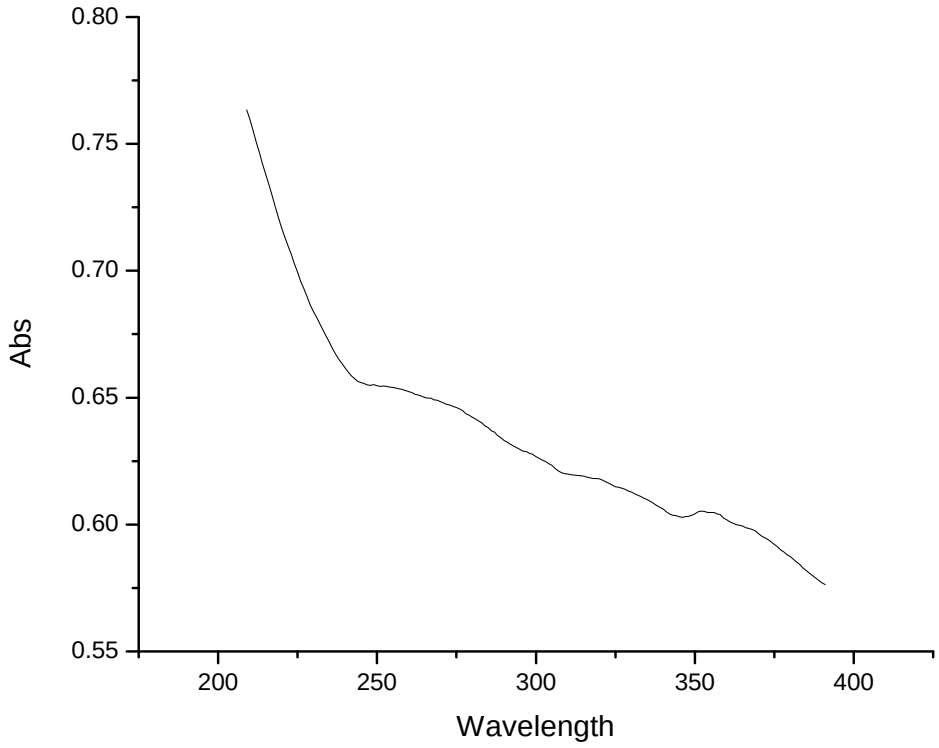


Figure-3: UV-Visible spectrum of [Zn(TZD)$_2$(BEN)$_2$]

IR and Far IR Spectra

The IR spectra give information about the functional groups present in the ligand which are entering into the co ordination sphere. The IR spectra of the free TZD showed v(C=O)at 3437cm^{-1},v(N-H) at 3452cm^{-1} and v(C-N) at 1286 cm^{-1}. The v(N-H) stretching frequency gets broadened in the Zn(II) and Cd(II) complexes at 3250cm^{-1} and 3626cm^{-1}.the benzoate ions shows the asymmetric and symmetric stretching vibrations of benzoate group in the region (1409-1547cm^{-1}) which get broadened. These observations indicate that the ligands have entered in to the coordination sphere of the Zn(II) and Cd(II) complexes. Zn(II) complexes at 1409cm^{-1} and at 1457cm^{-1} in Cd(II) complexes. Complexes in the far- IR spectrum, M-N coordinate of TZD atcm^{-1} and M-O coordination of benzoate at 419 cm^{-1} also shift at 450cm^{-1} and at 366cm^{-1} in Zn(II) and Cd(II) complexes respectively, confirm the ligating atoms of both the ligands.

^{1}H NMR Spectra of Zn(II) and Cd(II) Complexes

The 1H-NMR Spectrum of ligand 2,4 thiazolidinedione shows the N-H group chemical shift at 11.99 ppm and C-H group shift at 4.31 ppm. Benzoate ligand shows the aromatic proton

chemical shift values at 7.50ppm. In Zn(II) and Cd(II) Complexes the N-H proton value is shifted to downfield field at 11.45 ppm and 11.47ppm. and C-H value shifted to downfield 4.30ppm and 4.29ppm respectively. The benzoate aromatic chemical shift value 7.50-7.90 is shifted to down field in the complexes. These observation indicate the types of protons and entry of the ligands into the coordination sphere of the complexes.

^{13}C- NMR Spectra of Zn(II) and Cd(II) Complexes

The ^{13}C-NMR spectrum of free TLD shows the following chemical shift values (N=C=O, 170 ppm), (S-C, 37.2ppm) (S,C=O,167ppm) and the ^{13}C –NMR spectrum of benzoate ion shows the ortho carbon at 127-129ppm and meta carbon at 133 ppm. In Zn(II) and Cd(II) complexes all the above values get shifted slightly to downfield except N=C=O (170.7 ppm) except carbon atom.

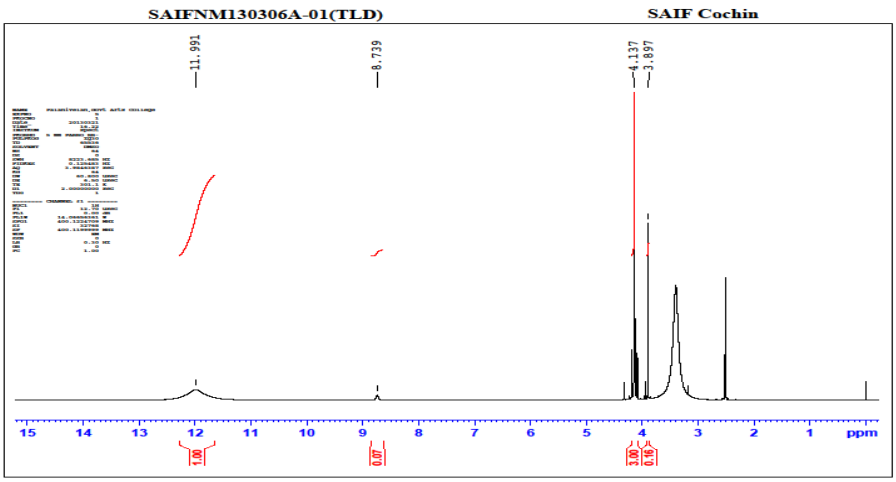


Figure.4 ^{1}H-NMR spectrum of TZD

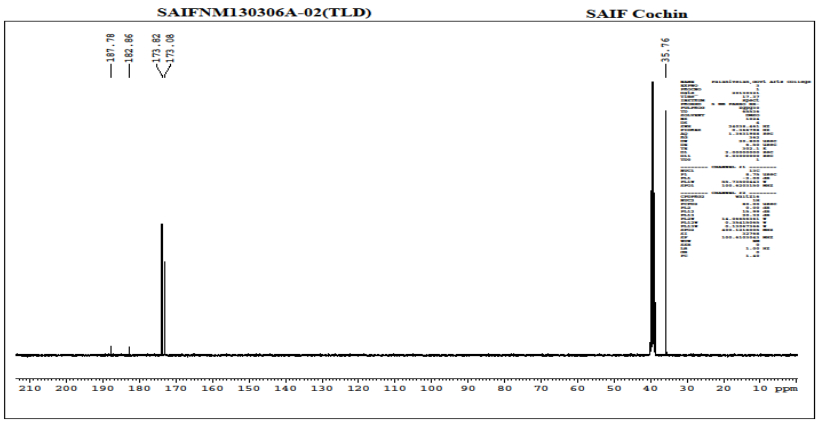


Figure.5 ^{13}C NMR spectrum of TZD

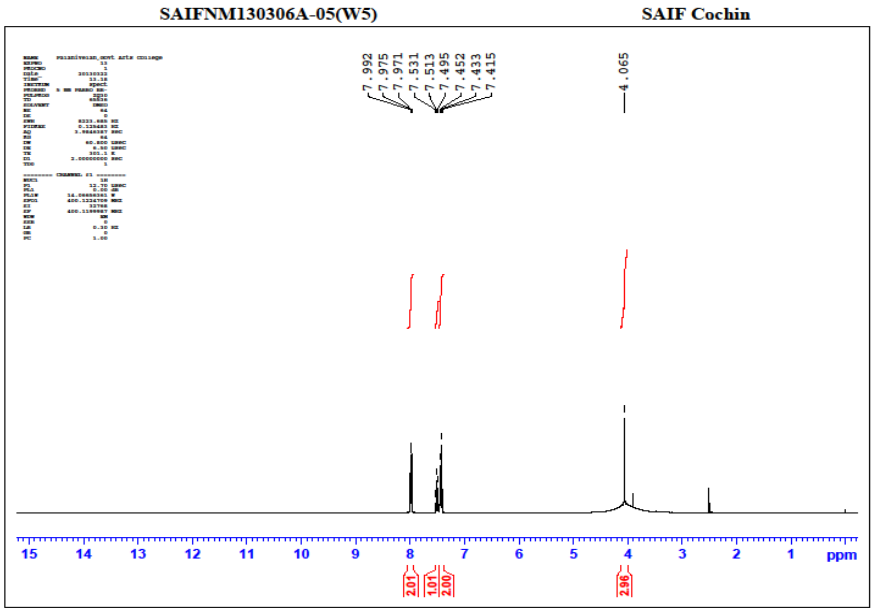


Figure-6 ^{1}H-NMR spectrum of Cd(II) complex

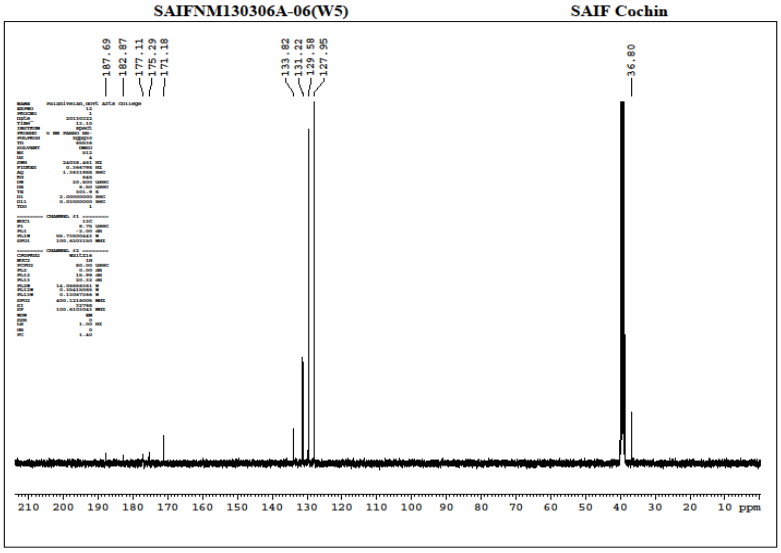


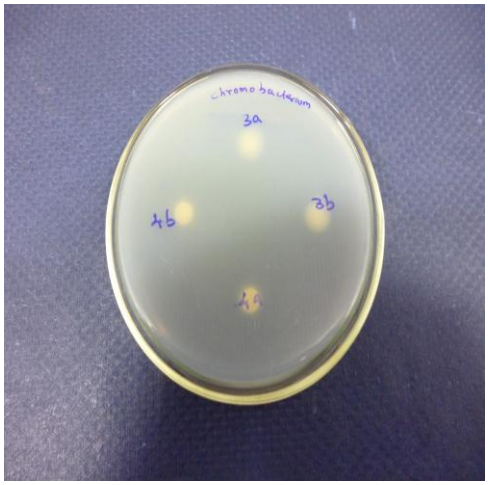
Figure-7 ^{13}C-NMR spectrum of Cd(II) complex

Biological activities[15]

The antibacterial and antifungal activities of TZD and its Zn(II) and Cd(II) complexes were determined by disc diffusion method by using Amikacin and ketoconazole as standards at 30µg/l and 50µg/l concentration. The following microorganisms were used: *Chrombactor, Burkol, solmonillatyfi, s.aurier, serratia, c.albicance* and *A.niger.*

Table-1: Antimicrobial activity data for the complexes

S.No.	TZD/Complex	Conc. (µg/l)	Microorganisms						
			chromo	***burkol***	**salmonella**	***S.aureus***	***Serratia***	***C.albicance***	***Aspergillus***
1	TZD	30	20	12	10	10	13	12	07
		50	22	16	15	12	15	13	09
1	$[Zn(TZD)_2(BEN)_2]$	30	23	15	11	13	14	12	07
		50	28	19	16	19	19	17	12
2	$[Cd(TLD)_2(BEN)_2]$	30	17	12	05	11	14	04	05
		50	25	18	12	18	17	05	05



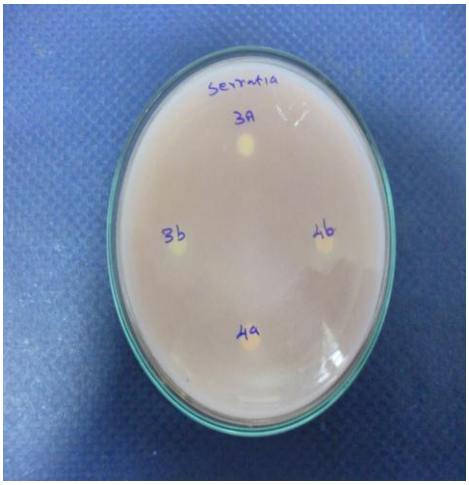


Fig.8 Zone of inhibition of $[Zn(TZD)_2(BEN)_2]$ Zone of inhibition of$[Cd(TLD)_2(BEN)_2]$

The results indicate that the complexes are highly active against the Microorganisms as compare to the ligands.

CONCLUSION

Cd(II) and Zn(II) complexes with TZD and benzoate ion (BEN) ion were prepared under microwave irradiation and characterized by various physico-chemical and spectral methods. The molecular formulae of the complexes are $[Zn(BEN)_2(TZD)_2]$ and $[Cd(BEN)_2(TZD)_2]$. The probable geometries of the complexes are square planar and pseudotetrahedral respectively.

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