

Complexes Of 4-Cyanobenzaldehydeisonicotinic Acid Hydrazone With Some Transition M(II) Sulphates. (M= Cu, Co, Ni)

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ABSTRACT: New complexes of 4-Cyanobenzaldehydeisonicotinic acid hydrazone (4-CBINH) with M(II) Sulphates (M= Cu, Co, Ni) have been synthesized and characterized. The complexes were characterized by elemental analysis, conductance, infrared and electronic spectral studies. The ligand and complexes were screened for antimicrobial activity. The electronic data indicate an octahedral coordination for the Ni²⁺ and Co²⁺ complexes while the Cu²⁺ complexes assumed a square planer geometry. The spectral data are diagnostic of a bidentate coordination via the carbonyl oxygen and the azomethine nitrogen while the sulphate ions are in the outer coordination sphere.

[Nwabueze J.N and Salami H.A. **Complexes Of 4-Cyanobenzaldehydeisonicotinic Acid Hydrazone With Some Transition M(II) Sulphates. (M= Cu, Co, Ni).** *N Y Sci J* 2013;6(2):102-104]. (ISSN: 1554-0200).

<http://www.sciencepub.net/newyork>. 16

Key Words: Cyanobenzaldehydeisonicotinic acid, hydrazone, Sulphates

Introduction

The remarkable biological activity of acid hydrazides R-CO-NH-NH₂, their corresponding aroylhydrazones R-CO-NH-N=CH-R', and the dependence of their activity on the mode of chelating with transition metal ions have been of significant importance in the past [1-3]. Hydrazones have also been known for their significant antimicrobial, anticonvulsant, analgesic, anti-inflammatory and antitumoral activities [4-6]. Isonicotinic acid hydrazone (INH) is a drug of proven therapeutic importance and is used for bacterial ailments, e.g., tuberculosis. Hydrazones derived from condensation of isonicotinic acid hydrazone with pyridine aldehydes have been found to show better antitubercular activity than INH [7]. Agarwa *et al* investigated the coordinating ability of INH-derivatives with metal ions [8]. Tri- and terdentate Schiff bases may contain ONO or ONS donor atoms. Their metal complexes may be monomeric, dimeric, trimeric or tetrameric with abnormal magnetic properties and characteristic structures.

As a continuation of our interest in the coordination behaviour of Schiff bases with isonicotinoylhydrazones [9], the synthesis and characterization of a series of Copper(II), Cobalt(II), and Nickel(II) complexes with the 4-cyanobenzaldehydeisonicotinic acid hydrazone (4-CBINH) ligand are reported herein.

Experimental

Ethylisonicotinate and 4-cyanobenzaldehyde were obtained from sigma-Aldrich chemical Ltd while the metal sulphates and other reagents and solvents used were from BDH Chemicals Ltd, England. They were all used without further purification.

Preparation of 4-cyanobenzaldehydeisonicotinic acid hydrazone (4-CBINH)

Isonicotinic acid Hydrazone was prepared from ethylisonicotinate and hydrazine hydrate using standard method [1]. The ligand 4-CBINH was then prepared as follows; 10g (0.27 moles) of Isonicotinic acid Hydrazone was mixed with 11.75g (0.08 moles) of 4-cyanobenzaldehyde in 200ml of absolute ethanol and refluxed for four hours in a 500ml round bottom flask. The mixture was left for 24 hours to crystallize. The milky colour crystals formed were dried over silica gel in a desiccator and weighed. (Yield 16.90g, 89.04%)

Preparation of the complexes

The complexes were prepared by the reaction between ethanolic solutions of the ligand in a 1:2 molar ratio.

Preparation of Cu-Sulphate/4-CBINH complex

0.64g (0.004 moles) of CuSO₄.5H₂O was dissolved in 40ml of water and 2.0g (0.008 moles) of the CBINH ligand was dissolved in 200ml of ethanol. The ligand solution was then added gently, with stirring, to the solution of the metal salt. Greenish crystals were formed. The crystals were filtered and dried over silica gel in a desiccator. (Yield 1.70g, 31.36%). The Cobalt(II), and Nickel(II) complexes were similarly prepared.

Elemental Analysis

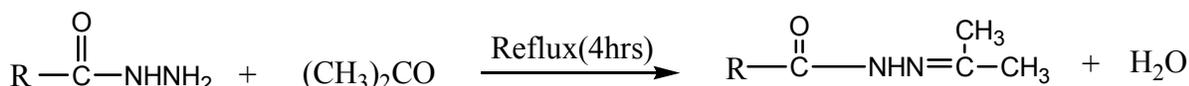
The percentage of metal in the complexes was determined complexometrically using EDTA while percentage sulphate was determined gravimetrically as sulphate by precipitation using BaCl₂.

Instrumental Measurement

Conductivity measurement in ethanol was made using WTW LF conductivity meter. IR spectra in Nujol were taken on a Mattson Genesis II FTIR Spectrophotometer while the electronic spectra were recorded using 21D Milton-Roy UV-VIS spectrophotometer.

Antimicrobial screening

Antimicrobial screening of the ligand, the metal salts and the complexes in aqueous methanol was carried out using nutrient agar. Petri dishes



The analytical data and some physical constants for the ligand and the complexes are shown in Table 1. The insolubility of the ligand in common organic solvents, their high melting/decomposition point and very low conductivity indicate that they are monomeric non electrolytes [3].

Infrared data

The diagnostic IR data for the ligand and complexes are shown in Table 2. The bands appearing in the spectra of the ligand between 1682-1650 cm^{-1} have been assigned to $\nu(\text{C}=\text{O})$ [10]. This band was lowered by 70-80 cm^{-1} on complex formation, indicating the involvement of the carbonyl group in bonding to the metal ions. The bands corresponding to $\nu(\text{C}=\text{N})$ located in the spectrum of the ligand is between 1665- 1595 cm^{-1} and in the complexes, between 1585-1535 cm^{-1} . This band underwent a shift to a lower wave number by 80-100 cm^{-1} on complex formation, indicating the involvement of the azomethine nitrogen in the bonding [11].

The SO_4^{2-} group belongs to the high symmetry T_d point group. Uncoordinated SO_4^{2-} group has one active IR vibration Located around 1100 cm^{-1} . On coordination the symmetry is lowered leading to the splitting of the band into multiplets. The $\nu(\text{SO}_4)^{2-}$ band in all the complexes is found around 1100 cm^{-1} as a singlet, this is consistent with an outer sphere sulphate group [12].

Electronic Spectra

The electronic spectra of the complexes are shown in Table 3. The spectra of the cobalt(II) complex show bands at ca 500nm and 520nm. The band at 520nm is a shoulder of the higher energy band. An octahedral coordination is therefore indicated. The bands have, therefore, been assigned to the $^4\text{T}_{2g}(\text{F})$ to $^4\text{T}_{1g}(\text{P})$ and $^4\text{T}_{2g}(\text{F})$ respectively [13]. The spectra of the copper(II) complexes show a single band located at ca 600nm. This $d \rightarrow d$ band is indicative of a square planer geometry for the

containing already jelled nutrient agar were inoculated with the microorganisms viz, *Candida albican*, *Pseudomonas amerusinosa* and *Escherichia coli*. The Petri dishes were incubated at 37C for 1 hr; this was done in duplicates. Antibacterial activity was measured as zone of inhibition around the disc.

Results And Discussion

The preparation of the hydrazone from the acylhydrazide is represented by the chemical equation below:

complexes [14]. Two bands are observed in the spectra of the nickel(II) complex at around 400nm and 550nm. The bands have been assigned to the transitions from the $^3\text{A}_{2g}$ ground term to the $^3\text{T}_{1g}(\text{P})$ and $^3\text{T}_{1g}(\text{F})$ respectively. An octahedral geometry is therefore inferred [15].

Antimicrobial screening

The results of the antimicrobial screening of the compounds are shown in Table 4. The antimicrobial activity of the compounds is insignificant probably due to the presence of few nitrogen atoms [16].

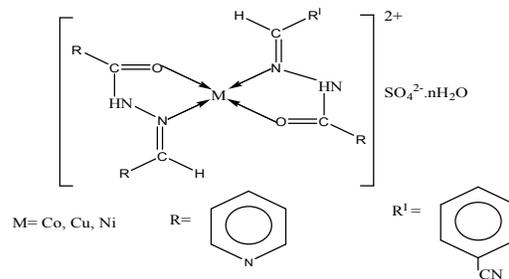


Figure I: Suggested structure for the complexes

Conclusion

The ligand 4-cyanobenzaldehydeisonicotinic acid hydrazone was successfully synthesized and it formed complexes with the title metal salts. The ligand acted as a neutral bidentate donor via the carbonyl oxygen and the azomethine nitrogen. The cobalt and nickel complex are octahedral while the copper complex has a square planer geometry. The anions appear to be in the outer coordination sphere. No significant antimicrobial activity was shown by the complexes. On the bases of their physicochemical studies the suggested structures for the complexes are presented in figure I.

Table 1: Analytical data and some physical constants of the ligand and metal complexes

Compound	Formula	Formula Weight (g mol ⁻¹)	Color	%Yield	%Metal (Calc.)	Solubility	m.p (°C)	Molar Conductivity (ohmcm ² mol ⁻¹)
INH	C ₆ H ₇ N ₃ O	137	White	55.24	-	-	-	-
CBINH	C ₁₇ H ₁₀ N ₄ O	250.03	Cream	89.04	-	EtOH	256(M)	-
(Cu)(CBINH) ₂ SO ₄ .H ₂ O	C ₂₈ H ₂₂ N ₈ O ₇ SCu	677.56	Green	31.36	9.37 (9.29)	DMSO	183(D)	0.277
(Co)(CBINH) ₂ SO ₄ .3H ₂ O	C ₂₈ H ₂₆ N ₈ O ₉ SCo	708.933	Pink	18.51	8.31 (8.30)	DMSO	115(D)	0.277
((Ni)(CBINH) ₂ SO ₄ .2H ₂ O	C ₂₈ H ₂₄ N ₈ O ₈ SNi	690.75	Light green	38.18	8.49 (8.47)	DMSO	237(D)	0.274

Table 2: Electronic Data for the Complexes

Compound	λ max (nm)	Assignment	Suggested geometry
(Cu)(CBINH) ₂ SO ₄ .H ₂ O	550	d→d	Square planer
(Co)(CBINH) ₂ SO ₄ .3H ₂ O	500	⁴ T _{2g} (F) → ⁴ T _{1g} (P)	Octahedral
((Ni)(CBINH) ₂ SO ₄ .2H ₂ O	410	³ A _{2g} → ³ T _{1g} (P)	Octahedral

Table 3: Diagnostic IR Data for the ligand and metal complexes

Compound	ν (OH)	ν(NH)	ν (C=N)	ν (C=O)	Δ(C=O)	Δ(C=N)	ν(SO ₄) ²⁻	ν (M-N)
CBINH	-	3182	1595	1643	70	87	1145	-
(Cu)(CBINH) ₂ SO ₄ .H ₂ O	-	3180	1567	1626	73	83	1149	502
(Co)(CBINH) ₂ SO ₄ .3H ₂ O	3395	3158	1545	1644	80	100	1135	615
((Ni)(CBINH) ₂ SO ₄ .2H ₂ O	3420	3181	1540	1643	76	80	1145	-

Table 4.5 : Antimicrobial activity for the ligand and their metal complexes

Compound	<i>Candida albican</i>	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>
CBINH	-	-	-
(Cu)(CBINH) ₂ SO ₄ .H ₂ O	-	-	-
(Co)(CBINH) ₂ SO ₄ .3H ₂ O	+	-	-
((Ni)(CBINH) ₂ SO ₄ .2H ₂ O	-	-	-

Key: + = Active

- = Inactive

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