

## Infrared Spectroscopic Characterization of Calcium and Barium Hydrazone Complexes

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### ABSTRACT

Hydrazones have attracted considerable interest on account of their biological activities. Introduction of calcium and barium metal ions into m- and p-nitrobenzoic hydrazones is expected to modify these biological properties for enhanced activity and versatility. The ligands were synthesized from the parent acids. The complexes have been characterized using C, H and N microanalyses and IR spectrometry. The IR spectral data of the ligands and complexes revealed bonding via the C=O and C=N groups. The suggested metal to ligand stoichiometries are: [M (m-NBH)<sub>x</sub>]Cl<sub>2</sub>.yH<sub>2</sub>O, x, y = 1 and 4 for M = Ca; x, y = 2 and 3 for M = Ba respectively.

[M(p-NBH)<sub>x</sub>]Cl<sub>2</sub>.yH<sub>2</sub>O, x, y = 1 and 12 for M = Ca; x, y = 1 and 3 for M = Ba respectively. The structural deductions are tentative pending future X-ray structural studies.

**Keywords:** barium, calcium, hydrazones, infrared spectroscopy

### 1. INTRODUCTION

The properties of hydrazones<sup>1-11</sup> have attracted considerable interest owing to their biological activities, such as anti-tumor, anti-bacterial, anti-viral, anti-hypertensive, anti-convulsant, anti-inflammatory, analgesic, vasorelaxant, anti-coagulant anti-protozoal activities. Hydrazones also have wide applications as analytical reagents in the spectrophotometric determination of cobalt and other metals in inorganic analysis<sup>12,13</sup>.

Calcium is required for the formation of bones and teeth, maintaining heart rhythm and in blood clotting<sup>14,15</sup>. Similarly, barium a heavier congener of calcium as equally received attention being in the same group (II) with calcium<sup>16,17</sup>.

Earlier studies have revealed that the formation of metal complexes modifies the behaviour and enhances the activity of hydrazones<sup>18-20</sup>. Reported synthesis of calcium and barium complexes of hydrazones is scanty in the literature. No work has yet been reported on calcium and barium complexes of m- and p-nitrobenzoic hydrazones.

In the present work, the synthesis and characterization of calcium and barium complexes of m- and p-nitrobenzoic hydrazones is reported.

### 2. EXPERIMENTAL

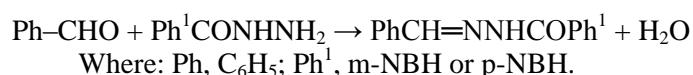
#### 2.1 Chemicals and reagents

The chemicals and reagents used were of analytical grade and were purchased from Aldrich and Fluka AG.

#### 2.2 Synthesis of ligands

The esters used in the ligands synthesis were first synthesized from their parent acids, while, the hydrazides were subsequently synthesized from the respective esters following the methods reported before<sup>6, 21-23</sup>. Consequently, equimolar mixture (0.05 mol) of benzaldehyde and the previously synthesized m- and p-nitro benzoic acid hydrazides, with few drops of conc. HCl in 25 ml ethanol, were heated under reflux for 2 hrs. After cooling, water was added to the reaction mixture, filtered and dried to yield the respective hydrazones<sup>6, 24-26</sup>.

The benzaldehyde and acid hydrazides condensation reaction for the synthesis of m- and p- nitrobenzoic hydrazones are summarized as follows:



#### 2.3 Preparation of Complexes

##### 2.3.1 [Ca (m-NBH)]Cl<sub>2</sub>.4H<sub>2</sub>O

Calcium complex of m-nitrobenzoic hydrazone (m-NBH) was prepared by stirring 0.5 g (1.90 mmol) m-nitrobenzoic hydrazone with 0.279 g (1.90 mmol) CaCl<sub>2</sub>.2H<sub>2</sub>O in 40 ml methanol for 16 hrs using a Griffin Minimag magnetic stirrer. The mixture was then refluxed for 2 hrs. An off-white precipitate was formed on cooling, which was filtered, washed thoroughly with methanol and dried in vacuum over silica gel (self indicating, 6-20 mesh)<sup>27-28</sup>.

##### 2.3.2 [Ca (p-NBH)]Cl<sub>2</sub>.12H<sub>2</sub>O

Equimolar amount of 0.5 g (1.90 mmol) p- nitrobenzoic hydrazone and 0.27 g (1.90 mmol) of CaCl<sub>2</sub>.2H<sub>2</sub>O in 40 ml methanol was stirred for 16 hrs in a magnetic stirrer. The mixture was then refluxed for 2 hrs and a brown precipitate

appeared on cooling. The solid, a calcium complex of p-nitrobenzoic acid was washed with methanol and dried over silica gel (self indicating, 6-20 mesh) <sup>7,27</sup>.

### 2.3.3 [Ba (m-NBH)<sub>2</sub>]Cl<sub>2</sub>.3H<sub>2</sub>O

[Ba (m-NBH)<sub>2</sub>]Cl<sub>2</sub>.3H<sub>2</sub>O was synthesized when 1.2 g (4.46 mmol) m-nitrobenzoic hydrazone was stirred with 1.09 g (4.46 mmol) BaCl<sub>2</sub>.H<sub>2</sub>O, in 60 ml methanol for 16 hrs. The mixture was then refluxed for 2 hrs. A grey precipitate was formed on cooling. The precipitate was washed several times with methanol and dried over silica gel (self indicating, 6-20 mesh) <sup>29,30</sup>.

### 2.3.4 [Ba (p-NBH)]Cl<sub>2</sub>.3H<sub>2</sub>O

Barium complex of p-nitrobenzoic hydrazone was synthesized using the same method as adopted for [Ba (m-NBH)]Cl<sub>2</sub>.3H<sub>2</sub>O, but instead of m-, p-nitrobenzoic hydrazone was used. The resultant mixture was then refluxed for 2 hrs and a light brown precipitate was washed and dried over silica gel (self indicating, 6-20 mesh) as reported earlier <sup>4,27</sup>.

### 2.3.5 Physicochemical measurements

The melting/decomposing temperatures of the ligands and complexes were determined using a calibrated Griffin melting point apparatus. The results are indicated in Tables 1 and 2. Calcium and barium were determined by EDTA titrations, after digesting with conc. nitric acid. Methyl thymol blue was used as the indicator <sup>31</sup>.

**Table-1:** Physical data of the ligands

Ligand	Formula	M.P (°C)	Colour
m-NBH	C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>	180-182	off-white
p-NBH	C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>	210-212	light yellow

Notes: M.P = melting point; m-NBH = m-nitrobenzoic hydrazones; p-NBH = p-nitrobenzoic hydrazones

**Table-2:** Elemental analysis and physical characteristics of the complexes

Item	[Ca (m-NBH)] - Cl <sub>2</sub> .4H <sub>2</sub> O	[Ca (p-NBH)] - Cl <sub>2</sub> .12H <sub>2</sub> O	[Ba (m-NBH) <sub>2</sub> ] - Cl <sub>2</sub> .3H <sub>2</sub> O	[Ba (p-NBH)] - Cl <sub>2</sub> .3H <sub>2</sub> O
Formula*	CaC <sub>14</sub> H <sub>19</sub> N <sub>3</sub> O <sub>7</sub> Cl <sub>2</sub>	CaC <sub>14</sub> H <sub>35</sub> N <sub>3</sub> O <sub>15</sub> Cl <sub>2</sub>	BaC <sub>14</sub> H <sub>28</sub> N <sub>6</sub> O <sub>9</sub> Cl <sub>2</sub>	BaC <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>6</sub> Cl <sub>2</sub>
m.p. (°C)	300-302	290-292	210-212	250-252
Colour	off-white	Brown	grey	light brown
% M	8.79 (8.86)	6.59 (6.72)	17.39 (17.16)	25.39 (25.84)
% C	37.25 (37.16)	27.50 (28.18)	41.09 (41.09)	31.41 (31.62)
% H	4.98 (4.24)	5.52 (5.92)	3.24 (3.53)	2.63 (3.23)
% N	9.57 (9.29)	7.66 (7.05)	10.55 (10.49)	7.36 (7.91)

\*Refer to Table-1 for nomenclature of ligands; figures in parentheses are the calculated values; m.p, melting point.

Elemental analyses for C, H and N were carried out by the micro-analytical laboratory at the University of Cape Town, South Africa.

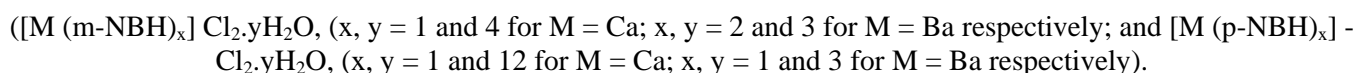
The solubility of the ligands and complexes were carried out in water, n-hexane, ethanol, methanol, acetone, petroleum ether and trichloromethane.

The infrared spectrum of the ligands and complexes were obtained using KBr pellets in the range 4000 – 500 cm<sup>-1</sup> on a Buck Scientific M 500 infrared spectrophotometer at Rotas Soilab, Ltd. Ibadan, Nigeria. The relevant spectra data is listed in Table 3. Representative spectra for the ligands and complexes are presented in four Figures as follows: 2 = m-NBH; 3 = p-NBH; 11 = [Ba (m-NBH)<sub>2</sub>]Cl<sub>2</sub>.3H<sub>2</sub>O ; 15 = [Ca (p-NBH)]Cl<sub>2</sub>.12H<sub>2</sub>O respectively.

## 3. RESULTS AND DISCUSSION

The melting/decomposition temperatures of the ligands, m- and p- nitrobenzoic hydrazones are shown in Table 1, 180 – 182 °C for m-NBH and 210 - 212 °C for p-NBH respectively. The compounds were off-white (m-NBH) and light yellow (p-NBH). These observations are in agreement with the properties of similar hydrazones reported earlier <sup>6,9</sup>. The ligands are insoluble in water and generally found to have poor solubility in the organic solvents used except in ethanol.

The C, H, N and metal contents of the complexes, along with their melting points and colour are presented in Table 2. The data indicates that the formulae of the complexes are:



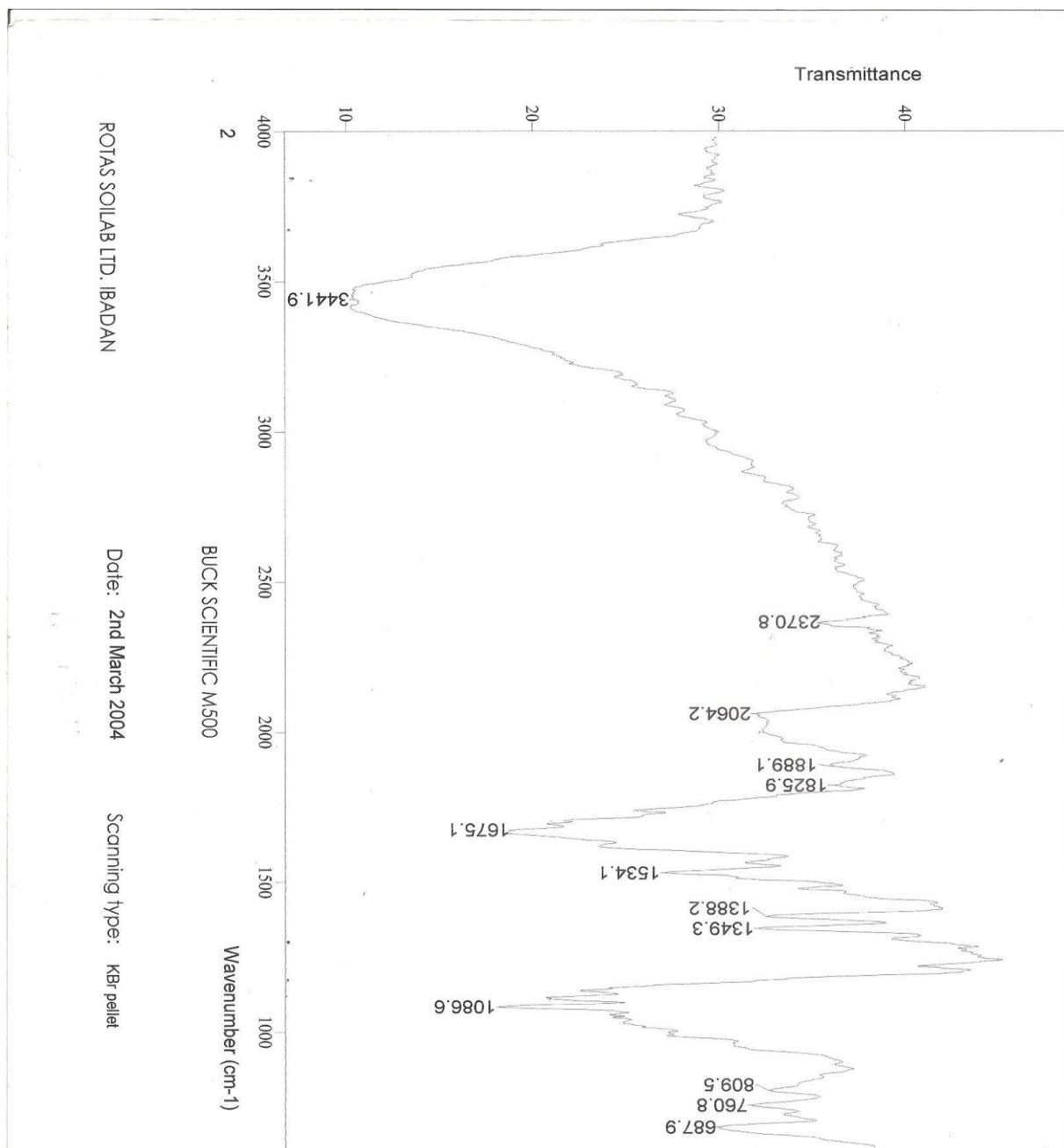
Similar metal to ligand stoichiometries have been reported before <sup>7-32</sup>. The complexes have sharp melting points ranging between 210–302 °C <sup>27</sup>. The complexes were mostly brownish (Table 2), however, [Ca (m-NBH)]Cl<sub>2</sub>.4H<sub>2</sub>O

was off-white and  $[\text{Ba}(\text{m-NBH})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  was grey in colour. Coordination complexes of group II metals that are off-white, grey and brownish in colour have been reported earlier<sup>27, 28, 33, 34</sup>. This is in spite of their non-transitional nature<sup>14-15</sup>.

The IR data of the ligands and its complexes (Table 3) revealed strong and weak absorption peaks in the range  $3567\text{--}3691\text{ cm}^{-1}$ . These bands have been attributed to  $\nu\text{ OH}$  vibrations<sup>7, 27</sup>. Similarly, the bands around  $1667\text{--}1697\text{ cm}^{-1}$  were assigned to  $\nu\text{ C=O}$ <sup>7-27, 35</sup>.

The  $\nu\text{ C=O}$  frequency in  $[\text{Ba}(\text{m-NBH})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  shifted to  $1667\text{ cm}^{-1}$  from  $1675\text{ cm}^{-1}$  in the ligand (m-NBH), whereas,  $\text{Ba}(\text{p-NBH})\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  shifted by  $18\text{ cm}^{-1}$  to lower frequency that is from  $1697\text{ cm}^{-1}$  in the free ligand, p-NBH to  $1679\text{ cm}^{-1}$  in the complex. These shifts to lower frequencies suggest that the carbonyl group is involved in barium to ligand bonding<sup>27-29</sup>. However, the  $\nu\text{ C=O}$  band shifted to higher frequency in  $[\text{Ca}(\text{m-NBH})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ , while the frequency for the complex  $[\text{Ca}(\text{p-NBH})]\text{Cl}_2 \cdot 12\text{H}_2\text{O}$  remained unchanged as compared to the ligand, p-NBH (Table 3).

These observations indicate the non-involvement of the carbonyl oxygen in coordination in these complexes<sup>3-7, 35</sup>. It should be noted from Table 3 that the bands  $1621\text{ cm}^{-1}$  and  $1614\text{ cm}^{-1}$  in the ligands (m-NBH and p-NBH respectively) due to  $\nu\text{ CN}$  shifted to higher frequencies in  $[\text{Ca}(\text{m-NBH})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ,  $[\text{Ca}(\text{p-NBH})]\text{Cl}_2 \cdot 12\text{H}_2\text{O}$  and  $[\text{Ba}(\text{p-NBH})]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  respectively, but remained unchanged in  $[\text{Ba}(\text{m-NBH})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ . This suggests that the C-N nitrogen was not involved in bonding to calcium and barium. Similar coordinating behaviour has been reported before<sup>3, 24, 27</sup>.



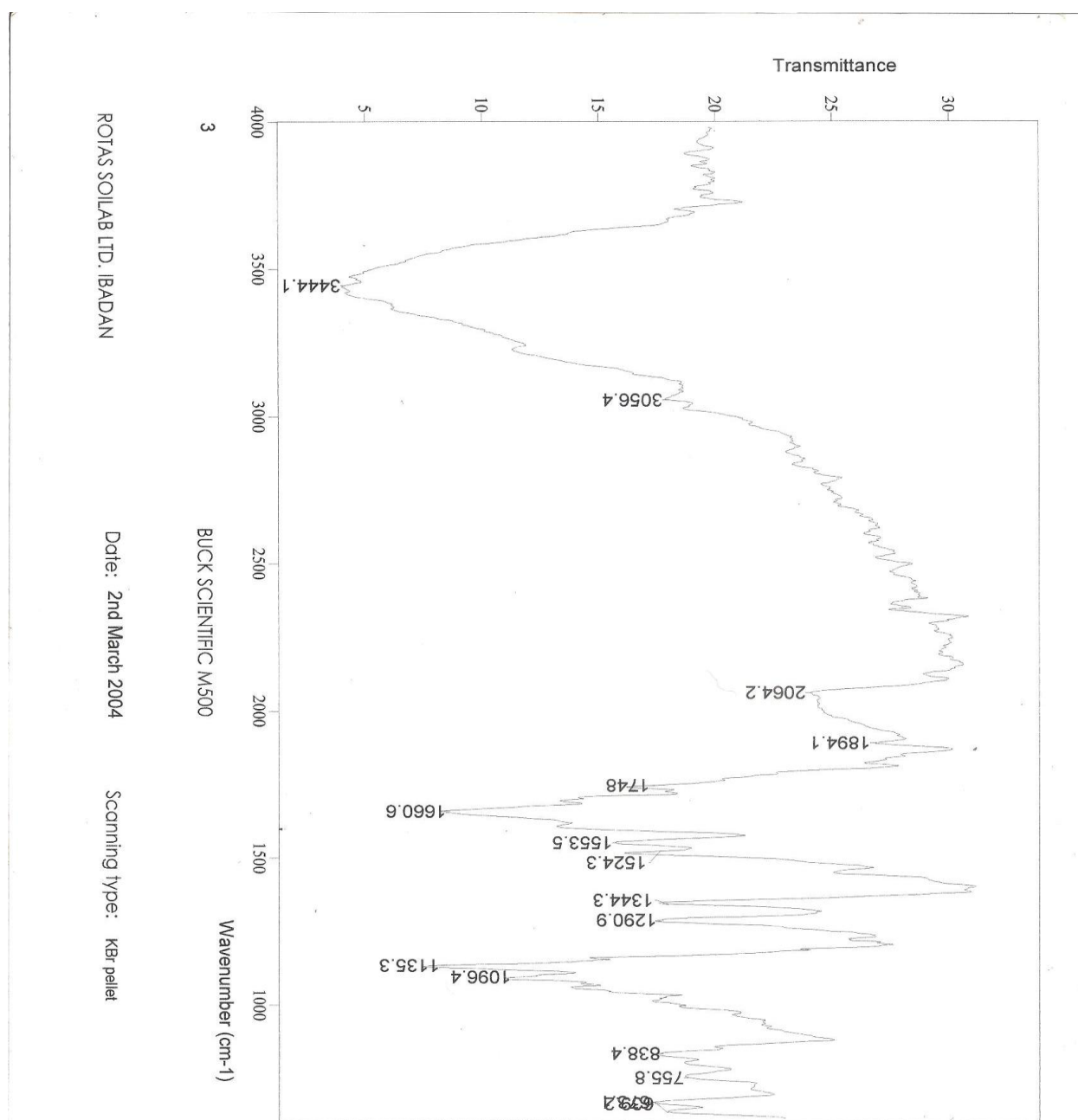
In the spectra of the ligands and their complexes (Table 3), except  $[\text{Ba}(\text{m-NBH})_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ , strong absorption bands ranging from  $1554\text{--}1598\text{ cm}^{-1}$  assigned to  $\nu\text{ C=N}$ <sup>3-7</sup>, shifted to lower frequencies by  $6\text{--}44\text{ cm}^{-1}$ . These frequency shifts associated with the C=N group, suggest bonding via this group.

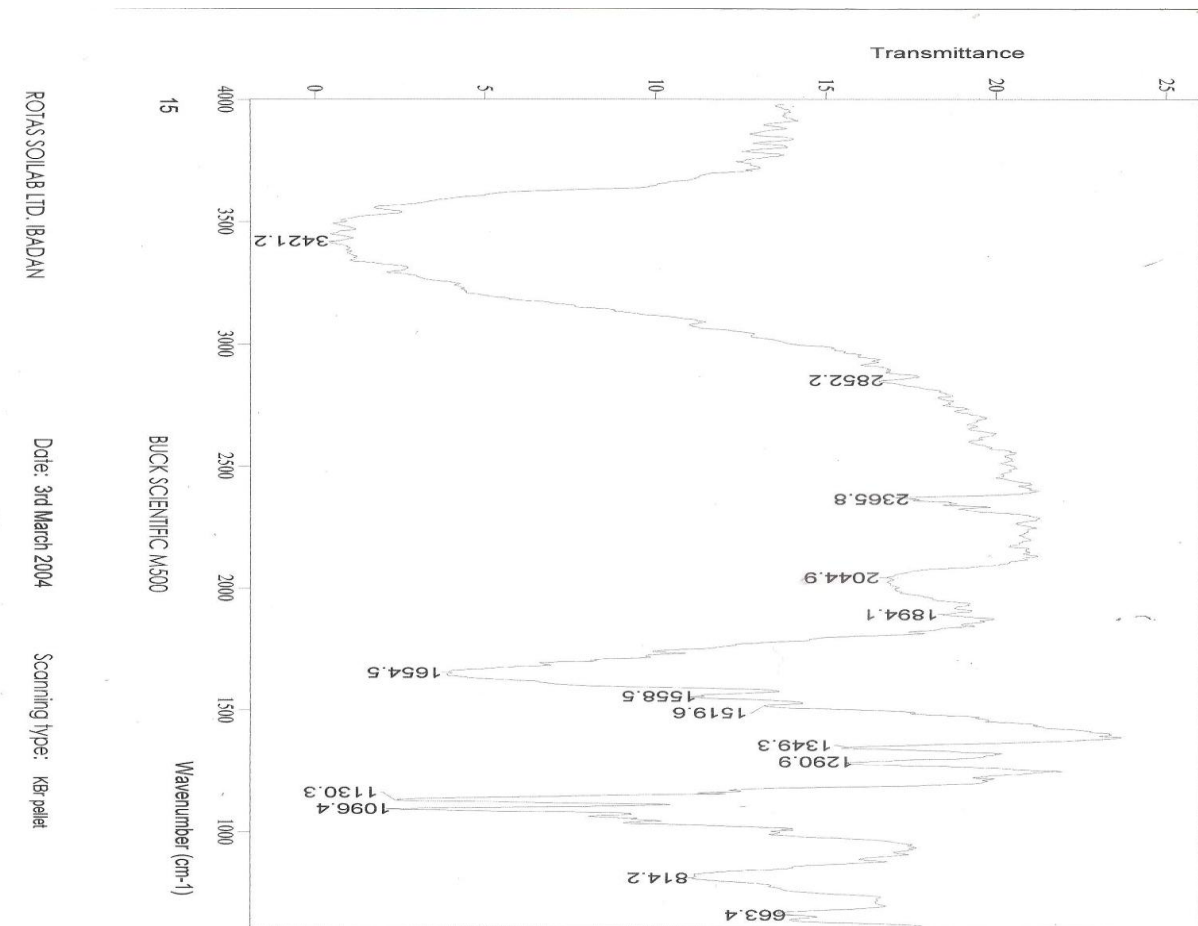
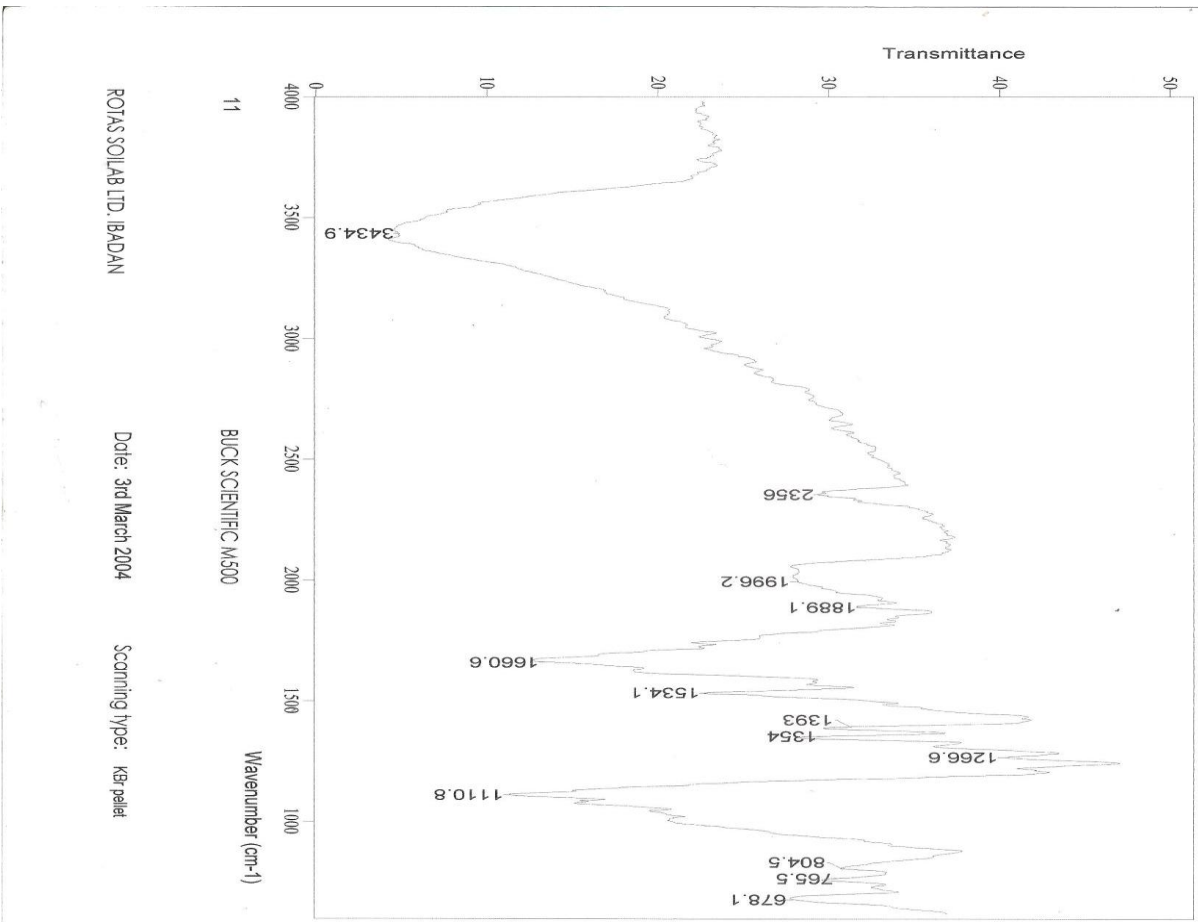
The bands,  $1534\text{ cm}^{-1}$  and  $1524\text{ cm}^{-1}$  in the ligands due to deformation NH, remained either unchanged or shifted to higher frequencies in the complexes suggesting that the NH group was not involved in bonding in the complexes<sup>4-24, 27, 36</sup>. The structural deductions for the complexes (Table-2) are tentative pending future X-ray structural studies.

**Table-3:** Relevant IR data ( $\text{cm}^{-1}$ ) of the ligands and complexes

Ligand/Complex	$\nu\text{ OH}$	$\nu\text{ C=O}$	$\nu\text{ CN}$	$\nu\text{ C=N}$	$\delta\text{ NH}$
m-NBH	3621 w	1675 s	1621 s	1576 s	1534 s
$[\text{Ca}(\text{m-NBH})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	3591 w	1697 s	1671 s	1570 s	1536 m
$[\text{Ba}(\text{m-NBH})_2] - \text{Cl}_2 \cdot 3\text{H}_2\text{O}$	3691 w	1667 s	1621 s	1591 s	1534 m
p-NBH	3667 w	1697 s	1614 s	1598 s	1524 m
$[\text{Ca}(\text{p-NBH})] - \text{Cl}_2 \cdot 12\text{H}_2\text{O}$	3567 s	1697 s	1656 s	1559 s	1524 m
$[\text{Ba}(\text{p-NBH})] - \text{Cl}_2 \cdot 3\text{H}_2\text{O}$	3671 w	1679 s	1651 s	1554 s	1530 m

Where: s, m, w =, strong, medium and weak respectively





#### 4. CONCLUSIONS

Complexes of calcium and barium m- and p- nitrobenzoic acid hydrazones were synthesized and characterized using metal, elemental and IR spectroscopic techniques. The IR spectral behavior suggested that the ligands C = O and C = N groups are involved in coordination to the metal ions. A final structural elucidation by X-ray diffraction studies and possible biological evaluation of the complexes is desirable.

#### 5. ACKNOWLEDGEMENT

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