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Benzil bisisonicotinoyl hydrazone complexes of tervalent metals Ti, Zr, Sn, Hf and Th

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ABSTRACT

Benzil bisisonicotinoyl hydrazone complexes of tervalent metals Ti, Zr, Sn, Hf, and Th have been prepared in different M: L molar ratios (2:1, 1:1 and 1:2), in different solvents (MeOH and DMF) and in different pH media. The complexes have been characterized by elemental, thermal and spectral (i.r. and electronic) analyses. Spectral studies indicate octahedral geometries. The title ligand acts as either one of the following:- Neutral bidentate (cis or skew form) chelating via the two pyridine nitrogen (complexes 1, 2) or one pyridine and one azomethine nitrogen (complex 3) Monobasic bidentate (skew) chelating via one azomethine N and enolate O, complexes (4-7). Dibasic tetradentate (cis form) chelating via the two azomethine N and the two enolate O (complex 8).

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INTRODUCTION

Isonicotinic acid hydrazide (INH) and hydrazones and their complexes are known for their biological activity as antibacterial, antitubercular and antitumour activities^[1-3]. They have been used also as analytical reagents^[3,4], moreover some transition metal complexes of isonicotinoyl hydrazone have been found to be useful in polymer coatings, inks and pigments^[5].

Transition metal complexes of related ligands, viz. acetone^[6], terephthaldehyde^[7], ohydroxyacetophenone^[8-11], acetylacetone, trifluoroacetylacetone and thionylacetone^[12], salicylaldehyde^[13,14], 2-hydroxynaphthaldehyde^[14], benzoylacetone^[15] and isatinisonicotinoyl hydrazones have been reported^[16-19]. In continuation of our work on hydrazones of INH and their complexes^[14-21], in this paper, we reported the synthesis and characterization of some tervalent metal complexes of the title ligand. The data are presented and discussed.

EXPERIMENTAL

The ligand Benzil bisisonicotinoyl hydrazone [H₂L] was prepared by reacting INH with benzil in 2:1 molar ratio. The well mixed-reactants were fused in an oven at 180 °C for ca. 1h. The product was crystallized from dioxan to remove unreacted benzil and INH. The yellow precipitate was crystallized from DMF to remove any traces of benzil monoisonicotinoyl hydrazone. The purity was confirmed by m.p., elemental analysis and t.l.c.

Preparation of the complexes

MeOH solution of the metal [IV] chloride or thorium nitrate and the ligand were mixed together in 2:1, 1:1 or 1:2 molar ratios. A few drops of NH₃ or NaOH were added to study the effect of pH on the product. Thorium complex in 2:1 M: L molar ratio was prepared in DMF to study primarily the solvent effect on the product. The reaction mixture was boiled under reflux on a water bath for at least 1h. The products precipitated

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were removed by filtration, washed several times with hot MeOH and dried under vacuo.

Characterization

Metal content were determined by a literature procedure^[22], d.t.a. curves were recorded on a Shimadzu DT-30 thermal analyzer in the rate of 10 °C.min⁻¹ in the

temperature range 30-700 °C., molar conductance was measured in DMF using Bibby conductimeter type MC1. Ir and electronic spectra were recorded on Perkin Elmer 1430 i.r. and 4β u.v.-vis. spectrophotometers and ¹H n.m.r spectra were recorded using a Varian EM-390 90 Hz DMSO as solvent. The physicochemical data are given in TABLES 1-3.

TABLE 1 : Colour, m.p., Λ_m analytical and thermal data of the ligand and its complexes

No.	Compound ¹	Colour	M.P Or (dec.) (°C)	Λ_m	Found (Calc.) %				Loss of H ₂ O% up to 135 °C	n ₁	135- 220 °C	n ₂
					C	H	N	Cl				
0	H ₂ L.1/2H ₂ O Prepared in MeOH	White	248	10.1	68.3(68.3)	4.6(4.6)	18.4(18.4)	-	2.1(2.0)	0.5	-	-
1	[Hf(H ₂ L) ₂ (H ₂ O)X]X ₃ .4H ₂ O	Orange red	>300	215	46.4(47.1)	3.9(3.9)	12.1(12.7)	11.5(10.7)	6.6(6.8)	4	1.3(1.4)	1
2	[Ti(H ₂ L)(H ₂ O)X ₃]X.5H ₂ O	Scarlet red	(205)	67	41.8(41.8)	4.1(4.3)	10.5(11.3)	19.9(19.0)	12.0(12.1)	5	2.4(2.4)	1
3	[Zr(H ₂ L)(H ₂ O)X ₈].6H ₂ O Prepared in MeOH+NH ₃	Yellow orange	(280)	41	30.3(30.5)	3.8(3.1)	8.7(8.2)	-(27.8)	10.9(10.6)	6	-	0
4	[Zr(HL) ₂ (H ₂ O)X].3H ₂ O	Orange	240	75	55.6(55.3)	4.4(4.1)	15.0(14.9)	5.8(6.3)	5.0(4.8)	3	1.7(1.6)	-
5	[Sn(HL)(H ₂ O)X ₃]	Orange red	>300	35	45.1(45.3)	3.1(3.1)	11.9(12.2)	15.1(15.5)	-	0	2.8(2.6)	1
6	[Hf(HL)(H ₂ O)X ₃].H ₂ O Prepared in DMF	Orange red	(280)	44	42.2 (41.6)	3.1 (2.8)	10.3 (11.2)	14.2 (14.2)	-	0	2.3(2.4)	1
7	[Th ₂ L(H ₂ O) ₂ X ₆] Prepared in MeOH+NaOH	Orange	>300	45	33.7(33.7)	2.4(1.9)	14.6(14.2)	-	-	0	3.2(3.2)	2
8	[TiOL(H ₂ O) ₂]	Scarlet red	(290)	42	57.7(57.1)	4.5(4.0)	15.0(15.4)	-	-	0	6.6(6.6)	2

¹X: Cl or NO₃ in case of Th complex; ² s.cm².mol⁻¹ (in DMF); n₁: no of lattice water; n₂: no of coordinated water

TABLE 2 : Electronic spectral bands (χ_{max} , nm) of the ligand and complexes.

Complex No	H ₂ L	1	2	3	4	5	6	7	8	Assignment
Band A	-	460	472	400	452	465	445	455	483	c.t arising from metal-ligand interaction
Band B	-	372	375	372	-	371	370	383	379	Intramolecular c.t. with n- π^* transition within 5-membered chelate ring
Band C	345	340	344	344	344	343	344	343	344	Intramolecular c.t. with n- π^* transition Within C=O of the INH
	336	-	-	-	331	-	336	-	-	
Band D	327	323	326	-	-	310	293	293	273	π - π^* transition of the imidol group
Band E	263	335	258	255	280	283	267	278	-	π - π^* transition of the C=N of the pyridyl ring
Band F	236	230	232	236	236	-	230	-	-	π - π^* transition of the C=N and/or phenyl ring

RESULTS AND DISCUSSION

The ligand [H₂L] may in principle exhibit keto-enol tautomerism involving the two PyCONH groups, giving three possible tautomers. It appears from the ana-

lytical data of the complexes TABLE 1 that the ligand is neutral when the preparation is made in the neutral methanol medium, monodeprotonated [HL⁻] in the weak basic medium [MeOH/NH₃] and doubly deprotonated [L²⁻] in the strong alkaline medium [MeOH/NaOH] or in a solvent of high dielectric constant [DMF]. In strong

alkaline solution, titanil complex (8) is obtained. All these complexes are diamagnetic [d^0 or d^{10}], and their colors vary from orange to scarlet red. They are air stable up to 70 °C.

Thermal analysis

Thermal data of the complexes TABLE 1 showed number of both lattice and coordinated water molecules. Complexes (1-3) prepared from neutral solution were found to be hexahydrated. On the other hand, complexes (4, 5) prepared from neutral or slightly basic solutions were found to have only one coordinated water molecule, except complex 4 which has four water molecules. While complexes 7 and 8 prepared from alkaline solution or from DMF were found to be dihydrated.

Molar conductance

The low molar conductance value in DMF [$35-45 \text{ s.cm}^2.\text{mol}^{-1}$] of the bimetal complexes (3,7) and of the monoligand complexes (5, 6, 8) show that they are non-electrolytes^[23]. On the other hand, Λ_m values for the complexes (1,2,4) are 215, 67 and 75 $\text{s.cm}^2.\text{mol}^{-1}$ indicating that they are 1:3, 1:1 and 1:1 electrolyte respectively.

Electronic spectra

The ligand shows five transitions bands. Band-A at 236, band-B at 263, band-C at 327, band-D at

336 and band-E at 345 nm. These transitions are attributed to $\pi \rightarrow \pi^*$ transition of free imide C=O, pyridine C=N and imidol C=N in a five membered H-bonded chelate ring [R_1]^[24], imide C=O in a 5-membered H-bonded chelate ring [R_2]^[25] and of C=N group localized in the coupled azomethine chromophore.

In solution, benzil exists as an equilibrium mixture of the skew and the cis tautomers, the cis form is stabilized by the formation of H-bond with a solvent molecule [S]^[26,27], the phenyl rings are nearly coplanar with the carbonyl groups^[27] Figure 1.

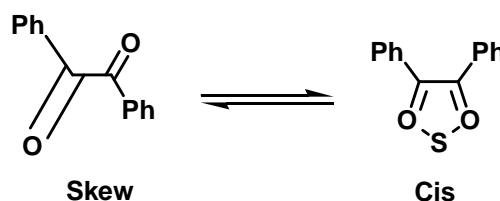


Figure 1: Benzil in skew and cis tautomers

Examination of the molecular model of benzil bisisonicotinoyl hydrazone, taking into account its electronic spectrum and assignments given before, shows that in an organic solvent [DMF], the ligand can be represented by [imide-imide] or [imidol-imidol] in tautomers of the skew form I or II or [imide-imidol] in the form III Figure 2.

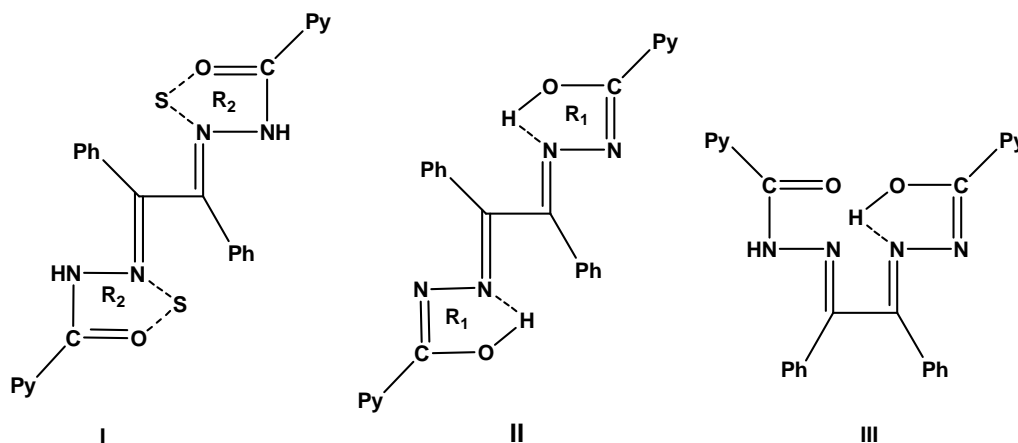


Figure 2 : Representation of the ligand by I [imide-imide], II [imidol-imidol] and III [imide-imidol]

The imidol form is more stable than the imide group due to the formation of H-chelate ring R_1 in the former. The imide group may be stabilized by the formation of H-chelate ring R_2 with a solvent molecule. In the cis form III the imide group is not solvated due to steric configuration. It is seen also that the skew form is more stable

as it has less steric configuration. The electronic spectra of the ligand and its complexes are given TABLE 2.

Band-A (483-400) nm: This band is absent in the ligand. It may be assigned to c.t. arising from metal–ligand interaction. The red shift observed in this band for complex 3 can be assigned to intramolecular H-bonded N

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atom of INH and C=O with the solvent N-S-O in a 5-membered chelate ring^[28]. The blue shift observed in the same band-A for complex 8 (483) nm may be due to more conjugation of the (C=N) around the metal ions.

The spectra of the complexes show non-ligand band B in 383-354 nm regions. Since the metal ions have either d^0 or d^{10} electronic configuration, no d-d band is expected and the last bands may, therefore be due to intramolecular charge transfer [c.t., with $n-\pi^*$ transitions within the 5-membered ring chelate ring of which the metal is a member^[29].

Band-C (344-331) nm is assigned to the intramolecular c.t. with $n-\pi^*$ transition of C=O of INH. While band-D (326-267) nm is assigned to $\pi-\pi^*$ transitions of C=N of the imidol group. Band-E 263 nm is assigned to $\pi-\pi^*$ transitions of the C=N of the pyridyl ring. This band shows hypsochromic shifts in complexes (1-3) indicating that the pyridyl group is coordinated in these complexes. On the other hand complexes 4-8 demonstrated a bathochromic shift indicating that the pyridine group is involved in more conjugated system arising from the enolization of the C=O of the imide group.

I.r and ^1H n.m.r. spectra of the ligand

The ^1H n.m.r spectra of the ligand in DMSO and

D_2O provided further evidence for the proposed structure. It shows a singlet at 11.2 p.p.m. which disappeared in D_2O that can be assigned to NH-O protons of the two imidol groups^[15].

The i.r. spectrum of the free ligand (TABLE 3) exhibits strong bands at 1688 cm^{-1} and 1660 cm^{-1} which may be assigned to $\nu(\text{C=O})$ and $\nu(\text{C=N})$ respectively. Medium bands appear at 3250 cm^{-1} [$\nu[\text{NH}]$] and 883 cm^{-1} [$\nu[\text{N-N}]$] show that, in the solid state the ligand exists in the keto form. The presence of lattice water is indicated by the presence of a broad band centered at 3450 cm^{-1} and two weaker bands at 845 and 710 cm^{-1} , these bands disappear upon dehydration at 110°C . Pyridine ring vibrations appear at 1410, 990, 633 and 435 cm^{-1} ^[16].

Examination of the molecular model of the ligand taking into account the steric effect and that the hydrazone exist in the syn and anti tautomers^[15] suggests that the title ligand exists in the cis IV [syn-anti] and/or the skew [syn-syn] V tautomers.

I.r. of the complexes

Comparison of the spectra of the complexes with that of the ligand TABLE 3 reveals the following observations:

TABLE 3 : Important i.r. spectral bands of the ligand and its complexes.

Compound	ν (Py)		ν (C=O) ν NH	ν (C=N) ν (N-N)	ν (NCO)	ν (M-O)	ν (M-N)	Other selected bands		
H_2L	1410	990	630	1688 3140	1600 883	-	-	-	-	
1.	1444	1055	690	1677 3140	1600 883	-	-	ν (M-OH ₂) ν (M-Cl)	1630 336	
2.	1440	1060	690	1678 3140	1600 880	-	-	ν (M-Cl) ν (M-OH ₂)	335 1637	
3.	1444	1060	690	1685 3140	1580 930	-	-	523 ν (M-Cl)	337	
4.	1408	985	634	1685	1580 925	1520 1320	473	522	ν (M-Cl) ν (M-OH ₂)	355 1637
5.	1405	990	626	-	1580 920	1550 1325	475	525	ν (M-Cl) ν (M-OH ₂)	320 1636
6.	1405	995	630	1680 3100	1580 925	1525 1330	475	542	ν (M-Cl) ν (M-OH ₂)	330 1630
7.	1410	990	630	-	1580 930	1550 1325	472	548	ν (M-NO ₃) ν (M-OH ₂)	1384,480 1630
8.	1410	990	630	-	1580 920	1520 1320	490	565	ν (M-OH ₂)	1630

All the metal complexes except (1, 2 and 3) show that the bands due to pyridine ring are displayed to high frequency indicating the involvement of the pyridine nitrogen in coordination^[30]. Similar alteration is not ob-

served in complexes 4-8 revealing that the pyridine ring nitrogen atom does not take part in coordination.

In complexes (4-8), the absence of bands at 3140 cm^{-1} and 1688 cm^{-1} with the appearance of more in-

tense band near 1600 cm^{-1} indicate that the CONH group is enolized and deprotonated^[31]. The appearance of $\nu(\text{N}=\text{C}=\text{O})$ at nearly 1530 cm^{-1} in these complexes suggested that the bonding to the metal occur through both deprotonated C-O groups

In all complexes except (1-3) $\nu(\text{N}-\text{N})$ band is observed at higher frequency compared to the free ligand, confirming the coordination of the azomethine nitrogen atom to the metal^[32].

The a-type metal ions like Ti^{4+} , Zr^{4+} , Hf^{4+} ^[33] would be expected to coordinate through carbonyl oxygen and non-ring nitrogen^[34]. We found exceptional cases as in the adduct complexes 1-3 where Hf, Ti and Zr ions coordinate through the ring nitrogen.

The spectra of complexes (1-4) show negative shift ($\approx 10\text{ cm}^{-1}$) in $\nu(\text{C}=\text{O})$, while the shift is minor ($\approx 3-8\text{ cm}^{-1}$) in complex (6). This indicate that the C=O group is free in complexes (1-4) while it hydrogen bonded in complex (6).

Coordination through ring nitrogen can be expected with b-type metal ions like Sn^{4+} ^[33]. This expectation has actually been incorrect for complex 5 where Sn

coordinates via azomethine N and enolate O.

On the other hand, the spectra of all complexes [except 3] display a new band at $[1637-1630]\text{ cm}^{-1}$ which is absent in the spectrum of the ligand, that band may be assigned to $\delta[\text{H}_2\text{O}]$ of coordinated water^[35-36].

$\nu[\text{M}-\text{Cl}]$, $\nu[\text{M}-\text{NO}_3]$, $\nu[\text{M}-\text{N}]$ and $\nu[\text{M}-\text{O}]$

The spectra of complexes 2-6 display new bands at $[337-320]\text{ cm}^{-1}$ assigned to $\nu[\text{M}-\text{Cl}]$. The occurrence of that band in that region indicates an octahedral geometry of these complexes^[37]. The presence of two strong bands at 1384 and 840 cm^{-1} in the spectrum of complex 7 suggests that the nitrate group is monodentate^[38]. The new bands appearing in the regions $(565-522)$ and $(490-453)\text{ cm}^{-1}$ are assigned to $\nu[\text{M}-\text{Py}]$ ^[39] and $\nu[\text{M}-\text{O}]$ ^[40] respectively.

Based on physical, analytical, molar conductivity and spectral results, taking into account that the exact geometry requires x-ray single crystal analysis which is not available, we can suggest octahedral geometries for the complexes which can be formulated as in Figure 3.

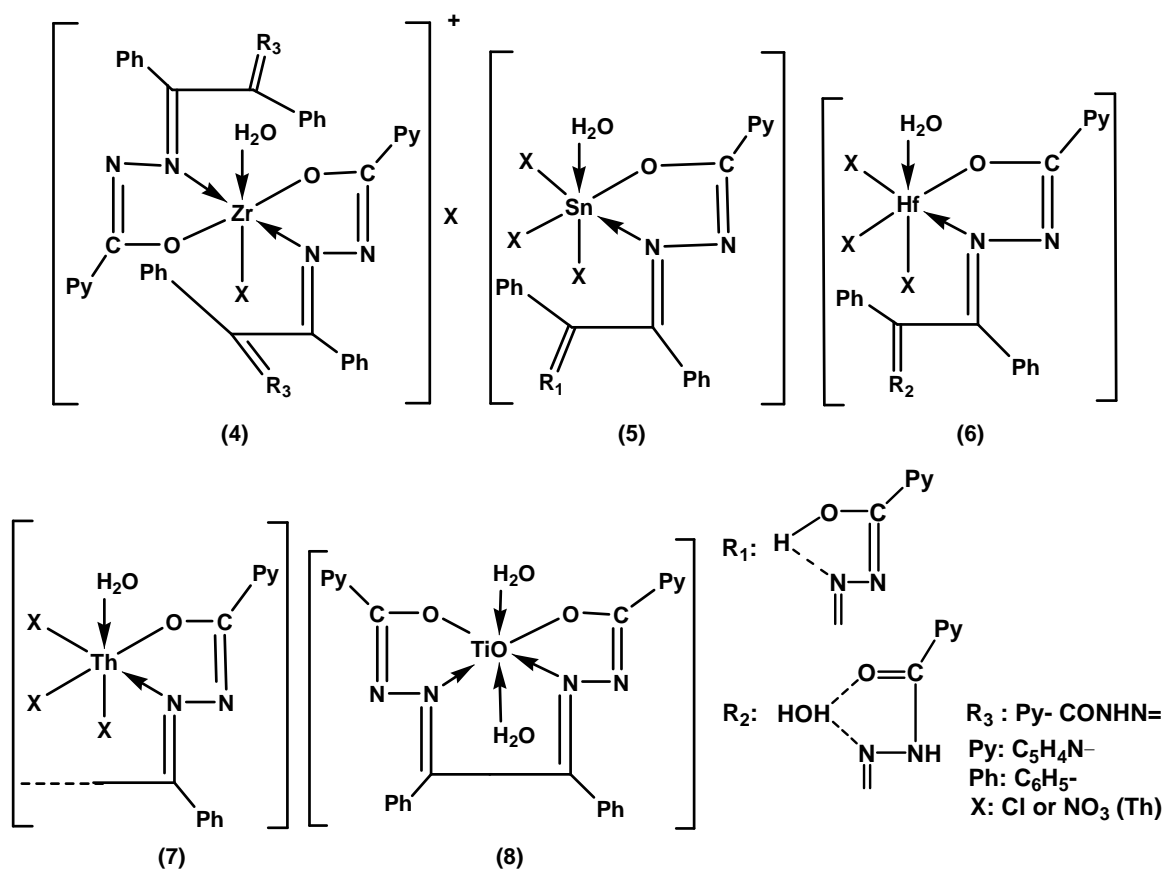


Figure 3: Proposed structures of the complexes.

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