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## Selective colorimetric sensing of nickel (II) ions using 2-hydroxy-5-nitrobenzaldehyde-4-hydroxybenzoylhydrazone ligand: Spectroscopic and DFT insights



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ABSTRACT

The abnormal levels of nickel (II) ions in body fluids have been linked to various ailments, and their ubiquitous environmental occurrence could pose a potential hazard. Hence, there is a pressing need to develop selective and miniaturized analytical techniques to efficiently monitor the level of nickel (II). In the present study, 2-hydroxy-5-nitrobenzaldehyde-4-hydroxybenzoylhydrazone (HNHBH) was synthesized and investigated as a potential colorimetric sensor for nickel (II) ions. A distinct color change was observed due to complex formation between HNHBH and nickel (II) ions. Both the free ligand and resulting complexes were characterized by UV-Vis, infrared and <sup>1</sup>H NMR spectroscopies. A theoretical DFT method has been implemented to understand the nature of complexation based on the calculated binding energies and frontier molecular orbitals. The computational approach used predicts that HNHBH adopts an imidic acid tautomeric form when it coordinates with the metal ion center. The selectivity of HNHBH towards nickel ions was evaluated by taking into account a number of factors, such as solvent, pH and EDTA effects.

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## 1. Introduction

The impact of nickel ions coupled with their ubiquitous environmental occurrence from anthropogenic and natural sources makes monitoring their level with the use of feasible means an important task [1,2]. Nickel compounds, except metallic nickel, are deemed carcinogenic to humans [1]. It has been proposed that nickel acts as a cofactor for some enzymes, such as urease [3,4], but the role of nickel in human physiology remains poorly understood. No consensus regarding whether nickel is an essential trace element for humans has been reached yet [1,3,4].

Trace analysis of nickel is often carried out through various methods such as atomic absorption spectroscopy [5,6] and inductively coupled plasma-mass spectroscopy [7]. These methods provide a good sensitivity and accuracy but can be costly and inconvenient due to the infrastructure and sample pre-treatment required, or when large numbers of samples need to be analyzed. Simpler alternatives that offer an acceptable sensitivity at a lower cost such as ion selective electrodes [8,9], UV–Visible absorption and fluorescent emission chemosensors [10] are being investigated. The colorimetric sensing of metal ions

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without the use of instrumentation is of a special interest as it is less labour-intensive compared to classical instrumental techniques [11,12] and has the potential to be developed into simple, convenient and cost-effective test kits [13].

A number of aroyl hydrazones were shown to function as colorimetric sensors for some metal ions, and their facile synthesis, tuneable electronic and steric properties and efficient chelating capability have been explored [14–19]. Sumita et al. reported the synthesis and spectroscopic studies of Co(III) arovl-hydrazone complexes with a characteristic oxidative and reductive electrochemistry [14]. Anthracene-based aroyl hydrazones were also synthesized and shown to readily form complexes with Co(III) and Ni(II) ions [16]. Aroyl hydrazones of 2phenylindole-3-carbaldehyde for the inhibition of the growth of cancer cells were also synthesized [18]. Metal complexes of aroyl hydrazones are reported to exhibit interesting biological and pharmaceutical activities and are of interest in several research fields including selective metal extraction and spectroscopic determination [19,20]. Hence this work aimed to investigate the potential application of 2-hydroxy-5nitrobenzaldehyde-4-hydroxybenzoylhydrazone (HNHBH) which is an aroyl hydrazones derivative as a promising colorimetric sensor for nickel (II). Computational modelling tool has been employed to understand the complexation nature of nickel ions with HNHBH in terms of binding energies, structural parameters and atomic charges. Comparison between computational and experimental results provides deep insights into the chemistry of the possibly formed complexes [21].

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## 2. Experimental

#### 2.1. Chemicals and materials

Metal salts used include nickel (II) acetylacetonate, copper (II) acetate and zinc (II) acetate (all of them were analytically pure and commercially purchased). All solvents used were of HPLC grade and used without any further purification.

The HNHBH ligand was synthesized following a previously reported method [22,23] and then tested with the salts of nickel (II) copper (II) and zinc (II) ions. Briefly, 0.30 g (2 mmol) of 4-hydroxyphenylhydrazide and 0.33 g (2 mmol) of 2-hydroxy-5-nitrophenyl aldehyde were dissolved in 25 mL MeOH and stirred for 3 h. The resulting product was filtered and washed three times with MeOH and Et<sub>2</sub>O and dried over fused CaCl<sub>2</sub>.

### 2.2. Methodology

## 2.2.1. Preliminary experiments

Solutions of HNHBH with tetrahydrofuran (THF)  $(2 \times 10^{-4} \text{ M})$  were prepared. Each metal salt in acetonitrile (ACN)  $(2 \times 10^{-3} \text{ M})$  was prepared and sonicated for 10 min. 10 µL of each metal salt solution was added to 1 mL of HNHBH ligand solutions in clean glass vials. While the mixture was shaken, any color changes were noted. After, another 10-µL quantity of the metal salt solution was added, and the process was repeated. The experiment was also carried out with the metal salts dissolved in THF.

### 2.2.2. Characterization of ligand-metal complexes

A 0.5-mL quantity of a ligand solution in THF ( $2 \times 10^{-4}$  M) was diluted with 2.5 mL of THF in a quartz cell and then scanned from 200 to 700 nm. The relevant metal salt solution in THF ( $2 \times 10^{-3}$  M) was added to the ligand solution in the quartz cell in 10-µL aliquots. The solution was mixed with a dropper and the spectra were recorded after each addition of the metal salt solution. The infrared spectroscopy was collected using KBr pellets containing a small amount of the analyte. Pellets were prepared and scanned from 4000 to 400 cm<sup>-1</sup>. For the <sup>1</sup>HNMR spectroscopy, equimolar solutions of the ligand and metal salts were prepared in DMSO  $d_6$  ( $2 \times 10^{-3}$  M). The HNHBH ligand was analyzed directly. The ligand-metal complexes were prepared by mixing equal volumes of the ligand and metal salt solutions. Purity of the ligand and metal-ligand complexes was verified using the energydispersive X-ray spectroscopy (EDX).

## 2.2.3. Effect of parameters

2.2.3.1. Metal interference effect. Interference solutions of calcium, zinc, magnesium, palladium and copper were prepared by adding 200  $\mu$ L of each metal salt solution in THF (2  $\times$  10<sup>-3</sup> M) to a microcentrifuge tube and manually shaking the mixture for 3 min. This solution was used for colorimetric titrations with the HNHBH ligand.

2.2.3.2. Solvent effect. To investigate the effect of other organic solvents, solutions of metal salts in ACN ( $2 \times 10^{-3}$  M) were used for colorimetric titrations. To investigate the effect of mixed aqueous solvents, solutions of metal salts were prepared in 50% THF mixed aqueous solutions ( $2 \times 10^{-3}$  M) from THF and nano-pure water. This solvent mixture was used to dilute the HNHBH ligand at 25% (w/v), 50% (w/v) and 75% (w/v), and the ligand and metal salts in mixed aqueous solutions were tested following the procedure described above. A colorimetric titration of HNHBH ligand ( $2 \times 10^{-4}$  M) and Ni(acac)<sub>2</sub> ( $2 \times 10^{-3}$  M) in a 50% THF mixed aqueous solution was also performed.

2.2.3.3. pH effect. Mixed aqueous solutions of 0.5 mL of the ligand (2  $\times$  10<sup>-4</sup> M) and 10  $\mu$ L of the metal salts (2  $\times$  10<sup>-3</sup> M) in glass vials were treated with 1–10  $\mu$ L of aqueous 0.5 M HCl followed by aqueous

**Fig. 1.** Color changes observed on adding HNHBH ligand to Ni(acac)<sub>2</sub>, Cu(OAc)<sub>2</sub> and Zn (OAc)<sub>2</sub> solutions. The most intense change was noticed in the case of nickel (II) solution.

0.5 M NaOH, and vice versa. A colorimetric titration of the ligand (2  $\times$  10<sup>-4</sup> M) and Ni(acac)<sub>2</sub> (2  $\times$  10<sup>-3</sup> M) in a 50% THF mixed aqueous solution with the addition of aqueous NaOH (0.5 M) and aqueous HCl (0.5 M) was carried out.

2.2.3.4. Ligand interference effect. 50% THF mixed aqueous solutions of tetrasodium ethylenediaminetetraacetate (Na<sub>4</sub>-EDTA) at various concentrations were prepared. 50% THF mixed aqueous solutions of various metal salts, Mg(OAc)<sub>2</sub>, Ca(OAc)<sub>2</sub>, Ni(acac)<sub>2</sub>, Cu(OAc)<sub>2</sub>, Zn(OAc)<sub>2</sub> and Pd (OAc)<sub>2</sub> ( $2 \times 10^{-3}$  M) were added in 10-µL aliquots to 0.5 mL of a Na<sub>4</sub>-EDTA solution ( $2 \times 10^{-4}$  M) in a glass vial, and any changes were noted. Mixed aqueous solutions of 0.5 mL of the HNHBH ligand ( $2 \times 10^{-4}$  M) and 10 µL of a metal salt ( $2 \times 10^{-3}$  M) in a glass vial were treated with 1–10 µL of Na<sub>4</sub>-EDTA solutions ( $2 \times 10^{-2}$  M and 2  $\times 10^{-4}$  M). A colorimetric titration of ligand ( $2 \times 10^{-4}$  M) and Ni (acac)<sub>2</sub> ( $2 \times 10^{-3}$  M) in a 50% THF mixed aqueous solution with the addition of Na<sub>4</sub>-EDTA ( $2 \times 10^{-2}$  M) and aqueous HCl (0.5 M) was carried out.



Fig. 2. (a) Amide-imidic acid tautomerism of HNHBH ligand, and (b) Possible resonance structures of HNHBH ligand as an amide tautomer.







## 2.3. Computation

Geometry optimization and electronic structure study of the investigated ligand were carried out using the density functional theory (DFT) approach employing the B3LYP hybrid functional with the  $6-31G^*$  and  $6-311 + G^*$  basis sets [24,25]. Structural geometry optimizations of the HNHBH ligand and formed complexes were carried out to the minima on the potential energy surfaces without constrains. The relative stability and vibrational frequencies of HNHBH were also computed. The optimized binding energies (BE) of the ligand towards three metal ions of Ni, Cu and Zn were calculated using the following equation:

Binding Energy (BE) = 
$$E_{complex} - \left(E_{\rm M}^{2+} + 2 \times E_{\rm HNHBH}\right)$$
 (1)

where  $E_{\text{complex}}$  is the total energy of the ligand-metal complex,  $E_{\text{M}}^{2+}$  and  $E_{\text{HNHBH}}$  are the total energies of the free metal ions and free ligand, respectively. All calculations were carried out using the Gaussian 09 suite [26].

#### Table 1

Selected characteristic infrared absorption frequencies of the amides (free) and imidic acids (coordinated to the metal ion) forms.

Amides		Imidic acids		
Wavenumber, $\nu/\mathrm{cm}^{-1}$	Assignment	Wavenumber, $\nu/cm^{-1}$	Assignment O—H stretch	
3300-3280 (m)	N—H stretch	3500-3000 (s)		
1680–1640 (vs)	C==O stretch	1675–1600 (m)	C=N	
	(Amide I band)			
1560-1530 (vs)	N-H bend	1615-1580	C=N-N=C	
	(Amide II band)			
1310-1290 (m)	C—N stretch	1160-1120 (s)	C—OH stretch	
630–570 (s)	NC==O bend	1440-1260	C—OH in-plane bend	
		(m-s; br)		
615–535 (s)	C=O out-of-plane bend	700-600	C—OH out-of-plane deformation	
520-430 (m-s)	C—C==O bend	(m-s; br)		

Notes: s = strong; m = medium; br = broad.



Fig. 4. Absorbance against wavelength ( $\lambda$ /nm) for ligand/THF with Ni(acac)<sub>2</sub>/THF. Some spectra were omitted for the sake of clarity.

## 3. Results and discussions

## 3.1. Characterization of the ligand and ligand-metal complexes

The solutions of 2-hydroxy-5-nitrobenzaldehyde-4hydroxybenzoylhydrazone (HNHBH) were observed to change color



B3LYP/6-311+G\*

## Relative stability (kcal/mol) (a) to (b)

B3LYP/6-31G\*

(a)
(b)

# 15.4 12.6

## Energy Barrier (kcal/mol) (a) to (b)

B3LYP/6-31G*	B3LYP/6-311+G*		
35.2	31.4		

		OH ( III )		
B3L	YP/6-31G*	B3LYP/6-311+G*		
(a)	3376	3385		
(b)	3644	3654		

Calculated  $v_{out}$  (cm<sup>-1</sup>)

Fig. 5. Optimized structures, relative stability, energy barriers and OH stretching frequencies for the amide forms of HNHBH (a) with and (b) without the intramolecular hydrogen bonding.



Fig. 6. Optimized metal-ligand complexes with Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions adopting an octahedral coordination environment.



Fig. 7. Absorbance against wavelength ( $\lambda$ /nm) for hydrazone ligand/THF with interference solutions in THF. Some spectra were omitted for the sake of clarity.

10.24 ppm were assigned to the two phenol and one amide protons, respectively, as shown in Fig. S1. A summary of the NMR analysis of the ligand showing detailed peak assignments is given in Table S1. The UV-Vis spectrum of the ligand complexation (Fig. 4) also suggests that the free ligand exists as an amide tautomer. The ligand in THF has an absorption maximum at 295 nm ( $\varepsilon_{295} = 39,700 \text{ cm}^{-1} \text{ M}^{-1}$ ) with a shoulder peak at 335 nm ( $\varepsilon_{335} = 21,800 \text{ cm}^{-1} \text{ M}^{-1}$ ). These are likely due to the overlapping absorption from the two delocalized electron systems in the amide tautomer of the ligand (Fig. 2b). In the colorimetric titration of the ligand with Ni(acac)<sub>2</sub> in THF (Fig. 4), two isosbestic points were observed at 308 and 349 nm, and the complex showed a new, broad absorption band at approximately 410 nm. The new absorption band could be attributed as a charge transfer band. The peak in the region of 295 nm was not deemed significant as Ni(acac)<sub>2</sub> absorbs at 295 nm ( $\varepsilon = 16,650 \text{ cm}^{-1} \text{ M}^{-1}$ ).

The infrared spectrum of the ligand-Ni complex (Fig. 3) indicates noticeable changes in the spectral region above 3000 cm<sup>-1</sup>. This region mainly describes the nature of the N—H and O—H bonds. The strong, broad infrared band appeared at 3433 cm<sup>-1</sup> explains the presence of a non-hydrogen bonded OH stretching vibration. It suggests that the intramolecular hydrogen bonding found in the amide form no longer exists upon ligand complexation. The frequency shift in the O—H stretching vibrations from the amide to imidic acid forms is supported with calculated DFT frequencies (Fig. 5). The  $v_{OH}$  stretching vibration was calculated to be 3385 cm<sup>-1</sup> when it is intramolecularly bonded, while it was calculated at 3654 cm<sup>-1</sup> in the imidic acid form. We are concerned here about the frequency difference rather than the absolute values which could deviate from the corresponding experimental values due to the difference between the gas and solid phases. The C=O stretching band  $(1654 \text{ cm}^{-1})$  in the free ligand amide spectrum has also disappeared, while the new band at 1615 cm<sup>-1</sup> can be attributed to the C=N-N=C stretching vibration supporting the formation of imidic acid tautomer after complexation. The <sup>1</sup>H NMR spectrum of the ligand-Ni complex (Fig. S2) shows three new peaks observed at 10.45, 8.59 and 5.68 ppm. The 5.68 ppm peak can be assigned to protons from the acetylacetonate anion, the peak at 8.59 ppm was assigned as an aromatic proton, while the 10.45 ppm peak could be linked to the amide proton which has become after complexation more deshielded due to the absence of the hydrogen bonding. The EDX spectrum of the complex confirmed the presence of the metal ions which were absent in the spectrum of the pure ligand (Fig. S3). The overall shift and subsequent appearance of new peaks upon the coordination of the ligands with the metal ion are considered a sign of the tautomeric exchange that allows complexation between the ligand molecules and the metal ions.

The conformational properties of the tautomeric forms of HNHBH have been further investigated theoretically to get some insights on the energetics and stability of the ligand before and after complexation. While the two tautomeric forms were predicted to exhibit comparable stabilities, the relative stability between the amide form with the intramolecular hydrogen bond and the imidic acid form without that sort of bonding was calculated to be as high as 12 kcal/mol (Fig. 5). The transition state on the potential energy scan (PES) resulting from rotating the hydroxyl proton outward of the hydrazonic nitrogen corresponds to a noticeably high rotational energy barrier of about 30 kcal/mol. It is predicted that upon introducing the metal ions, the hydroxyl group is forced to rotate outwards in order to allow for the complexation between the HNHBH ligand and the metal ion to take place in a 2:1 ratio, as optimized at the B3LYP/6-311 +  $G^*$  level of theory and presented in Fig. 6. This is also evidenced in the IR spectra which show a blue-shifted strong band in the region of OH absorption upon addition of the metal ion compared to the case of the free ligand.

#### 3.2. Effect of parameters

#### 3.2.1. Metal interference effects

The interference solutions used contained six metal ions, namely Mg, Ca, Ni, Cu, Zn and Pd, each of which is of a concentration of approximately  $3 \times 10^{-4}$  M. The ligand was observed to be very sensitive to metal ions. When treated with interference solutions, a solution of



Fig. 8. Frontier orbitals of HNHBH depicting the HOMO and LUMO orbital energies before (a) and after complexation with (b) Ni<sup>2+</sup>, (c) Cu<sup>2+</sup> and (d) Zn<sup>2+</sup> metal ions.

#### Table 2

Binding energies of metal ions complexes with HNHBH ligand as calculated at the B3LYP/  $6-31G^*$  and B3LYP/ $6-311 + G^*$  levels of theory.

Metal ion	Binding energy (Kcal/mo	nergy (Kcal/mol)		
	B3LYP/6-31G*	B3LYP/6-311 + G*		
Ni <sup>2+</sup>	-486.4	-464.6		
Cu <sup>2+</sup>	-417.4	-397.2		
$Zn^{2+}$	-399.2	-378.2		

HNHBH in THF turned from colourless to pale yellowish-green. The UV– Vis spectral pattern is similar to that of the ligand-Ni complex in THF (Fig. 4). However, the peak wavelength of the charge transfer band has gradually shifted from 400 to 390 nm upon the addition of the interference solutions, and three isosbestic points were observed at 244, 344 and 380 nm.

Comparing the spectrum in Fig. 7 with the individual spectra of the ligand with nickel (II), copper (II) and zinc (II) ions, the charge transfer band shape suggests that zinc (II) interfered with the formation of the ligand-Ni complex more than copper (II) did. Hence the formation of the ligand-Ni complex was influenced by the presence of the zinc (II) ions and, to less extent, copper (II) ions, but not magnesium (II), calcium (II) or palladium (II) ions.

The nature of interaction between the ligand and the metal ions was investigated on the basis of calculated frontier molecular orbitals (MOs). The charge transfer behaviour of any two reactants depends on the spatial distribution of their frontier orbitals as well as the energy gap maintained. The frontier orbitals of the HNHBH ligand before and after complexation were calculated and depicted in Fig. 8. The MO interaction map shows that the free ligand LUMO was primarily confined on the hydrazonic group, which suggests a more likely binding site available for the metal ion. Upon complexation with metal ions, a corresponding energy shift in a form of an overall decrease in the energy gap was expected. The Ni(II) ion complex exhibits the most significant shift and consequently the most stable complexation among the three metal ions, in agreement with the trend observed in the color change when a complex forms. Furthermore, the coordination energies were estimated for Ni(II), Cu(II) and Zn(II) ions according to Eq. (1). The HNHBH-Ni (II) complex was calculated to possess the highest binding energy as listed in Table 2. The observed selectivity of the ligand towards nickel compared to the other metal ions could be attributed to the size that suits the octahedral type of coordination environment resulting with the relatively least tilted orientation while binding to the metal ion center (Fig. 6).

#### 3.2.2. Solvent effects

The effect of polar solvents (acetonitrile and water) on the color change has been also explored. Fig. S4 shows the UV–Vis spectrum of the ligand-Ni complex in acetonitrile (ACN). The spectrum appears similar to that of the complex in pure THF (Fig. 4). However, in the ACN solvent, the selectivity of the ligand for nickel (II) was slightly improved and yielded a darker yellowish-green solution than the case for the THF solvent. Interestingly, the isosbestic points moved from 308 to

285 nm and from 349 to 347 nm, and the charge transfer band shifted from 410 to 405 nm. Such a small hypsochromic shift could be due to the addition of ACN which is more polar than THF. The reason for the dark yellowish-green formation could be due to the ACN solvent stabilizing non-bonding orbitals through hydrogen bonding, leading to an increase in the amount of energy required to excite an electron originating from a non-bonding orbital.

Moreover, the complexation in water has been investigated. Since HNHBH is hardly soluble in water, a 50:50 ratio of water and THF was used. The ligand in a 50% THF mixed aqueous solution had an absorption maxima at 296 nm and a shoulder peak at 335 nm, which is similar to the case of the ligand in THF. The spectrum of the ligand-Ni complex in a 50% THF mixed aqueous solution was also similar to that of the ligand-Ni complex in THF (Fig. 4), with a charge transfer band at 400 nm and two isosbestic points at 293 and 347 nm. The slight hypsochromic shift observed was similar to the case of ACN, since water is also a more polar solvent compared to THF.

#### 3.2.3. pH effects

The ligand-metal complex is expected to be sensitive to the pH of the solution, as the ligand is expected to coordinate with the metal ion through the lone pairs of electrons on the oxygen and nitrogen atoms. While the addition of a base is expected to deprotonate the oxygen and nitrogen atoms and hence enhance the ligand ability to bind to the metal ion, the addition of an acid is expected to protonate the oxygen and nitrogen atoms and thus disrupt the formation of the complex or even regenerate the ligand in its free form. NaOH was chosen as the base for the investigation of the pH effect after verifying that a solution of the ligand did not change color when treated with neutral solution of sodium chloride. The addition of a few drops of the acid or base to the solution of the ligand or the ligand-metal complex caused a distinct color change without a significant change of pH. Furthermore, the color change was observed to be independent of the composition of the mixed aqueous solution.

Adding NaOH to a mixed aqueous solution of the ligand and a metal salt increased the selectivity of the ligand for nickel (II) (Table 3). On a subsequent addition of HCl to the basic solution, however, the bright yellow color was retrieved indicating a higher selectivity for nickel ions in basic conditions. The addition of HCl to a mixed aqueous solution of the ligand and a metal salt other than nickel (II) resulted with a colourless solution, and the addition of nickel (II) to the same solution turned it pale green-yellow.

To further investigate the pH phenomenon, a UV–Vis spectrum was measured at alkaline conditions (Fig. 9a). The addition of NaOH caused the charge transfer band of the ligand-Ni complex to broaden, and its peak value was observed to slightly shift from 400 to 394 nm. The subsequent addition of HCl was tested (Fig. 9b), and a clear back-shift was observed. However, on further increase of the HCl concentration, no change in the absorption pattern was observed.

The Mulliken atomic charge distribution of the HNHBH ligand was calculated (Fig. 10) and used to predict the chemical reactivity at different pH values. Atomic charges provide useful insights of relevance to the electronic nature of the molecule, from which possible bonding, antibonding or non-bonding features could be deduced [30]. For the

Table 3

Color observations for HNHBH ligand in a 50:50 THF and water mixture with individual metal salts and mixtures of metal salts at acidic and basic conditions.

Metal salt		$Mg(OAc)_2$	Ca(OAc) <sub>2</sub>	Ni(acac) <sub>2</sub>	$Cu(OAc)_2$	$Zn(OAc)_2$	Pd(OAc) <sub>2</sub>	Mixed metal salts with Ni(acac) <sub>2</sub>	Mixed metal salts without Ni(acac) <sub>2</sub>
pH 7		Very, very pale green-vellow	Very, very pale green-vellow	Pale green-vellow	Very pale green-vellow	Very, very pale green-vellow	Extremely pale green-vellow	Greenish-yellow	Very, very pale green-vellow
Addition	NaOH	Pale green-yellow	Pale green-yellow	Bright	Pale	Pale green-yellow	Pale green-yellow	Bright yellow	Pale green-yellow
of				yellow	green-yellow				
	HCl	Colourless	Colourless	Pale	Colourless	Colourless	Colourless	Pale	Colourless
				green-yellow				green-yellow	



**Fig. 9.** Graphs represent the absorbance against wavelength  $(\lambda/nm)$  for the hydrazone ligand with Ni(acac)<sub>2</sub> in a 50% THF mixed aqueous solution upon (a) the addition of NaOH; and (b) upon consecutive additions of NaOH and HC. Some spectra were omitted for the sake of clarity.

HNHBH complex, remarkably negatively charged oxygen atoms of the hydroxyl and carbonyl groups were calculated. This is in agreement with the experimental observations in which the addition of a strong acid would result in the discoloration of the complex due to the competent protonation of the carbonyl and hydroxyl oxygen atoms. A subsequent addition of a base turned the solution bright yellow as this would deprotonate the binding sites and hence availed them to coordinate with the metal ions.

## 3.2.4. EDTA effects

The influence of EDTA on the ligand-metal complex formation was also investigated. A mixture of metal salts was first introduced to a 50% THF aqueous solution of HNHBH. The aqueous solution is 1 M of Na<sub>4</sub>-EDTA. The result of the absorption study is shown in Fig. S5. At the acidic condition, a colourless solution was observed. While with the basic solution, a bright yellow color was observed (which is similar to the case without the addition of EDTA). At the basic condition, EDTA alone caused a pale yellow color to occur without the presence of HNHBH. These observations clearly indicate that at the basic condition there is a competition between HNHBH and EDTA in coordinating with nickel (II) ions, with more preference for the ligand over EDTA.

A UV–Vis absorption test was conducted for a solution with only the ligand and EDTA in order to find out if any sort of specific interaction takes place between HNHBH and EDTA. The results presented in Fig. S6 show the effect of EDTA on HNHBH. It was noted that two new peaks emerged at 369 and 416 nm, and two isosbestic points were observed at 269 and 344 nm. Such a change was found to be reversible on addition of HCl (as shown in Fig. S7). This suggests that at an acidic condition, the ligand is no longer bound to nickel (II) ions. As such, the use of HCl offers the possibility of regenerating free ligands from the complex, and this has a potential application in the development of a reusable sensor. A summary of the UV–Vis data of the free ligand, ligand-Ni complex and affecting parameters is presented in Table S2.



Fig. 10. Mulliken atomic charges of the HNHBH ligand complex with Ni<sup>2+</sup> ion as calculated at the B3LYP/6-311 + G\* level. The arrows indicate potential sites for possible protonation.

## 4. Conclusion

In this work, a hydrazone derivative; 2-hydroxy-5nitrobenzaldehyde-4-hydroxybenzoylhydrazone (HNHBH), was synthesized and investigated as a potentially selective colorimetric sensor for nickel (II) ions. HNHBH complexation with metal ions is predicted to take place via an internal rotation of the hydroxyl group overcoming the intramolecular hydrogen bonding followed by an amide - imidic acid tautomerism. DFT calculations showed that the free hydrazone ligand exists as an amide form but turned into an imidic acid form upon coordination with metal ions. While zinc (II) and copper (II) ions were shown to have a mild interference with the formation of the ligand-Ni complex, the interference of other metals with the ligand could not be ascertained. The selectivity of the HNHBH ligand towards nickel (II) ions improved slightly in the presence of a small amount of ACN, yet diminished significantly in THF-water mixed aqueous solutions. Reacting the ligand-Ni complex in a mixed aqueous solution with EDTA followed by the addition of HCl appeared to successfully regenerate the original ligand.

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#### Appendix A. Supplementary data

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