



RESEARCH PAPER

Spectrophotometric Determination and Corrosion Inhibitory of Co (II), Ni (II), Cu (II), and Zn (II) Complexes Derived from Nicotinic Acid Hydrazide

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ABSTRACT

Metal complexes formed by the reactions of Nicotinic acid Hydrazide (NAH) with copper (II), Cobalt (II), Nickel (II), and Zinc (II) sulphate ions were prepared and characterized by their infrared, electronic, magnetic moment, elemental analysis, solubility, molar conductivity, and melting point as well as their corrosion inhibition properties using the Weight Loss Method (WLM). The infrared spectra analysis showed the participation of the carbonyl group or the aromatic ring in the coordination of the metal and the ligands due to the presence of $\nu(\text{N-H})$, $\nu(\text{O-H})$, $\nu(\text{C=N})$, $\nu(\text{N-N})$, $\nu(\text{C=N})$, $\nu(\text{M-N})$ and $\nu(\text{M-O})$ bonds; the electronic spectra data shows that the ligands and the metal complexes absorbed in the visible region due to charge transfer processes from the energy in the visible light due to the presence of $\sigma\text{-}\sigma^*$, $\pi\text{-}\pi^*$, and $n\text{-}\pi^*$ transitions and hence, provide evidence that they are all coloured compounds (Harvey, 2000); the magnetic moment shows that all the metal complexes were paramagnetic except the zinc hydrazide metal complex which is diamagnetic; the elemental analysis showed that the metal to ligand ratio of the complexes is 1:2, the solubility data showed that the metal complexes were insoluble in distilled water, methanol, acetone, chloroform, ethyl acetate and dimethyl sulfoxide but were soluble in ethanol which indicates that the metal complexes are polymeric in nature; the molar conductivity analysis showed that the metal complexes exhibited weak ionic character which indicates that the ligands are part of the coordinate structure of the complexes; the melting point of the metal complexes increased from cobalt to nickel to copper to zinc metal complex thus, the zinc metal complex had the lowest melting point; the corrosion inhibition analysis using Weight Loss Method (WLM) showed that the nickel metal complex had the highest inhibition ability, followed by the zinc metal complex, then the copper metal complex and finally, the cobalt metal complex which indicates that the strength of adsorption of the metal complexes depended on the charge on the anchoring group rather than the heteroatoms.

Keywords: Nicotinic acid hydrazide, Inhibitory, Corrosion, Metal complexes, Weight loss.

INTRODUCTION

In a world where there is heavy dependence or reliance on the use of metals and alloys; protecting metals from corrosion therefore, has been paramount on the hearts and minds of the chemists whose concern has always been to help reduce or curb this threatening condition or phenomena over the past decade (Ragab *et al.*, 2015). Corrosion problems have ravaged and sunk deep into the fabrics of the chemical industry which deal with these metals and alloys and has affected a wide range of application and products causing the degradation and the failure of components and systems over time in the processing and manufacturing industries respectively (Zarghi *et al.*, 2011). The control of corrosion of metals and alloys is a very

expensive process as many industries spend huge sums of money to mitigate this scourge. A review of literature shows that many hydrazides have been used widely in medicine, catalysis, and analytical chemistry (Walaa *et al.*, 2014). However, the use of hydrazide metal complexes to inhibit corrosion is scarce and thus, there is a need for a broad spectrum of hydrazide complexes that are cheap and affordable to be synthesized and employed in the control of corrosion (Waeel, 2013)..

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This investigation is aimed at preparing the Nicotinic acid hydrazide [NAH] ligands, nicotinic acid hydrazide [NAH] complexes using Co (II), Ni (II), Cu (II), and Zn (II) sulphates and determining the corrosion inhibitory properties of these complexes so synthesized.

METHODOLOGY

Preparation of the Ester and the Nicotinic acid hydrazide (NAH)

The ester were prepared using a modified Fisher-Speier's Method (Brian *et al.*, 1989). 37.0 g (0.300 moles) of nicotinic acid was reacted with 36 ml (0.616 moles) of absolute ethanol saturated with 19 ml (0.539 moles) of concentrated hydrochloric acid in a 250 ml round bottom flask and refluxed for 5 hours at 80°C in a water bath. In order to minimise the reagents used and prevent loss of material during refluxing, 37.0 g was used; 5 hours and 80 °C was also used as prescribed by the method adopted in order to provide the environmental condition that is suitable for the process. [Weight = 35.0 g and Yield = 77.2%]

Preparation of Nicotinic Acid Hydrazide [NAH]

The nicotinic acid hydrazide [NAH] was prepared by the hydrazinolysis of ester with hydrazinemonohydrate (NH₂NH₂.H₂O) (Kumar *et al.*, 2012). 35.0 g (0.232 moles) of ester was reacted with 11 ml (0.354 moles) of hydrazinemonohydrate in a 250 ml round bottom flask and heated for 15 minutes under reflux in a water bath at 80°C. After 15 minutes, 19 ml (0.325 moles) of absolute ethanol was added into the solution until a clear solution was observed. The mixtures were left overnight to crystallise. The resulting crystals were

recrystallized with a minimum quantity of ethanol. The final crystals obtained were dried over CaCl₂ in a desiccator and weighed. [Weight = 22.0g and Yield = 69.2%].

Preparation of the metal complexes

(0.027 moles) of each of, CuSO₄.6H₂O, NiSO₄.6H₂O, CoSO₄.7H₂O and ZnSO₄.7H₂O were dissolved in 5 ml of distilled water then, 3.75g (0.027 moles) of [NAH] were also dissolved in 5ml of absolute ethanol. The metal salt solutions were added with constant stirring to the solution of the [NAH] and heated for about 10 minutes. The mixture was left overnight to crystallise. The resulting crystals were recrystallized with a minimum quantity of ethanol. The final crystals obtained were dried over CaCl₂ in a desiccator and weighed. The weights and yields were as follows: 6.5g and 62.3% for copper complex, 7.0g and 64.9% for nickel complex, 9.3g and 82.3% for cobalt complexes, and 8.5g and 74.2% for zinc complex respectively.

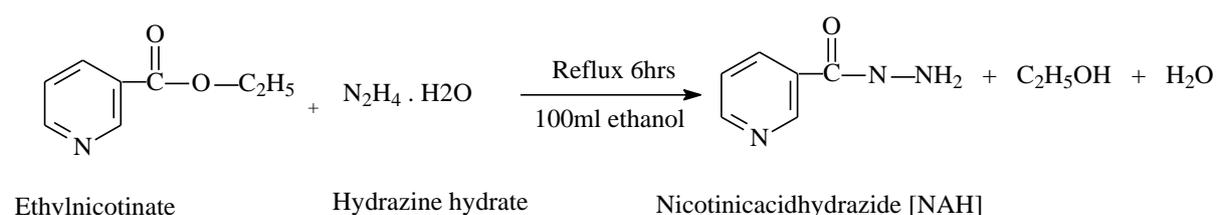
Weight Loss Method (WLM) for Corrosion Testing.

The method as described in the literature (Kavita *et al.*, 2014) was modified and adopted. The mild steel was perforated, cleaned and weighed. Two (250 ml) beakers were used to which 1.0M HCl was added to each beaker and a coupon each and labelled **I** and **II** respectively. The first beaker represented the control system and to the second beaker, 0.12g of the ([M(NAH)₂SO₄]_n(H₂O)) was added also and this last process was carried out for all the ([M(NAH)₂SO₄]_n(H₂O)) metal complexes. After 72 hours (3 days), the coupons were removed, washed and weighed on a weighing balance in grams up to 0.000.

RESULTS AND DISCUSSION

The Hydrazide

The preparation of the ligand can be represented by the equation below:



The hydrazide obtained was milky crystals which gave a moderate yield. It is quite stable in air. It could be stored for months without any appreciable change.

The Complexes

The metal (II) complexes were synthesized using equi-molar quantities of the metal (II) sulphate salts of Co, Ni, Cu and Zn respectively as shown below:



Melting point of the hydrazide and complexes

The melting point result of the ligand (nicotinic acid hydrazide) and metal(II) complexes are shown in Table 1. The results show high melting points ranging from 155-205°C indicative of the high purity of the metal (II) complexes and the nicotinic acid hydrazide (Nwabueze and Salawu, 2012).

Conductance data of the hydrazide and complexes

The Conductance data for the metal (II) hydrazide complexes on Table 1 shows that all the metal complexes are non- electrolytic in nature and thus, exhibit weak ionic character.

Table 1: Some Physical Constants, molar conductivity and the Melting point for the Ligand and Metal (II) Complexes.

Complexes	Molecular formula	Molecular weight	Yield (%)	Colour	Melting point (°C)	Molar Conductivity (ms/c)
[NAH]	C ₆ H ₇ N ₃ O	137.14	69.20	Milky	155	0.80
[Cu(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SCu	487.83	62.30	Light-blue	178	0.14
[Ni(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SNi	482.99	64.90	Light-green	220	0.14
[Zn(NAH) ₂ SO ₄].H ₂ O	C ₁₂ H ₁₆ N ₆ O ₇ SZn	453.37	74.20	White	197	0.99
[Co(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SCo	483.21	82.30	Pink	201	0.08

Solubility of the hydrazide and complexes

The ligand (nicotinic acid hydrazide) and the metal (II) hydrazide complexes prepared were soluble in ethanol but insoluble in other organic solvents as shown in Table 2.

Table 2: Solubility test for the ligand and Metal (II) Complexes.

Complexes	Distilled water	Ethanol	Acetone	Methanol	Ethyl acetate	DMSO	Chloroform
[NAH]	NS	S	NS	NS	NS	NS	NS
[Cu(NAH) ₂ SO ₄].3H ₂ O	NS	S	NS	NS	NS	NS	NS
[Ni(NAH) ₂ SO ₄].3H ₂ O	NS	S	NS	NS	NS	NS	NS
[Zn(NAH) ₂ SO ₄].H ₂ O	NS	S	NS	NS	NS	NS	NS
[Co(NAH) ₂ SO ₄].3H ₂ O	NS	S	NS	NS	NS	NS	NS

Note: S = Soluble, NS = Not Soluble

Elemental analysis of the complexes

The elemental analysis data in Table 3 is given in (mg/l). The concentration over the absorption from Table 7 on atomic absorption spectroscopic data gives the percentage composition. The result shows that the metal to ligand ratio of the complexes is 1:2.

Table 3: The Elemental Data for the Ligand/Metal (II) Complexes.

Complexes	%M	%H ₂ O	%SO ₄ ²⁻
	Calculated (experimental)	Calculated (experimental)	Calculated (experimental)
[NAH]	-	-	-
[Cu(NAH) ₂ SO ₄].3H ₂ O	12.95 (13.01)	10.97 (11.08)	19.58 (19.69)
[Ni(NAH) ₂ SO ₄].3H ₂ O	12.21 (12.16)	10.89 (11.18)	19.90 (21.22)
[Zn(NAH) ₂ SO ₄].H ₂ O	14.38 (14.42)	4.07 (3.97)	21.22 (21.17)
[Co(NAH) ₂ SO ₄].3H ₂ O	12.15 (12.20)	11.25 (11.18)	19.90 (19.87)

Infrared Spectra

The relevant IR spectra assignment is shown on Table 4. The relevant IR spectra for the ligand and metal (II) complexes are explained as shown below.

Table 4: Relevant Infrared spectra data for the ligand and complexes in KBr/NaCl Pellet in cm⁻¹.

Compounds	N-H	C=O	C=N	N-N	M-N	M-O	SO ₄ ²⁻	H ₂ O
[NAH]	3669	1733	1396	1242	-	-	-	-
[Cu(NAH) ₂ SO ₄].3H ₂ O	3231	1610	1517	1302	616	466	1063	3996
[Ni(NAH) ₂ SO ₄].3H ₂ O	3277	1607	1510	1387	612	402	1072	3753
[Zn(NAH) ₂ SO ₄].H ₂ O	3265	1617	1511	1319	607	387	1070	3875
[Co(NAH) ₂ SO ₄].3H ₂ O	3282	1617	1507	1387	608	393	1079	3736

Electronic Spectra

The electronic spectra and the magnetic data are represented in Table 5. The electronic spectrum for the zinc hydrazide complex ([Zn(NAH)₂SO₄].H₂O) showed a band at 361.00 nm (27700 cm⁻¹) assigned to ¹A₁ (π-π* due to the presence of C=C, C=O, or C=N groups) transition (Geoffrey, 1980, Salawu and Abdulsalam, 2011) and suggestive of a tetrahedral geometry. The cobalt hydrazide complex ([Co(NAH)₂SO₄].3H₂O) showed a band at 786 nm (12720 cm⁻¹) assigned to ⁴T_{1g} - ²T_{2g} (n-π* due to water molecules) transition and suggests an octahedral geometry (Vidya and

Mini, 2014). The copper hydrazide complex ([Cu(NAH)₂SO₄].3H₂O) showed a band at 419.00 nm (23900 cm⁻¹) and assigned to ²E_g - ²T_{2g} (π-π* due to the presence of C=C, C=O, or C=N groups) transition which is suggestive of a distorted octahedral geometry due to Jahn-teller effect (Rathakrishnan *et al.*, 2014). The nickel hydrazide complex ([Ni(NAH)₂SO₄].3H₂O) showed a band at 783.50 nm (12800 cm⁻¹) due to ³A_{2g} - ³T_{1g} (n-π* due to the presence of water molecules) transition and is suggestive of an octahedral geometry (Ushma and Sunil, 2014).

Table 5: Electronic Spectra and Magnetic susceptibility for the Ligand/Metal (II) Complexes.

Metal complexes	λ_{\max} (nm)	Assignment	Colour	Geometry
NAH	366.5	Charge transfer	Milky	-
[Co(NAH) ₂ SO ₄].3H ₂ O	786	⁴ T _{1g} - ² T _{2g}	Light blue	Octahedral
[Zn(NAH) ₂ SO ₄].H ₂ O	361	¹ A ₁	Light green	Tetrahedral
[Cu(NAH) ₂ SO ₄].3H ₂ O	419	² E _g - ² T _{2g}	White	Octahedral
[Ni(NAH) ₂ SO ₄].3H ₂ O	783.5	³ A _{2g} - ³ T _{1g}	Pink	Octahedral

Corrosion Inhibitory of the Metal (II) complexes

The corrosion inhibitions of the metal (II) hydrazide complexes in Table 6 shows that the cobalt hydrazide complex showed higher

inhibition abilities probably because of the presence of more vacant, low-energy electron orbitals for electron transfer or sharing with the metal (Papavinasam, 2000).

Table 6: % Inhibition Efficiency of the Hydrazide Metal (II) Complexes.

Compounds	Initial weight (g)	Final weight (g)	Loss in weight (g)	Corrosion rate	% inhibition efficiency
Control (blank)	2.967	2.748	0.219	0.00051	-
HCl + [Cu(NAH) ₂ SO ₄].3H ₂ O	2.910	2.811	0.099	0.00023	54.8 %
HCl + [Ni(NAH) ₂ SO ₄].3H ₂ O	2.896	2.835	0.061	0.00014	72.2 %
HCl + [Zn(NAH) ₂ SO ₄].H ₂ O	2.998	2.935	0.063	0.00015	71.2 %
HCl + [Co(NAH) ₂ SO ₄].3H ₂ O	2.989	2.853	0.136	0.00032	37.9 %

Magnetic susceptibility of the metal (II) complexes

The Molar Magnetic susceptibility data is given in Table 7 and the magnetic moment was calculated using the relationship: $\mu / \mu_B = 797.5 \sqrt{X_{\text{mol}} \cdot T}$

Where μ = Magnetic moment, μ_B = Bohr Magneton, X_{mol} = Molar Magnetic susceptibility and is given as the Magnetic susceptibility (X_{gram}) \times Relative Molecular Mass, and T = temperature.

The magnetic moment (μ_{eff}) for the complexes is given in Table 7 and the value for the Co²⁺ hydrazide complex is 4.95 B.M observed for Octahedral Co²⁺ complexes (Geoffrey, 1980),

and for the Ni²⁺ hydrazide complex is 3.11 B.M for octahedral Ni²⁺ complexes (Wala *et al.*, 2014). The (μ_{eff}) for the Cu²⁺ hydrazide complex is 1.93 B.M observed for an octahedral Cu²⁺ complex (Salawu *et al.*, 2011). The Zn²⁺ hydrazide complex has the (μ_{eff}) of 0.41 B.M observed for a tetrahedral Zn²⁺ complex.

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Table 7. The Atomic Absorption Spectroscopic Data for the Metal, Sulphate and Water constitutes in the complexes as well as the Molar magnetic susceptibility Data (Mag. Suscep.)

Samples	M		SO ₄ ²⁻		H ₂ O		Mag. Suceptibility (X _{mol})
	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	
[Cu(NAH) ₂ SO ₄].3H ₂ O	0.0065	0.0500	0.0050	0.0260	0.0021	0.0191	1.965 x 10 ⁻⁸
[Ni(NAH) ₂ SO ₄].3H ₂ O	0.0049	0.0400	0.0055	0.0280	0.0020	0.0184	5.103 x 10 ⁻⁸
[Zn(NAH) ₂ SO ₄].H ₂ O	0.0056	0.0450	0.0018	0.0085	0.0023	0.0565	8.869 x 10 ⁻¹⁰
[Co(NAH) ₂ SO ₄].3H ₂ O	0.0059	0.0490	0.0112	0.0560	0.0017	0.0151	1.293 x 10 ⁻⁷

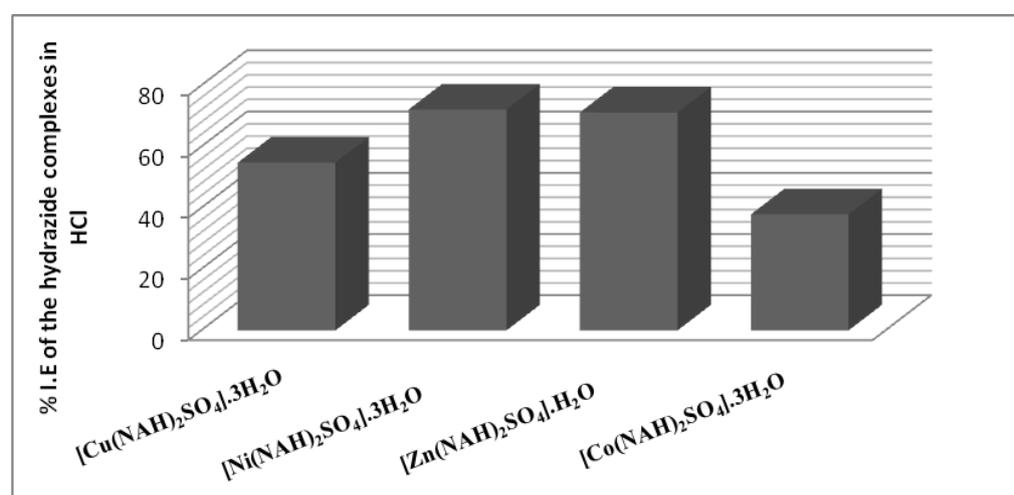
**Figure 1.0:** Percentage Inhibition Efficiency for the Hydrazide Metal (II) Complexes.

Figure 1.0 indicate that the nickel metal complex ($[\text{Ni}(\text{NAH})_2\text{SO}_4]\cdot\text{H}_2\text{O}$) and the zinc (II) hydrazide metal complex ($[\text{Zn}(\text{NAH})_2\text{SO}_4]\cdot\text{H}_2\text{O}$) has the highest inhibition efficiencies of 72.2% and 71.2% respectively, followed by the copper (II) hydrazide metal complex ($[\text{Cu}(\text{NAH})_2\text{SO}_4]\cdot\text{H}_2\text{O}$) with the inhibition efficiency of 54.8%. However, the cobalt (II) hydrazide metal complex

($[\text{Co}(\text{NAH})_2\text{SO}_4]\cdot\text{H}_2\text{O}$) has the least inhibition efficiency of 37.9%. The inhibition efficiency of the metal (II) hydrazide complexes increased as the electron density on the heteroatoms increased however, that the strength of adsorption depended on the charge on the anchoring group rather than the heteroatoms.

Conclusion

From the results of this study, the following conclusions can be drawn:

- i. Nickel complex proved to be an effective inhibitor of corrosion in 2 M hydrochloric acid solution followed by Zinc complex.
- ii. The inhibitor efficiency increases with increased inhibitor concentration.
- iii. The oxygen atoms in nickel and zinc complexes are electron rich and served as a good adsorption site using weight loss method.

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