

Synthesis and characterization of Bi (III) metal complexes derived from N/O donor ligand and their derivatives

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Abstract: A series of novel Bismuth(III) complexes of some Nitrogen and Oxygen donor ligands like *N'*-(2-oxo-2, 3-dihydro-1H-indol-3-yl) benzohydrazide (L-1), 2-hydroxy-*N'*-(2-oxo-2,3-dihydro-1H-indol-3-yl)benzohydrazide(L-2), 2-(2-hydroxyphenyl)-4,5-di- phenyl imidazol (L-3) and 2-(2-hydroxynaphthyl)-4,5-diphenyl imidazol (L-4) were prepared in ethanol by the reaction of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with ligands in 1:1 molar ratio. All these synthesized bismuth derivatives were characterized as monomer by elemental analysis, IR, ¹H NMR, UV-Vis, and Mass spectroscopy techniques.

Key Word: Bismuth complexes, Benzhydrazide, Imidazol, Chelating ligand, N, O donar Ligand

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I. Introduction

The coordination chemistry of bismuth (III) is incredibly sparse when put next to alternative metals¹⁻⁶. Bismuth and its compounds have medicative applications⁷ in treatment of a spread of epithelial duct disorders, as well as internal organ and small intestine ulcers, dyspepsia, symptom and rubor⁸⁻⁹ and have an instantaneous medication result on the gastritis and ulcer, inflicting bacteria, and helicobacter pylori¹⁰⁻¹². Pretreatment with bismuth complexes forestall the toxic aspect effects of the antitumor drug, cis-platine, while not compromising its anticancer activity¹³⁻¹⁴. It binds preferentially to the human body fluid siderophilin¹⁵. Bismuth compounds became engaging candidates to be used as reagents in organic synthesis¹⁶⁻¹⁷, in semiconductors, cosmetic preparations, alloys and metallurgic additives, and in exercise of metallic element nuclear fuels¹⁸. Bi (III) ions are extracted directly as ion-pairs with some cations exploitation completely different solvents¹⁹. Compounds of Bi(III) have received raised interest recently because of their multiple applications in various areas as well as medication, materials, organic synthesis, and chemical change²⁰⁻²³. Despite the fact that bismuth may be a p-block element, it's one in every of the additional golden of that a part of the table and forms stable complexes with Schiff bases and N and O donor ligands. in keeping with Pearson's hard-soft acid-base theory²⁴, Bi(III) may be a borderline metal particle, however it's a high affinity for multidentate ligands containing O and N donor atoms. Hence, these ligands are extremely variable ligands towards Bi(III). the soundness constants of those Bi(III) complexes are typically terribly high. As result, these complexes are stable and may be isolated even at low pH. whereas Bi(III) incorporates a sturdy affinity to change, within the presence of those powerfully chelating ligands it's stable up to pH ten²⁵. Increasing variety the quantity of donor atoms of the ligands and also the number of chelating rings fashioned typically leads to higher stability of the complexes. Hydrazone and Imidazole derived Schiff base ligands constitute an important class of heterocycles ligands being the core fragment of different natural products and biological systems. They occupy a unique place in the field of medicinal chemistry owing to their potent biological activity. They are well known to possess many pharmacological properties and to play a very important role in diverse biochemical processes. Many substituted imidazoles ligands display wide range of biological applications such as antiprotozoal, antifungal, and antihypertensive agents. During this paper, we've got synthesized the Bi(III) complexes with benzoyal hydrazone ligand and it's group derivative or imidazol ligand and its derivative.

II. Material And Methods

All the reactants and solvents used were of analytical grade. Pentahydrated Bismuth nitrate was purchased from Thermo-fisher Scientific (India). Isatin and hydrazone was obtained from Sigma-Aldrich. The solvents used in the experimental work, are of analytical grade and purchased from Rankem, India, and dried before using, by conventional methods. All manipulations for the syntheses of complexes were carried out in strictly anhydrous conditions. Precursors and Ligands were prepared according to the literature method²⁶⁻²⁸. The elemental analyses were performed on Thermo scientific Flash 2000. IR spectra [4000–400 cm⁻¹] were recorded with dry KBr pellets on a SHIMADZU, FT-IR 8400 spectrometer. ¹H and ¹³C{¹H} NMR data were collected on JEOL FX 300 FTNMR spectrometer in CDCl₃ solution at 300.4 MHz and 75.45 MHz frequencies for ¹H and

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra. ESI-mass spectra of some of the complexes were obtained on THERMO Finning LCQ Advantage max ion trap spectrometer using methanol solvent. The molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer fitted in a glass assembly (supplied by JSGW, India) in anhydrous benzene. Melting points of solids were determined in sealed capillaries, and the decomposition temperatures of sticky solids were determined on a melting point block. Absorption spectra of complexes were recorded using UV-Vis spectrophotometer from 200 to 800 nm range.

General Procedure

Synthesis of Ligands

Preparation of N'-(2-oxo-2, 3-dihydro-1H-indol-3-yl) benzohydrazide (L-1) and (Z)-2-hydroxy-N'-(2-oxo-2,3-dihydro-1H-indol-3-yl) benzohydrazide (L-2)

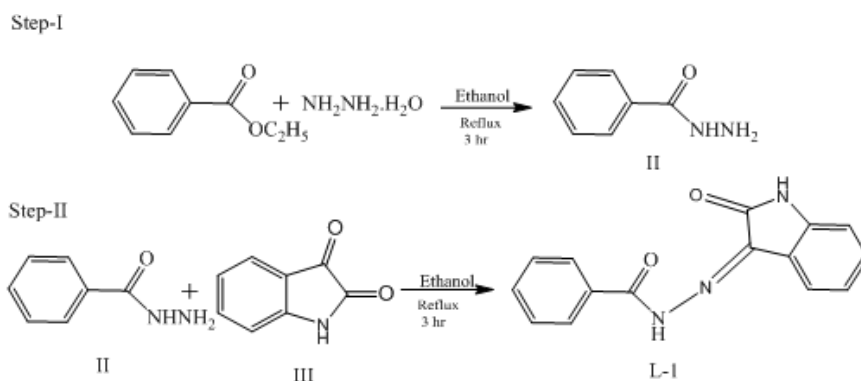
N'-(2-oxo-2, 3-dihydro-1H-indol-3-yl) benzohydrazide (L-1) and its hydroxyl derivative (L-2) were synthesized as previously reported method [27] by the reaction of isatin (III), (0.01 mole) and benzohydrazide (II) or salicyloyl hydrazide (II) (0.01 mole) in 20 ml ethanol solvent. These reaction mixtures were traces of acetic acid and refluxed for 3 hrs. The reaction mixtures were evaporated on water bath and the residue were poured onto crushed ice. These solid product obtained were separated by filtration and washed with cold water and then dried in vacuum. (L-1) m.p:286⁰C, Yield: 80%, (L-2) m.p:294⁰C, Yield: 80%

Synthesis of 2-(2-hydroxyphenyl)-4,5-diphenyl imidazol (L-3)

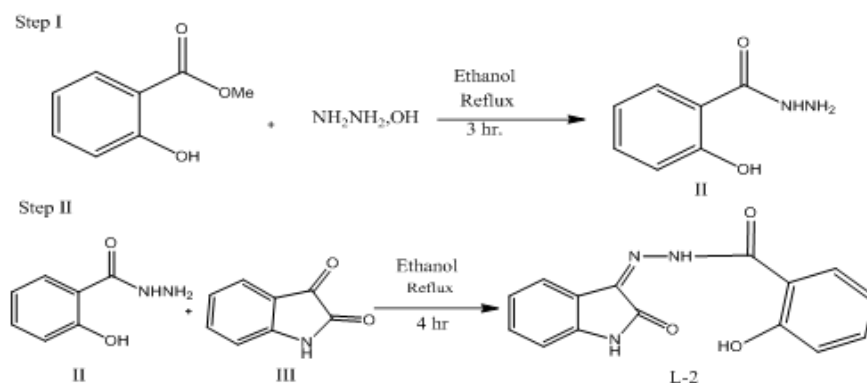
The ligand was synthesized by the reaction of benzyl (5mmol, 1.05 g), salicylaldehyde (5mmol, 0.610g) and ammonium acetate (80mmol, 6.16g) under refluxing in glacial acetic acid (20ml) for 4 h. The mixture was poured into 100ml deionized ice water. After cooling a gray color solid was generated and crystallized with ethanol. Yield -90%, M.P-213⁰C

2.2.3 Synthesis of 2-(2-hydroxyphenyl)-4,5-diphenyl imidazol (L-4)

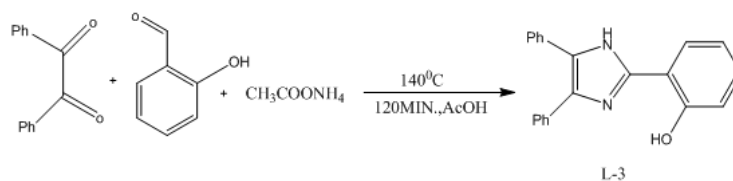
Ligand 2-(2-hydroxyphenyl)-4,5-diphenyl imidazol (HNPI) was synthesized by the refluxing of benzyl (5mmol, 1.05g), naphthalaldehyde (5mmol, 0.862g) and ammonium acetate (80mmol, 6.16g) in glacial acetic acid (20ml) for 4 h. The mixture was poured into 100ml deionized ice water and neutralized with aq. NH₃ to found crude solid, which was filtered and recrystallized with ethanol. Yield – 80%, M.P=190⁰C



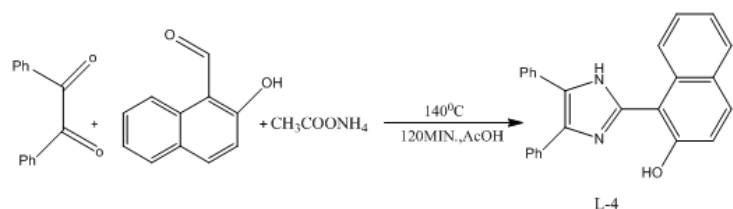
Scheme 1. Synthesis of N'-(2-oxo-2, 3-dihydro-1H-indol-3-yl) benzohydrazide (L-1)



Scheme 2. Synthesis of (Z)-2-hydroxy-N'-(2-oxo-2, 3-dihydro-1H-indol-3-yl) benzohydrazide (L-2)



Scheme 3. Synthesis of 2-(2-hydroxyphenyl)-4, 5-diphenyl imidazol (L-3)

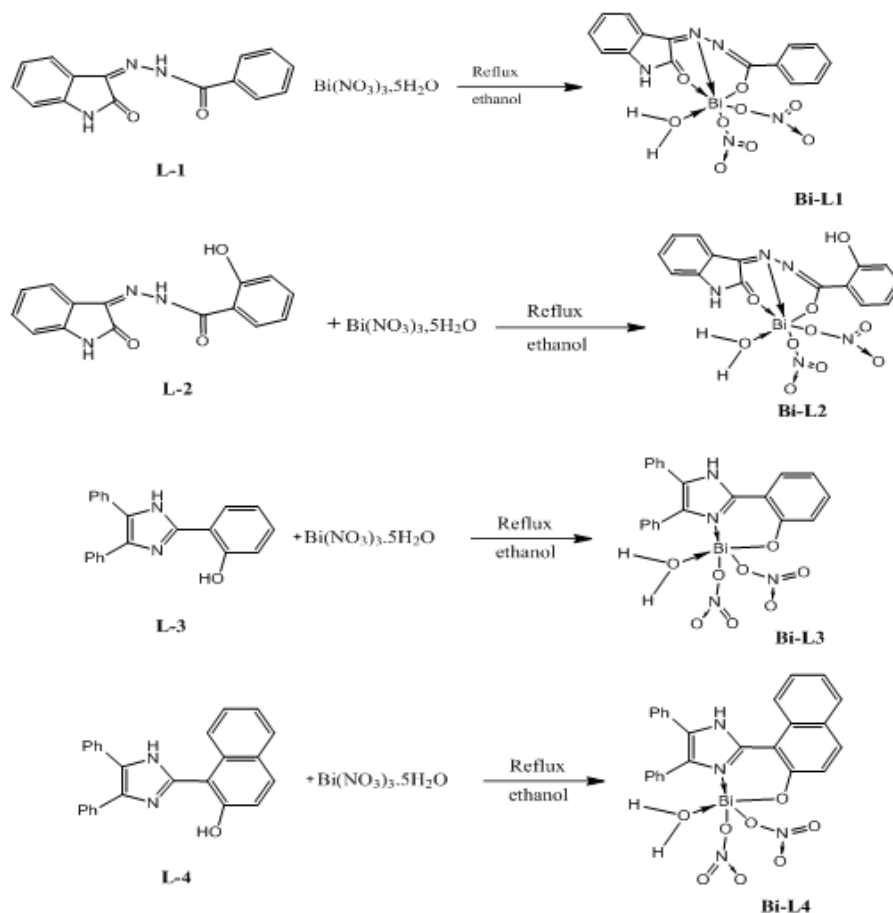


Scheme 4. Synthesis of 2-(2-hydroxyneptyl)-4, 5-diphenyl imidazol (L-4)

2.3 Synthesis of bismuth (III) complex

The metal complex of the Bismuth nitrate is produced by above-prepared ligands. The ethanoic solution of Bismuth nitrate pentahydrate (1 mmol) was dissolved drop wise in hot ethanolic solution of ligand (1 mmol) in a round bottom flask with 10 ml ethanol. Few drops of dilute ammonia were added to the reaction mixture to maintain its pH in the range of 7.5 to 8.0 and refluxed it's about for 3 hours. The resulting precipitate of complex formed was filtered and washed with ethanol and desiccated in vacuum.

Similar route have been employed for the preparation of other above said ligands complexes of bismuth (III) nitrate. The Physical and analytical properties of ligands and its bismuth(III) complexes are given in the table 1.



Scheme 5: Synthesis of Bi (III) Complexes

III. Result and Discussion

A systematic study of the reaction of bismuth nitrate pentahydrate with hydrazone or imidazol ligands in 1:1 molar ratio in EtOH have been carried out. The reaction can be represented by following equation as shown in scheme 5.

Several analytical techniques were used to characterize the bismuth (III) complexes, including microanalysis (CHN), spectral studies (IR, ¹H, ¹H NMR, and mass). All the reactions (scheme 5) were found to be quite facile and quantitative yielded orange to yellow color solids and mostly soluble in organic solvents. The molecular weight measurement data indicates that these complexes are monomeric in nature. These ligands are behaved as a bidentate ligand via both the N and O atom of the ligands.

Table-1: Physical Properties of ligands & metal complexes

S.N.	Molecular Formula	Compound Code	M.P	Color	Analytical Data found/cal.%				Mol. Wt Found/cal.
					C	H	N	Bi	
1	C ₁₅ H ₁₁ N ₃ O ₂	L-1	286	Orange	67.87 (67.92)	4.14 (4.18)	15.81 (15.84)	-	267.20 (265.27)
2	C ₁₅ H ₁₁ N ₃ O ₃	L-2	294	Yellow	64.08 (64.05)	3.92 (3.94)	14.89 (14.94)	-	281.40 (281.27)
3	C ₂₁ H ₁₆ N ₂ O	L-3	213	White solid	80.73 (80.75)	5.18 (5.16)	8.95 (8.97)	-	315.30 (312.37)
4	C ₂₅ H ₁₈ N ₂ O	L-4	190	Grey	82.73 (82.85)	5.03 (5.01)	7.71 (7.73)	-	363.60 (362.43)
5	C ₁₅ H ₁₂ BiN ₅ O ₉	BiL-1(1)	>300	Orange	29.33 (29.28)	2.08 (1.97)	11.20 (11.38)	33.84 (33.97)	616.50 (615.27)
6	C ₁₅ H ₁₂ BiN ₅ O ₁₀	BiL-2(1)	>300	Light yellow	28.61 (28.54)	1.86 (1.92)	11.15 (11.09)	33.21 (33.10)	632.40 (631.27)
7	C ₂₁ H ₁₇ BiN ₄ O ₈	BiL-3(3)	140	Pale yellow	38.14 (38.08)	2.49 (2.59)	8.53 (8.46)	31.58 (31.55)	663.20 (662.37)
8	C ₂₅ H ₁₉ BiN ₄ O ₈	BiL-4(4)	>300	Pale yellow	42.22 (42.15)	2.73 (2.69)	7.73 (7.86)	29.54 (29.33)	714.60 (712.43)

IR Spectra

The important IR spectral vibrations and their assignments of bismuth complexes are presented in table 2. These IR vibrations of all the complexes have been made comparing with spectra of free ligand and their ligands derivatives. The (NH) and (C=O) absorption bands of amido group which appeared at 3233 cm⁻¹, 3200 cm⁻¹ and 1624 cm⁻¹, 1686 cm⁻¹ in the spectra of free ligand (L-1 & L-2) were not observed in the spectra of bismuth complexes. The appearance of a new band in the IR spectra of these

complexes at 472–549 and 480–551cm⁻¹ region, assigned to ν(Bi-N), ν(Bi-O) also support the coordination of N and O to the bismuth metal ion [24,25], respectively. The new ν(C=N) mode observed at 1535 cm⁻¹ in the spectra of hydrazones undergoes small shifts (1624-1670) in the spectra of the complexes suggests that N atom of the ligand moiety attached to the indole ring also coordinating to the metal ion in complexes formation. This information may further supported by the appearance of a new weak to medium intensity band at 472-482cm⁻¹ due to ν(Bi-N) and 547-551cm⁻¹ stretching vibrations due to (Bi-O).The presence of broad absorption spectrum at 3340 cm⁻¹ confirm the presence of water molecule in the complexes. On the basis of the above the IR spectral data it is indicated that, all the above mentioned complexes, the ligand appeared to bind with metal via O,N and O in tridentate fashion in hydrazone and bidentate with imidazol .

Table 2. Important IR spectral data (cm⁻¹) of ligands and its corresponding bismuth (III) complexes

Compounds	IR absorption band (cm ⁻¹)					
	ν(O-H)	ν(N-H)	ν(C=N)	ν(C=O)	ν(Bi-N)	ν(Bi-O)
L-1	-	3233-3440	1535	1693-1624	-	-
Bi-L1	-	3444	1624	-	472	549
L-2	3450	3443-3200	1659	1724-1686	-	-
Bi-L2	3450	3446	1670	-	-	551
L-3	3417	3208 3417	-	-	-	-
Bi-L3	-	3202	-	-	482	547
L-4	3410	3220	-	-	-	-
Bi-L4	-	3204	-	-	473	551

¹H NMR Spectra

The expected NMR spectral data of ligands and their metal complexes are shown in table 3. However, in some cases due to the poor solubility of the complexes in CDCl₃, the ¹³C NMR spectra could not be resolved. These data have been made by the comparison of the spectra of free ligands and other related bismuth complexes, and also corroborate the results observed from the IR spectral studies. The signal appeared at δ 11.2 ppm due to –NH proton in spectra of free ligand, was absent in spectra of all these complexes, suggested that deprotonation was take place during the complexation and ligand attached to the bismuth in an ionic and neutral form. The hydroxyl proton resonances of the free ligands L-3 & L-4 (δ 12.95 & 12.72) were absent in ¹H NMR spectra of both the complexes, indicating deprotonation of the ligand and their bonding to the meta atom. The presence of signal at 5.2 ppm in the ¹H NMR spectra of the Bi(III) complexes further confirm the water molecule.

The other protons of ligand moiety like aromatic protons was appeared as a multiplete in the region δ 6.5–8.0 ppm in spectra of complexes and almost same as ligand with small deviation. In all the bismuth complexes, other proton resonance of the ligand moiety attached to the metal was appeared at the expected position with desirable multiplicities (table-3).

Table 3. ¹H NMR spectral data of the ligands and its corresponding bismuth (III) complexes

Compounds	Chemical Shift (δ ppm)		
	-NH	-OH	Aromatic
L-1	13.95(s,1H), 11.2(s,1H)	-	6.8-8.0 (m,9H)
Bi-L1	13.95(s,1H)	-	7.2-7.8 (m, 9H)
L-2	11.15(s,1H), 10.85(s,1H)	12.19(s,1H)	6.5-7.8(m, 9H)
Bi-L2	11.24(s,1H)	12.34(s,1H)	6.5-8.0(m, 9h)
L-3	13.05(s,1H)	12.95(s, 1H)	6.9-8.2(m, 14H)
Bi-L3	13.14(s,1H)	-	7.2-7.8 (m, 14H)
L-4	9.37(s,1H)	12.72(s,1H)	6.9-7.4(m, 19H)
Bi-L4	9.43(s,1H)	-	7.1-7.4(m, 19H)

Mass spectra

The ESI mass spectral studies of ligands and their metal complexes [BiL-1] (1), [BiL-2] (2), [BiL-3] (3) and [BiL-4] (4) indicate their monomeric nature. The characteristics molecular ion peak of ligands and their complexes are shown in Table 3. The molecular ion peak (M+1) of complexes (1), (2), (3) and (4) appears at m/z 616.0, 632.0, 663 and 713.0, respectively, thus confirming the formation a metal ion complex in 1:1 ratio.

Table 4. Molecular ions vs m/z values of ligands and complexes (1), (2), (3) and (4)

Compounds	Molecular Ion Peak	m/z value
L-1	C ₁₅ H ₁₁ N ₃ O ₂ (M+1)	266
L-2	C ₁₅ H ₁₁ N ₃ O ₃ (M+1)	281
L-3	C ₂₁ H ₁₆ N ₂ O (M+1)	313
L-4	C ₂₅ H ₁₈ N ₂ O (M+1)	363
BiL-1(1)	C ₁₅ H ₁₂ BiN ₃ O ₉ (M+1)	616
BiL-2(1)	C ₁₅ H ₁₂ BiN ₃ O ₁₀ (M+1)	632
BiL-3(3)	C ₂₁ H ₁₇ BiN ₄ O ₈ (M+1)	663
BiL-4(4)	C ₂₅ H ₁₉ BiN ₄ O ₈ (M+1)	713

Efforts to obtain good quality crystals of the complexes were unsuccessful. In the absence of crystal structures, it is difficult to comment on the solid state structure of the complexes. Nevertheless, the above studies do indicate the possibility of the structures which are shown in scheme 5.

IV. Conclusion

A series of bismuth(III) complexes isolated during the demonstrated that the interaction of bismuth nitrate with N/O donor ligands of benzohydrazide or imidazole in 1:1 stoichiometry and are found to be mononuclear. Their structures have been established on the basis of spectral studies. Monofunctional bidentate behaviour of ligands with metal was suggested on the basis of spectral data like elemental analysis, IR, ESI-Mass, ¹H NMR.

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