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Synthesis, charectrization and antimicrobial activity of bis(Hydroxyisonitrosobenzoylacetone) thiocarbohydrazone with zinc(II), mercury(II), tin(II) and lead(II) complexes

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Abstract
Ligand Bis (hydroxyisonitrosobenzoylacetone) thiocarbohydrazone, $(HINBA)_2$ tcz have been synthesized by the interaction of thiocarbohydrazone with isonitrosobenzoylacetone in 1:2 molar ratio carried out in presence of methanol. The metal complexes of Zn(II), Hg(II), Sn(II) and Pb(II) with the ligand Bis(hydroxyisonitrosobenzoylacetone)thiocarbohydrazone have been prepared and characterized with the help of some physicochemical methods such as elemental analyses, magnetic susceptibility, IR, PMR, spectral data, thermal analysis and electrical conductance measurements. It has been found that the ligand and complexes are non- electrolytic in nature. Spectral measurements showed that the ligand was coordinated to metal ion through carbonyl and oximino groups. The magnetic moments and electronic, spectral data indicate octahedral geometry for the metal complexes. The newly prepared ligand and its metal complexes are subjected to antimicrobial against selected microbial strains.

Keywords: Antimicrobial activity, Zinc (II), Mercury (II), Tin (II), Lead (II), metal complexes, synthesis, characterization

Introduction

Metal complexes of β-diketone as well as thio compounds have been widely used in coordination chemistry due to their versatility and antimicrobial activity [1-3] Isonitrosobenzoylacetone belongs to isonitrosoketone or carbonyl monooxime which is responsible for the formation of coloured complexes with various transition metal ions [4-6] It is also used for the rapid extraction and spectrophotometric determination of metal ions [7-8] Thiocarbohydrazide is useful in analytical chemistry for the identification and estimation of both organic and inorganic compounds [9]. Antitubercular activity of thiocarbohydrazide have been studied *in vitro* against Mycobacterium tuberculosis (BCG strain)10 Both the hydrazine groups of thiocarbohydrazide are very reactive and predominantly form his derivatives with aldehydes and ketone [10-11]. The present investigation mainly deals with the synthesis and characterization of mononuclear Zn(II), Hg(II), Sn(II) and Pb(II) complexes using multidentate ligand Bis(hydroxyisonitrosobenzoylacetone) thiocarbohydrazone (HINBA), tcz derived from condensation of isonitrosobenzoylacetone with thiocarbohydrazone. The preliminary screening of the ligand as well as its metal complexes for antibacterial, antifungal and antitubercular activity is reported.

Materials and Methods

Physical Measurements: The elemental microanalyses of C, H, N and S were carried out with a Thomas and Coleman Analyzer-Carlo Erba 1106 while the metal content in the complexes were determined by standard methods. The molar conductance values of the complexes were measured in Dimethylformamide (DMF) (10^{-3} M solution) using an Elico digital conductivity meter (CM-180). IR spectra was recorded on a Perkin-Elmer 1600 Series FTIR spectrometer in KBr pellets. PMR was recorded on a Bruker AMX-500 spectrometer in DMSO-d_δ and chemical shifts are reported in δ unit relative to tetramethyl silane (TMS) used as internal standard. Magnetic susceptibility measurements were carried out by employing the Gouy's method using $Hg[Co(SCN)_4]$ as a calibrant. The effective magnetic moments were calculated after diamagnetic correction for ligand component using Pascal's constants [12]. Thermogravimetric studies of the complexes were made by recording the change in weight on increasing the temperature from room temperature to 700 °C at a heating rate of 10 °C per minute. All the chemicals used were of AR grade. The C.P. grade chemicals, whenever used, were purified by standard methods. Isonitrosobenzoylacetone [4] and thiocarbohydrazone [13] were prepared in the laboratory by the reported methods.

Synthesis of Ligand Bis(hydroxyisonitrosobenzoylacetone) thiocarbohydrazone $(HINBA)_2$ tcz: The reaction between thiocarbohydrazone (1.06 g, 0.01 mole) and isonitrosobenzoyl- acetone (3.82 g, 0.02 mole) was carried out in 50 ml of methanol, in the presence of a trace amount of concentrated hydrochloric acid. The reaction mixture was stirred for one hour at room temperature. The white solid was separated by filtration, and recrystallised from ethanol. Yield, 4.02 g (88%).

Synthesis of $[Zn(INBA)_2$ tcz$].H_2O$: A quantity of zinc chloride 1.36 g (0.01 mole) dissolved in 50 ml of distilled water was added slowly to a solution of 4.52 g (0.01mole) of $(HINBA)_2$ tez in 50 ml of methanol. The mixture was refluxed for two hours, cooled properly and poured on the crushed ice. A green colored compound was separated. It was filtered and washed with distilled water followed by 40% methanol and dried in vacuum. Yield, 4.68 g (87%).

Synthesis of [Hg(INBA)$_2$ tcz).H$_2$O : A solution of mercury chloride 2.71g (0.01mole) dissolved in 50 ml of distilled water was added slowly to a solution of 4.52 g (0.01mole) of (HINBA)$_2$ tez in 50ml methanol. The mixture was refluxed for two hours, cooled properly and poured on the crushed ice. A brown colored compound was separated. It was filtered and washed with distilled water followed by 40% methanol and dried in vacuum. Yield, 5.46 g (81%).

Synthesis of [Sn(INBA)$_2$tez].H$_2$O: A quantity of stannous chloride 2.78 g (0.01 mole) in 50 ml of distilled water was added slowly to a solution of 4.52 g (0.01 mole) of (HINBA)$_2$tez in 50 ml of methanol. The mixture was refluxed for two hours, cooled properly and poured on the crushed ice. A yellow colored compound was separated. It was filtered and washed with distilled water followed by 40% methanol and dried in vacuum. Yield, 4.96 g (84%).

Synthesis of [Pb(INBA)$_2$ tcz]. H$_2$O: A solution of 1.70 g (0.01 mole) of lead chloride in 50 ml of distilled water, was added dropwise to a solution of 4.52 g (0.01mole) of (HINBA), tcz in 50 ml of methanol. The mixture was refluxed for two hours, cooled properly and poured on the crushed ice. A yellow colored compound was separated. It was filtered and washed with distilled water followed by 40% methanol and dried in vacuum. Yield, 5.58 g (82%).

Determination of antimicrobial activity: The minimum inhibitory concentrations (MIC µg mL^{-1} of the ligand and complexes were ascertained by using different biological strains such as *S. aureus, S. typhii, Candida albicans. T. mentagrophytes, T. rubrum and M. tuberculosis* according to the method described elsewhere [14].

Results and Discussion

The analytical and physical data of the ligand and its metal complexes were shown in Table-1. The complexes were brightly colored and thermally stable upto 120°C. They were insoluble in water and common organic solvents but soluble in DMF. DMSO, chloroform at room temperature [15]. The analytical data of the metal complexes indicate that the complexes have 1:1 metal-ligand stoichiometry. The values of molar conductance in DMF solution (10^{-3} M) were in the range 0.047- 0.051 ohm^{-1} cm^{2}mol^{-1} suggesting a non-electrolytic nature of the complexes [16].

Table 1: Analytical and Physical Data of the Ligand and its Metal Complexes

Compound/Empirical Formula/ (Molecular Weight)	Colour	Yield (%)	M.p. (^{0}C)	Elemental Analysis (Calcd/found)					Molar Conductance ohm^{-1} cm^2 mol^{-1}
				%M	%C	%N	%H	%S	
(HINBA)$_2$tcz $C_{21}H_{20}N_6O_4S$ (452.4)	White	88	183	-	55.70 55.49	18.56 18.45	4.42 4.32	7.07 6.92	0.045
[Zn(INBA)$_2$tcz].H$_2$O $ZnC_{21}H_{20}N_6O_5S$ (533.7)	Green	87	180	12.25 12.18	47.21 47.14	15.74 15.71	3.75 3.79	5.99 5.88	0.048
[Hg(INBA)$_2$tcz].H$_2$O $HgC_{21}H_{20}N_6O_5S$ (688.9)	Brown	81	145	29.98 29.86	37.67 37.58	12.55 12.49	2.98 2.91	4.78 4.70	0.051
[Sn(INBA)$_2$tcz].H$_2$O $SnC_{21}H_{20}N_6O_5S$ (587.1)	Red	84	128	20.21 20.16	42.92 42.85	14.30 14.22	3.40 3.33	5.45 5.40	0.047
[Pb(INBA)$_2$tcz].H$_2$O $PbC_{21}H_{20}N_6O_5S$ (675.6)	Yellow	82	172	30.66 30.58	37.30 37.24	12.43 12.34	2.96 2.91	4.73 4.66	0.049

Infrared Spectra: IR spectral data of the compounds and their assignments were shown in Table-2. The strong bands at 3482 cm and 3307 cm¹ in the ligand (HINBA), tcz are attributed to the hydrogen bonded γOH stretching frequency of the oxime group and the stretching vibrations of γNH respectively [17-18] In the spectrum of the ligand, the strong absorption peak at 1595 cm^{-1} and 1507 cm^{-1} can be ascribed to νC=N of azomethine and νC=N of oxime respectively. The characteristic absorptions of the ligand at 1668 cm and 1311 cm can be assigned to vC=0 and vC=S respectively. In the IR spectra of [Zn(INBA),tcz].H$_2$O, [Hg(INBA), tcz]. H$_2$O, [Sn(INBA),tez]. H$_2$O and [Pb(INBA), tcz). H$_2$O a broad shoulder absorption in the range 3206-3308 cm^{-1} is observed indicating the presence of coordinated water molecule in the complexes [9]. The band at 1672-1685 cm in the complexes are attributed to νC=0 stretching [19] The absorption bands in the range 1450-1554 cm^{-1} are attributed to νC-N of oxime which indicates the possibility of coordination of oximino nitrogen to the metal ion [20]. Shift in the frequencies of the groups except νC-N of azomethine [21] suggest that they are involved in the complex formation. The characteristic shift to νC-S mode was observed in the range 1301-1337 cm suggests that the thiocarbonyl sulfur is one of the bonding sites in the complexes. The appearance of νM-N and νM-O stretching frequencies further confirm the involvement of nitrogen atom of oxime and oxygen atom of carbonyl group in the complex formation.

Table 2: Infrared Spectral Data of the Ligand and its Metal Complexes. [v in cm^{-1}]

Compound	ν_{OH}	$\nu C=O$	$\nu C=N$ azomethine	$\nu C=N$ oxime	$\nu C=S$	$\nu M-N$	$\nu M-O$	$\nu M-S$
(HINBA)tcz	3482	1668	1595	1507	1311	-	-	-
[Zn(INBA)$_2$tcz].H$_2$O	3211	1678	1594	1554	1335	754	694	594
[Hg(INBA)$_2$tcz].H$_2$O	3210	1679	1595	1495	1337	764	695	593
[Sn(INBA)$_2$tcz].H$_2$O	3206	1685	1597	1450	1326	770	694	598
[Pb(INBA)$_2$tcz].H$_2$O	3308	1672	1596	1510	1301	748	689	601

PMR sipectra: The PMR data and assignments of (HINBA)$_2$ tcz are given in Table-3 The PMR spectrum of (HINBA)$_2$ tcz in DMSO-d, exhibited signal at δ12.159 which was assigned to the proton of =NOH group. Aromatic

protons were observed between δ7.245 - δ7.691 in the ligand. The ligand showed the presence of singlet signals at δ9.851 due to - NH proton. The niethyl proton of ligand was observed at δ2.167. The oximino proton was disappeared in [Zn(INBA)$_2$ tcz].H$_2$O [Hg(INBA)$_2$ tcz]. H$_2$O, [Sn(INBA)$_2$tcz]$_2$ H$_2$O and [Pb(INBA)$_2$ tcz]$_2$ H$_2$O complexes which indicates the proton of the =NOH group is replaced during complexation. The phenyl protons of complexes are observed as multiplets in the range δ7.096 - δ7.863. The methyl protons of the complexes were observed in range δ2.101 - δ2.314. The NH proton signal is not resolved and not seen in the spectra of the complexes. The signal for TMS appears at the extreme right of spectrum with 8 equal to 0 ppm.

Table 3: PMR Spectral Data of the Ligand and its Metal Complexes

Compound	PMR DMSO –d_δ /TMS (δ ppm)
(HINBA)$_2$tcz	2.167 (s, 6H 2xCH$_3$), 7.245 – 7.691 (m, 10H aromatic) 9.851 (s, 2H 2xNH), 12.159 (s, 2H 2 x NOH)
[Zn(INBA)$_2$tcz].H$_2$O	2.287 (s, 6H 2xCH$_3$), 7.263 – 7.813 (m, 10H aromatic)
[Hg(INBA)$_2$tcz].H$_2$O	2.314 (s, 6H 2xCH$_3$), 7.096 – 7.314 (m, 10H aromatic)
[Sn(INBA)$_2$tcz].H$_2$O	2.304 (s, 6H 2xCH$_3$), 7.205 – 7.863 (m, 10H aromatic)
[Pb(INBA)$_2$tcz].H$_2$O	2.101 (s, 6H 2xCH$_3$), 7.236 – 7.691 (m, 10H aromatic)
	2.101 (s, 6H 2xCH$_3$), 7.236 – 7.637 (m, 10H aromatic)

Electronic spectra: The electronic absorption spectrum of (HINBA), tcz display strong band at 28,169 and 31,746 cm^{-1} due to intra-ligand transition assignable most probably to n→ л* and л→ л* electronic transitions. The electronic absorption spectrum of [Zn(INBA)$_2$tcz]. H$_2$O, [Hg(INBA)$_2$ tcz]. H$_2$O, [Sn(INBA)$_2$tcz]. H$_2$O and [Pb(INBA)$_2$tez]. H$_2$O complexes shown intra-ligand transition band which shifted to higher wavelength than ligand band positions. Magnetic mornent of all these complexes exhibits diamagnetic nature. These evidences support the octahedral geometry of the complexes and results are shown in Table-4.

Table 4: Magnetic Moment values, Electronic Spectral data and their assignments of the Ligand and its Metal Complexes

Compound	μ_{eff}	Bands (cm^{-1})	Assignment
(HINBA)$_2$tcz	-	28, 169 31, 746	Intra-ligand transition Intra-ligand transition
[Zn(INBA)$_2$tcz].H$_2$O	Diamagnetic	32, 258 46728	Intra-ligand transition Intra-ligand transition
[Hg(INBA)$_2$tcz].H$_2$O	Diamagnetic	35, 211 46, 082	Intra-ligand transition Intra-ligand transition
[Sn(INBA)$_2$tcz].H$_2$O	Diamagnetic	35, 087	Intra-ligand transition Intra-ligand transition
[Pb(INBA)$_2$tcz].H$_2$O	Diamagnetic	46, 082	Intra-ligand transition Intra-ligand transition
		35, 714 46, 082	Intra-ligand transition Intra-ligand transition

Thermal Studies: Thermal analysis of the complexes shows that they are thermally stable to a varying degree. The complexes show a gradual but insignificant loss in weight up to 100-110°C indicating absence of any water of crystallization. The thermal analysis clearly indicates the presence of one coordinated water molecule with the central metal ion. The metal complexes initially show the loss of coordinated water in the temperature rangel 110- 180°C with further increases in temperature in the range investigated, the complexes show decomposition by fragmentation and thermal degradation of organic part of the metal complexes, finally resulting in the corresponding metal sulphides. The result of the thermal studies indicating the presence of one coordinated water molecule in metal complexes as shown in Table- 5.

Table 5: Thermo gravimetric Data for the Metal Complexes

Compound	Temp. range (^{0}C)	Weight loss in (%)		Group/Moiety Lost	Metal Sulphides Residue (%)	
		Calcd.	Found		Calcd.	Found
[Zn(INBA)$_2$tcz].H$_2$O	110-150 150-170 270-650	3.37 16.49 81.70	3.40 16.56 81.78	-H$_2$O -H$_2$O+CH$_2$N$_4$ - H$_2$O+CH$_2$N$_4$ C$_{20}$H$_{16}$N$_2$O$_4$	18.26	18.20
[Hg(INBA)$_2$tcz].H$_2$O	110-140 140-200 200-620	2.69 13.16 65.19	2.75 13.20 65.26	-H$_2$O -H$_2$O+CH$_2$N$_4$ - H$_2$O+CH$_2$N$_4$ C$_{20}$H$_{16}$N$_2$O$_4$	34.78	34.41
[Sn(INBA)$_2$tcz].H$_2$O	110-160 160-230 230-640	3.06 14.99 74.27		-H$_2$O -H$_2$O+CH$_2$N$_4$ - H$_2$O+CH$_2$N$_4$ C$_{20}$H$_{16}$N$_2$O$_4$	25.68	25.65
[Pb(INBA)$_2$tcz].H$_2$O	110-200 200-250 250-650	2.66 13.03 64.54		-H$_2$O -H$_2$O+CH$_2$N$_4$ - H$_2$O+CH$_2$N$_4$ C$_{20}$H$_{16}$N$_2$O$_4$	35.41	35.48

Antimicrobial studies: Table-6 shows the results of the antimicrobial activity test. The antimicrobial activity of ligand and complexes were screened against several microorganisms at 200 µg/mL. It was evident from the preliminary data that the compounds at screening concentration used show a strong or a moderate activity against the microorganisms tested. All complexes were more active than the ligand.

Table 6: Antimicrobial Activity (MIC mg/mL) of the Ligand and its Metal Complexes

Compound	Antibacterial Activity		Antifungal Activity			Antitubercular Activity
	1	2	3	4	5	6
(HINBA)$_2$tcz	40	40	200	200	200	200

$[Zn(INBA)_2tcz].H_2O$	40	20	40	40	40	100
$[Hg(INBA)_2tcz].H_2O$	40	40	40	40	100	100
$[Sn(INBA)_2tcz].H_2O$	20	40	40	40	40	40
$[Pb(INBA)_2tcz].H_2O$	20	40	20	40	20	40

Conclusion

Present investigation mainly deals with the synthesis characterization and antimicrobial activity of ligands and its metal complies. The metal complies of Zn(II), Ag(II), Sn(II) and *p*b(II) with the ligand Bis (Hydroxyisonitrobenzoyl acetone) Thiocarbohydrazone have been characterized with the help of physic-chemical methods. It has been found that the ligand and complexes are non-electrolytic in nature. Analytical and physical data of ligand and its metal complexes were aseertained by different biological stairs. Thiocarbohydrazone is used in analytical chemistry for the identification of organic and inorganic compound. The Infrared spectral data of metal compounds and their assignment in ligand are attributed to the hydrogen bonded of oyime groups.

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