

Full Length Research Paper

Synthesis, characterization and corrosion inhibition of Co (II), Ni (II), Cu (II), and Zn (II) complexes derived from nicotinic acid hydrazide

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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).

Key words: Ligand, Metal Complexes, Corrosion.

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. A review of literature shows that many hydrazides have been used widely in medicine, catalysis, and analytical chemistry (Nwabueze and Salawu, 2012). However, the use of hydrazide metal complexes to inhibit corrosion is scarce and so there is a need for a broad spectrum of hydrazide complexes to be synthesized and employed in the control of corrosion.

MATERIALS AND METHODS

Hydrazine hydrate (NH₂NH₂.H₂O), nicotinic acid, absolute ethanol, methanol, CuSO₄.6H₂O, NiSO₄.6H₂O, ZnSO₄.7H₂O, CoSO₄.7H₂O,

CaCl₂, concentrated HCl and acetone were of reagent grade and were obtained from commercial sources (Sigma-Aldrich Chemical Limited) and used without further purification. All solvents used were of analytical grade.

Preparation of the ester and nicotinic acid hydrazide (NAH)

The ester was prepared using the Fisher-Speier's method (Brian et al., 1989). Here, 37.0 g (0.300 mole) of nicotinic acid was reacted with 36 Hydrazine hydrate (NH₂NH₂.H₂O), nicotinic acid, absolute ethanol, mL (28.4 g; 0.616 mole) of absolute ethanol saturated with 19 mL (19.3 g, 0.539 mole) of concentrated hydrochloric acid in a 250 mL round bottom flask and refluxed for 5 h at 80°C in a water bath and the NAH was prepared by the hydrazinolysis of ester with NH NH .H O (Kumar et al., 2012). The ester of exactly 35.0 g (0.232 mole) was reacted with 11 mL (11.3 g; 0.354 mole) of NH₂NH₂.H₂O in a 250 mL round bottom flask and heated for 15 min under reflux in a water bath at 80°C. After 15 min, 19 mL (15.0 g; 0.325 mole) of absolute ethanol was added into the solution

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Table 1. Some physical constants, molar conductivity and the Melting point for the ligand and metal (II) complexes.

Ligand/Complex	Molecular formula	Molecular weight	Yield (%)	Colour	Molar conduct (ms/cm)	Temperature (°C)
NAH	C ₆ H ₇ N ₃ O	137.14	69.2	Milky	0.8	155
[Cu(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SCu	487.83	62.3	Light Blue	0.14	205
[Ni(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SNi	482.99	64.9	Light Green	0.14	175
[Zn(NAH) ₂ SO ₄].H ₂ O	C ₁₂ H ₁₆ N ₆ O ₇ SZn	453.37	74.2	White	0.99	184
[Co(NAH) ₂ SO ₄].3H ₂ O	C ₁₂ H ₂₀ N ₆ O ₉ SCo	483.21	82.3	Pink	0.08	195

Table 2. Solubility test for the ligand and metal (II) complexes.

Ligand/Complex	Distilled water	Ethanol	Acetone	Methanol	Ethyl acetate	DMSO	Chloroform
NH	NS	S	NS	NS	NS	NS	NS
[Co(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
[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

Table 3. The elemental data for the ligand/metal (II) complexes.

Compound	Found	%M	%H ₂ O	%SO ₄ ²⁻
NAH	Calculated	-	-	-
[Co(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 (19.87)
[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)

until a clear solution was observed. The mixtures were left overnight to crystallize. The resulting crystals were recrystallized with a minimum quantity of ethanol. The final crystals obtained were dried over CaCl₂ in a dessicator and weighed: [Weight = 35.0 g and Yield = 77.2% for ester and Weight = 22.0 g and Yield = 69.2% for NAH].

Preparation of the [Cu(H₂O)₃(NH)₂SO₄], [Ni(H₂O)₃(NH)₂SO₄], [Co(H₂O)₃(NH)₂SO₄], and [Zn(H₂O)(NH)₂SO₄] metal complexes

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

and weighed. Two (250 mL) beakers were used to which 1.0 M HCl was added to each beaker and a coupon each and labeled I and II, respectively. The first beaker represented the control system and to the second beaker, 0.12 g 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 h (3 days), the coupons were removed, washed and weighed on a weighing balance in grams up to 0.000.

RESULTS AND DISCUSSION

The melting point of the ligand and metal complexes is shown in Table 1. The results show high melting points ranging from 155 to 205°C indicative of the high purity of the metal complexes. The conductance data in Table 1 shows that all the metal complexes are non-electrolytic in nature and thus exhibit weak ionic character. The hydrazide metal complexes were soluble in ethanol but insoluble in other organic solvents as shown in Table 2. The elemental analysis data in Table 3 is given in mg/kg (mg/L). The concentration over the absorption from Table 4 on atomic absorption spectroscopic data gives the percentage composition. The result shows that the metal to ligand ratio of the complexes is 1:2. The corrosion

Table 4. The relevant infrared spectra data for the ligands/complexes in KBr/NaCl pellets in cm^{-1} .

Ligand/Metal complex	N-H	C=O	C=N	N-N	M-N	M-O	SO ₄ ²⁻	H ₂ O
NAH	3669	1733	1396	1242	-	-	-	-
[Co(NAH) ₂ SO ₄].3H ₂ O	3282	1617	1507	1387	608	393	1079	3736
[Zn(NAH) ₂ SO ₄].H ₂ O	3265	1617	1511	1319	607	387	1070	3875
[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

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

Metal complex	μ_{eff} (B.M)	λ_{max} (nm)	Assignment	Assignment	Geometry
NAH	-	366.50	Charge transfer	-	-
[Co(NAH) ₂ SO ₄].3H ₂ O	4.95	786.00	⁴ T _{1g} - ² T _{2g}	Paramagnetic	Octahedral
[Zn(NAH) ₂ SO ₄].H ₂ O	0.41	361.00	¹ A ₁	Diamagnetic	Tetrahedral
[Cu(NAH) ₂ SO ₄].3H ₂ O	1.93	419.00	² E _g - ² T _{2g}	Paramagnetic	Octahedral
[Ni(NAH) ₂ SO ₄].3H ₂ O	3.11	783.50	³ A _{2g} - ³ T _{1g}	-	Octahedral

Table 6. % Inhibition efficiency of the hydrazide metal (II) complexes.

S/N	Compound	Initial wt. (g)	Final wt. (g)	Loss wt. (g)	Corrosion rate	% Inhibition efficiency
1	Control (Blank)	2.967	2.748	0.219	0.00051	-
2	HCl + [Cu(NAH) ₂ SO ₄].3H ₂ O	2.910	2.811	0.099	0.00023	54.8
3	HCl + [Ni(NAH) ₂ SO ₄].3H ₂ O	2.896	2.835	0.061	0.00014	72.2
4	HCl + [Zn(NAH) ₂ SO ₄].H ₂ O	2.998	2.935	0.063	0.00015	71.2
5	HCl + [Co(NAH) ₂ SO ₄].3H ₂ O	2.989	2.853	0.136	0.00032	37.9

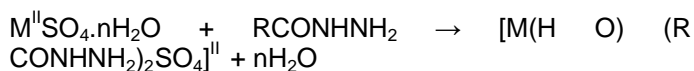
inhibitions of the metal complexes in Table 6 show that the cobalt hydrazide complex showed higher inhibition abilities probably, because of the presence of more vacant, low-energy electron orbitals for electron transfer or sharing with the metal (Papavinasam, 2000). The molar magnetic susceptibility data is given in Table 7 and the magnetic moment was calculated using the relationship as follows:

$$\mu_{\text{B}} = 797.5 \sqrt{X_{\text{mol}}} \cdot T$$

where μ = magnetic moment, μ_{B} = Bohr Magnetron, X_{mol} = molar magnetic susceptibility and is given as the magnetic susceptibility (X_{G}) \times relative molecular mass, and T = temperature.

The magnetic moment (μ_{eff}) for the complexes is shown in Table 5 and the value for the Co²⁺ hydrazide complex is 4.95 B.M observed for octahedral Co²⁺ complexes (Wala et al., 2014) and for the Ni²⁺ hydrazide complex is 3.11 B.M for octahedral Ni²⁺ complexes (Geoffrey, 1980). 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. The hydrazide complexes were synthesized using equi-molar quantities of the metal (II) sulphate salts of Co, Ni, Cu and Zn, respectively as follows:



where M is Co, Ni, Cu or Zn and n = 1, 2, 3,7.

Infrared spectra

The relevant IR spectra assignment is shown in Table 4. The relevant IR spectra for the ligand and metal (II) complexes are explained in Table 8.

Electronic spectra

The electronic spectra and the magnetic data are shown

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.).

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

Table 8. The relevant IR spectra for the ligand and metal (II) complexes.

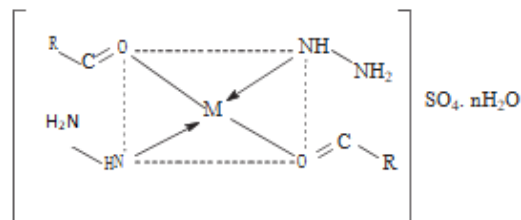
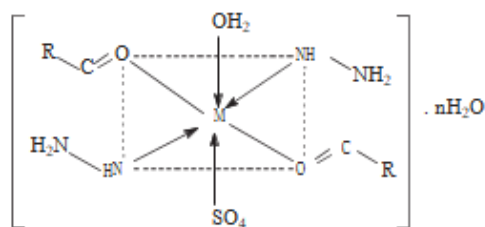
Band	Frequency(cm ⁻¹)	Assignment
v(O-H)	3431-3876	Watermolecules
v(C=N)	1396-1453	Azomethine in bonding
v(N-H)	3231-3669	Azomethine confirmed
v(N-N)	1213-1242	Azomethine confirmed
V(SO ₄ ²⁻)	1050-1153	Inner sphere coordination
v(C=O)	1600-1733	Conjugation with double bond and resonance effect

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 (δ-δ* due to the presence of C=C, C=O, or C=N groups) transition (Geoffrey, 1980) 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-δ* due to water molecules) transition and suggests an octahedral geometry (Vidya and Mini, 2014). The copper hydrazide complex [Cu(NAH) SO₄].3HO showed a band at 419.00 nm (23900 cm⁻¹) and assigned to ²E_g - ²T_{2g} (δ-δ* 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-δ* due to the presence of water molecules) transition and is suggestive of an octahedral geometry (Hamud, 2013).

Conclusion

On the basis of the physicochemical properties, the following structures are suggested for the 1:2 octahedral and tetrahedral geometry for the hydrazide metal complexes where M = Co (II), Ni (II), Cu (II) and Zn (II) and R = C₆H₅N-



CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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