



Complexes of Cu(II) and Ni(II) Sulphate with Acetone and Acetaldehyde Hydrazones Derived from Valeric Acid and Isovaleric Acid

H.D. ALIYU* and A.S. OJO

Department of Chemistry, University of Abuja, Abuja, Nigeria

*Corresponding author: E-mail: dedeji22@yahoo.com

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Eight complexes of Ni(II) and Cu(II) sulphates with valeric acid and isovaleric acid hydrazones of acetone and acetaldehyde were synthesized and characterized. The hydrazones act as a bidentate ligands coordinating through the oxygen of the carbonyl and the azomethine nitrogen, while the SO_4^{2-} ions occurs in the outer sphere complex. The microbial activities of the ligands and their metal complexes are encouraging.

Key Words: Complexes, Cu(II), Ni(II), Hydrazones, Valeric acid, Isovaleric acid.

INTRODUCTION

Much attention is given to acylhydrazones and some other hydrazines derivatives because of their biological and physiological activities¹. They generally exhibit strong antibacterial activity which is enhanced on complexation to some transition metal ions². Generally the acylhydrazones are tridentate ligands and the coordination chemistry of these ligands is of interest^{3,4}. We report here the Cu(II) and Ni(II) sulphate complexes of acetone and acetaldehyde valeric and isovaleric acid hydrazones and their biological activity.

EXPERIMENTAL

Valeric acid, isovaleric acid, hydrazine, ethanol, Ni(II) sulphate and Cu(II) sulphate and all other organic solvents are products of BDH Ltd.

Valeric acid hydrazide: 8.37 mL (8.62 g, 0.17 mol) of hydrazine hydrate was added to 18.85 mL (17.5 g, 0.17 mol) of valeric acid in 50 mL of ethanol in a 250 mL round bottom flask was refluxed for 6 h, on a water bath. The mixture was concentrated and left to stand for 2 days. The resulting crystals was dried over silica gel in a vacuum desiccator.

Acetaldehyde valeric acid hydrazone (AVAH): 9 g (0.08 mol) of valeric acid hydrazide in 20 mL of ethanol was refluxed with 4.4 g (0.1 mol) of acetaldehyde in a 250 mL round bottom flask for 6 h. The resulting solution was concentrated and left to crystallize after 1 week. The same procedure was employed for the synthesis of acetaldehyde valeric acid hydrazone (AAVAH), acetone isovaleric acid hydrazone (AIVAH) and acetaldehyde acetone isovaleric acid hydrazone (AAIVAH).

Synthesis of complexes [Ni(AVAH)]: 1.60 g (0.0113 mol) of acetone valeric acid hydrazone was dissolved in 30 mL of ethanol and was added into 1.4 g (0.0056 mol) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 20 mL of deionized distilled water gently, while stirring. The resulting green crystal was filtered, recrystallized and dried over silica gel in a vacuum desiccator.

Similar procedure was followed for the preparations of [Ni(AAVAH)], [Cu(AVAH)] [Cu(AAVAH)], [Ni(AIVAH)] [Ni(AAIVAH)], [Cu(AIVAH)] and [Cu(AAIVAH)].

The IR spectra of the ligands and complexes were run on perkin-elmer 1750 Ft spectrophotometer, while the electronic spectra were run on pe-unicam ps-750 UV-Visible spectrophotometer in ethanol and the magnetic susceptibility on MBS auto magnetic susceptibility balance, the melting point of the ligands and complexes were taken on a gahlen hamp melting point apparatus. The metal and SO_4 ions were determined according to standard method⁵ while the microbial screening was by Agal-well diffusion method⁶ against the following microbes *i.e.*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Klebsiella pneumoniae* and *Shigella flexneri*.

RESULTS AND DISCUSSION

The molecular formula of the ligands are shown below:



and



Their Ni(II) and Cu(II) complexes gave a 1:2, M:L ratio, according to the general equation.

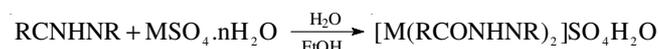


TABLE-1
 PHYSICO-CHEMICAL PROPERTIES OF THE COMPOUNDS

Compound	m.f.	m.w. (g)	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)				
					C	H	N	S	M
AVAH	C ₇ H ₁₄ N ₂ O	142	Brown	146	50.06 (59.15)	9.72 (9.86)	19.58 (19.62)	-	-
AAVAH	C ₈ H ₁₆ N ₂ O	156	Brown	148	60.87 (61.15)	10.12 (10.26)	17.76 (17.95)	-	-
AIVAH	C ₂ H ₁₄ N ₂ O	142	Brown	142	58.96 (59.15)	9.68 (9.86)	19.46 (19.62)	-	-
AAIVAH	C ₈ H ₁₆ N ₂ O	156	Brown	144	61.10 (61.15)	10.12 (1.26)	17.82 (17.95)	-	-
N ₁ (AVAH) ₂ SO ₄ ·H ₂ O	C ₁₄ H ₃₀ N ₄ O ₆ NiS	441	Light Brown	194	37.72 (38.10)	6.58 (6.80)	12.62 (12.70)	7.12 (7.26)	13.12 (13.37)
Cu(AVAH) ₂ SO ₄ ·H ₂ O	C ₁₄ H ₃₀ N ₄ O ₆ CuS	446	Dark green	198	37.60 (37.67)	6.48 (6.73)	12.48 (12.56)	7.10 (7.17)	14.12 (14.35)
N ₁ (AAVAH) ₂ SO ₄ ·H ₂ O	C ₁₆ H ₃₄ N ₄ O ₆ NiS	469	Green	142	40.82 (40.94)	7.12 (7.25)	11.72 (11.94)	6.78 (6.82)	12.32 (12.58)
Cu(AVAH) ₂ SO ₄ ·H ₂ O	C ₁₆ H ₃₄ N ₄ O ₆ CuS	474	Blue	166	40.12 (40.50)	7.02 (7.17)	11.62 (11.81)	6.42 (6.75)	13.28 (13.50)
N ₁ (AIVAH) ₂ SO ₄ ·H ₂ O	C ₁₄ H ₃₀ N ₄ O ₆ NiS	461	Green	188	38.01 (38.10)	6.28 (6.80)	12.46 (12.70)	7.12 (7.20)	13.18 (13.37)
Cu(AIVAH) ₂ SO ₄ ·H ₂ O	C ₁₄ H ₃₀ N ₄ O ₆ CuS	446	Blue	157	37.42 (37.67)	6.52 (6.80)	12.46 (12.56)	6.88 (7.17)	14.18 (14.35)
N ₁ (AAIVAH) ₂ SO ₄ ·H ₂ O	C ₁₆ H ₃₄ N ₄ O ₆ NiS	469	Green	186	40.68 (40.74)	7.12 (7.25)	11.82 (11.94)	6.68 (6.82)	12.46 (12.58)
Cu(AAIVAH) ₂ SO ₄ ·H ₂ O	C ₁₆ H ₃₄ N ₄ O ₆ CuS	474	Blue	178	40.18 (40.50)	7.12 (7.17)	6.58 (11.81)	6.56 (6.75)	13.28 (13.50)

 TABLE-2
 MAGNETIC AND ELECTRONIC DATA

Compound	λ_{\max} (cm ⁻¹)	Assignment	μ_{eff} B.M.	Stereochemistry
Ni(AVAH) ₂ SO ₄ ·H ₂ O	25641	³ A _{2g} → ³ T _{1g} (p)	2.38	Distorted Octahedral
	137336	³ A _{2g} → ³ T _{1g} (f)		
Cu(AVAH) ₂ SO ₄ ·H ₂ O	12315	d-d	1.24	Distorted Octahedral
	23774	³ A _{2g} → ³ T _{1g} (p)		
Ni(AVAH) ₂ SO ₄ ·H ₂ O	13736	³ A _{2g} → ³ T _{1g} (f)	2.34	Distorted Octahedral
	12048	d-d		
Cu(AVAH) ₂ SO ₄ ·H ₂ O	12048	d-d	1.26	Distorted Octahedral
	27486	³ A _{2g} → ³ T _{1g} (p)		
Ni(AIVAH) ₂ SO ₄ ·H ₂ O	13728	³ A _{2g} → ³ T _{1g} (f)	2.32	Distorted Octahedral
	12288	d-d		
Cu(AIVAH) ₂ SO ₄ ·H ₂ O	12288	d-d	1.26	Distorted Octahedral
	295851	³ A _{2g} → ³ T _{1g} (p)		
Ni(AIVAH) ₂ SO ₄ ·H ₂ O	13736	³ A _{2g} → ³ T _{1g} (f)	2.33	Distorted Octahedral
	12048	d-d		
Cu(AIVAH) ₂ SO ₄ ·H ₂ O	12048	d-d	1.28	Distorted Octahedral

 TABLE-3
 KEY IR BANDS (cm⁻¹) OF THE LIGANDS AND COMPLEXES

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\Delta\nu(\text{CO})$	$\nu(\text{C=N})$	$\Delta\nu(\text{C=N})$	$\nu(\text{SO}_4)$
AVAH	-	3203	1710	-	1589	-	-
N ₁ (AVAH) ₂ SO ₄ ·H ₂ O	3428	3210	1641	69	1461	128	1093
Cu(AVAH) ₂ SO ₄ ·H ₂ O	3442	3188	1642	68	1465	124	1105
AIVAH	-	3220	1728	-	1592	-	-
N ₁ (AIVAH) ₂ SO ₄ ·H ₂ O	3448	3216	1629	99	1459	133	1089
Cu(AIVAH) ₂ SO ₄ ·H ₂ O	3492	3216	1664	64	1441	131	1099
AAVAH	-	3195	1656	-	1548	-	-
N ₁ (AAVAH) ₂ SO ₄ ·H ₂ O	3488	3178	1621	35	1459	89	1086
Cu(AVAH) ₂ SO ₄ ·H ₂ O	3462	3180	1612	44	1461	87	1093
AAIVAH	-	3195	1662	-	1535	-	-
N ₁ (AAIVAH) ₂ SO ₄ ·H ₂ O	3496	3192	1633	29	1461	74	1097
Cu(AAIVAH) ₂ SO ₄ ·H ₂ O	3448	3188	1666	14	1454	81	1083

Their physicochemical properties are given in Table-1, shows a moderate melting points and are soluble in both the polar and non polar solvents.

Electronic properties: Their electronic data in ethanol are shown in Table-2. Reveal a *d-d* transition for the Cu(II) complexes around 12000 cm⁻¹ of a distorted octahedral symmetry, while the Ni(II) complexes gave two bands, which has been assigned to the spin allowed transitions ³A_{2g} → ³T_{1g} (p) and ³A_{2g} → ³T_{1g} (f) usually observed for distorted octahedral symmetry of Ni(II) complexes(1). The room temperature magnetic moment for both Ni(II) and Cu(II) complexes fall in the range of 1.24-1.28 and 2.32-2.38 BM, respectively and are within the range for distorted octahedral complexes⁷.

IR spectra: The relevant features of IR bands for the ligands and complexes are shown in Table-3. The broad band, around 3400 cm⁻¹ is been attributed to the $\nu(\text{OH})$ of water of crystallization which obscured the $\nu(\text{NH})$ bands. The amide I band $\nu(\text{C=O})$ in the ligand, located around 1662 and 1682 for AVAH and AAVAH respectively is been lowered between by between 14-99 cm⁻¹ in the spectra of the complexes due to the coordination *via* the carbonyl oxygen⁸. The vibrational frequency of the azomethine group $\nu(\text{C=N})$ is similarly altered indicating coordination *via* the nitrogen of this group^{4,8}. The stretching vibration of the SO₄²⁻ is observed as a sharp singlet around 1100 cm⁻¹ implying that the group is acting as a counter ion.

TABLE-4
ANTIMICROBIAL SCREENING OF THE LIGANDS AND COMPLEXES

Compound	<i>Staphylococcus aureus</i>	<i>Pseudomonas aeruginosa</i>	<i>Bacillus subtilis</i>	<i>Shigella flexneri</i>	<i>Kiebsiella pneumoniae</i>
AVAH	+	-	+	-	-
N ₁ (AVAH) ₂ SO ₄ .H ₂ O	++	-	-	++	++
Cu(AVAH) ₂ SO ₄ .H ₂ O	-	++	-	++	++
AIVAH	+	-	+	-	-
N ₁ (AIVAH) ₂ SO ₄ .H ₂ O	++	-	-	++	++
Cu(AIVAH) ₂ SO ₄ .H ₂ O	++	-	-	-	-
AAVAH	-	-	-	-	-
N ₁ (AAVAH) ₂ SO ₄ .H ₂ O	-	-	-	-	++
Cu(AAVAH) ₂ SO ₄ .H ₂ O	++	++	++	++	++
AAIVAH	-	-	-	-	-
N ₁ (AAIVAH) ₂ SO ₄ .H ₂ O	-	-	-	-	-
Cu(AAIVAH) ₂ SO ₄ .H ₂ O	-	-	-	-	-

+ = partially active, ++ = moderately active and - = not active

Microbial activity: The microbial screening of the ligands and complexes as given in Table-4, shows no activity against the tested organisms for the ligands AAVAH and AAIVAH and their Cu(II) and Ni(II) complexes, with exception of Cu(AAVAH) complex which gave a moderate activity. In the case of AVAH and AIVAH, which are partial active against some of the microbes shows moderate activity on complexation.

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