

Synthesis, FTIR and Electronic Spectra Studies of Metal (II) Complexes of Pyrazine-2-Carboxylic Acid Derivative

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Abstract

Aminolysis of pyrazine-2-carboxylic acid was carried out through an intermediate ethyl pyrazinoate formed by a reaction between pyrazine-2-carboxylic acid and ethanol in the presence of concentrated sulfuric acid under reflux which was then reacted with 2-Aminopyridine under same reflux and the final product proposed theoretically N-(pyridin-2-yl)pyrazine-2-carboxamide a novel compound was characterized using FTIR spectroscopy, UV/Visible spectroscopy and other physical measurement such as melting point determination, solubility were determined. The FT-IR spectrum of the proposed compound showed absorption shift different from the starting ligand(POA) having (NH) stretch at 3323 cm⁻¹ and (3349 cm⁻¹, 3256 cm⁻¹) of A1 and A2 ligands respectively, (CO) stretch at 1665 cm⁻¹ and 1678 cm⁻¹ for PYPC1 and PYPC2 respectively. The complexes A3 and A5 spectra studies showed a Cu-N, Cu-O, Co-N, and Co-O coordination.

Keywords: Aminolysis; Pyrazine-2-carboxylic acid; Refluxing; Absorption; Solubility; Copper; Cobalt; Spectra studies

Introduction

Transition metal ions are playing an important role in biological processes in human body [1]. Ogunniran et al., [2] have proved that physical properties and antimicrobial activities are enhanced upon complexation. The use of metal in the complexing of ligand especially drug based ligand has become a vibrant and growing aspect of research among inorganic chemists and biologist over the last few decades resulting in a variety of exciting and valuable drugs which are already in the market [3].

Pyrazinamide is a first line anti-tuberculosis drug commonly used in the formation of different metal complexes and various compounds possessing the -NHCO- groups were found to inhibit photosynthetic electron transport [4]. Pyrazine-2-carboxylic acid derivative are commonly used in the formation of metal complexes.

This research work is focused on the synthesis, FTIR and UV/Visible spectrophotometry characterization of pyrazine-2-carboxylic acid derivative ligand and metal complexes with the synthesized ligand with Cu(II) and Co(II) metal ions also melting point determination and solubility test were observed for purity of the synthesized ligand and metal complexes.

Materials and Methods

Materials

Analytical grade of Cobalt(II) sulphate heptahydrate and Copper(II) sulphate pentahydrate were used as such without further purification. Pyrazine-2-carboxylic acid and absolute ethanol was purchased from Sigma Aldrich, UK. 2-Aminopyridine was also purchased from Lobal Chemie, Mumbai, India. Concentrated sulphuric acid was purchased from Fishers Scientific UK. All other solvents used were of analytical grade.

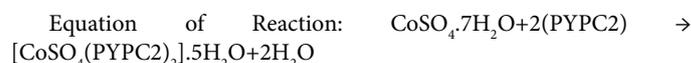
Synthesis of N-(pyridine-2-yl)pyrazine-2-carboxamide (PYPC)

A mixture of pyrazine-2-carboxylic acid (1.19 g; 10 mmol) and the corresponding ethanol (20 ml) in few drops of concentrated sulphuric acid was refluxed for 7 hours [5] then 1.99 g of 2-aminopyridine (21 mmol) was added then refluxed for 5 hours and excess 2.07 g of 2-aminopyridine (22 mmoles) was also added and further refluxed for

4 hours. A dark brown solid (PYPC1) was formed on cooling at room temperature and recrystallize from ethanol to form a white precipitate (PYPC2) with colourless crystals [6].

Synthesis of [CoSO₄(PYPC2)₂].5H₂O

An aqueous solution of CoSO₄.7H₂O (5mmole; 1.405 g) was mixed with a methanolic solution of PYPC2 (2.00 g, 10 mmol) and heated in boiling water while stirring for 30 minutes. A light brown precipitate with crystals was formed on cooling at room temperature for 24 hours. The same method was applied for ethanolic solution synthesis of the same complex with same ratio used in the methanolic synthesis but heated at temperature of 80°C for 1 hour and resulting solution was allowed to evaporate slowly at room temperature for 5 days. A dark brown precipitate with crystals was formed.



Synthesis of [CuSO₄(PYPC)₂].3H₂O

An aqueous solution of CuSO₄.5H₂O (5 mmole; 1.248 g) was mixed with a methanolic solution of PYPC2 (10mmol) and heated in boiling water while stirring for 20 minutes. A grey precipitates with crystals was formed on cooling at room temperature for 24 hours.



Results and Discussion

Some physical and spectroscopic data of the ligands and their metal complexes are presented in the Tables 1 and 2.

All the complexes showed a melting point value and the ligand synthesized showed a low melting point compared with the starting

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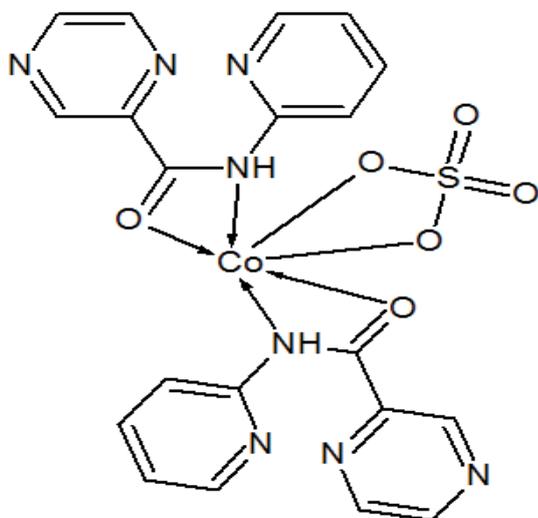


Figure 1: Proposed structure of $[CoSO_4(A2)_2] \cdot 5H_2O$ complex.

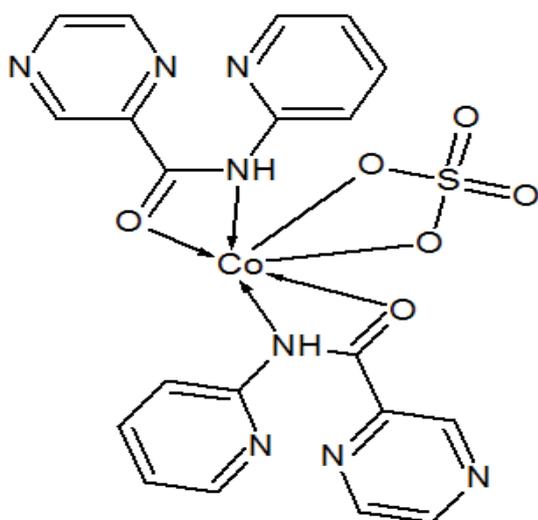


Figure 1: Proposed structure of $[CoSO_4(A2)_2] \cdot 5H_2O$ complex.

material pyrazine-2-carboxylic acid (225°C). The two complexes synthesized were crystalline in nature.

All the complexes are insoluble in the available solvents but slightly soluble in de-ionized water and the ligand is soluble in ethanol and methanol on heating, slightly soluble in de-ionized water.

Infrared spectra of synthesized ligand and metal complexes

The infrared spectra of the ligand, its derivatives and complexes were measured from 400 to 4000 cm^{-1} . A sharp absorption band occurs in the region 3000-3400 cm^{-1} of the amide group assigned to $\nu(NH)$ vibrations [7]. The band at (3349 cm^{-1} , 3256 cm^{-1}) and 3323 cm^{-1} in the spectrum of N-(pyridine-2-yl) pyrazine-2-carboxamide (PYPC2 and PYPC1) respectively is attributed to $\nu(NH)$ of the amide group but when compared to the Pyrazine-2-carboxylic acid spectrum there was a shift in the frequency of an $\nu(OH)$ 3065 cm^{-1} of the carboxylic acid to a higher frequency in the region of the $\nu(NH)$. A strong and sharp absorption occurs in the region of 1680-1630 cm^{-1} assigned to carbonyl group of an amide [8]. For ligand N-(pyridine-2-yl) pyrazine-2-carboxamide (PYPC1 and PYPC2) a strong and sharp absorption band occurs at 1665 cm^{-1} and 1678 cm^{-1} respectively which is assigned to C=O stretching different from the 1732 cm^{-1} and 1715 cm^{-1} bands of the Pyrazine-2-carboxylic acid ligand. The characteristic absorption bands in the region 1725-1700 cm^{-1} is attributed to a C=O of a carboxylic acid [8]. The sharp absorption band of C=O stretching observed at 1678 cm^{-1} of the free A2 ligand shifted to a lower frequency in the A3(1641 cm^{-1}), and A5(1640 cm^{-1}) complexes. This indicates the coordination of PYPC2 through the carboxyl group [9]. The N-H stretch observed at 3349 cm^{-1} and 3256 cm^{-1} of the free A2 ligand also shows a slight shift in lower frequency of the complexes having A3(3254 cm^{-1}), with exception to A5(3431 cm^{-1}) that shows a slight increase in the frequency which indicate the coordination of amide nitrogen. The absorption band at (461 cm^{-1} , 442 cm^{-1}) and (409 cm^{-1} , 463 cm^{-1}) of A3 and A5 complexes respectively are attributed to Co-N while (696 cm^{-1} , 625 cm^{-1}) and (542 cm^{-1}) of A3 and A5 respectively are attributed to Co-O (Tables 3 and 4).

The UV spectra of the free ligand displayed a sharp band at 240 nm and 296 nm which is due to intra-ligand charge transfer transition of N-(pyridine-2-yl) pyrazine-2-carboxamide (PYPC1) ligand. In the UV/visible region of the Co(II) complex (Figure 1) two peaks were observed at 324 nm and 960 nm which are due to charge transition from metal to ligand and d-d transition (${}^4T_1g \rightarrow {}^4T_1g(p)$) respectively. The Cu(II) complex (Figure 2) showed two peaks, one sharp (at 295 nm) and the other broad at 650 nm which were also due to charge transition from ligands to metal and d-d transition (${}^2e_{g(D)} \rightarrow {}^2b_{1g(D)}$) respectively.

Compound	Physical State	Melting Point (°C)	Colour	% Yield
PYPC1	Crystalline	161°C	White	70
PYPC2	Semi-Solid	N/A	Dark-Brown	65
Co(II) Complexes (A3)	Crystalline	>300	Dark brown	62
Cu(II) Complex (A5)	Crystalline	>300	Grey	64

Table 1: Physical properties of ligand and complexes.

Compound	De-ionised water(RT/warm)	Ethanol (RT/warm)	Methanol (RT/warm)	Acetone (RT/warm)	THF (RT/warm)	ACN (RT/warm)
PYPC1	S/SS	INS/S	INS/S	INS/INS	INS/INS	INS/INS
Co(II) complex	SS/SS	INS/INS	INS/INS	INS/INS	INS/INS	INS/INS
Cu(II) complex	SS/SS	INS/INS	INS/INS	INS/INS	INS/INS	INS/INS

S=Soluble; SS=Sparingly Soluble; INS=Insoluble; RT=Room temperature

Table 2: Solubility of ligands and metal complex in different solvents.

Ligands/Complex	Assignment (cm ⁻¹)								
	u(O-H)	u(N-H)	u(C-N)	u(C=N)	u(C-O)	u(C=O)	u(C-H)	u(M-N)	u(M-O)
Pyrazine-2-carboxylic acid (POA)	3065Sh,m	-----	-----	1649w	1053Sh,S	1732Sh,s 1715Sh,s	2803Sh,w	-----	-----
A1	-----	3323br,S	1381Sh,w 1325Sh,w	1622Sh,S	1124Sh,S	1665Sh,S	2970Sh,m 2841Sh,m	-----	-----
A2	-----	3349Sh,w 3256Sh,w	1339Sh,w 1258Sh,w	1605br,w	1155Sh,w	1678Sh,S	2812Sh,w 2756Sh,w	-----	-----
Co(II) Complex (A3)	-----	3254br,m	1356Sh,S	1586Sh,S	1163Sh,m	1641Sh,S	-----	461Sh,m 442Sh,w	696w 625w
Co(II) complex (A4)	-----	3261br,m	1356Sh,S	1586Sh,S	1163Sh,S	1641Sh,S	2704w	463Sh,S 442Sh,w	698w 625w
Cu(II) complex (A5)	-----	3431br,w	1354Sh,S	1589Sh,m	1163Sh,m	1640Sh,S	2764w 2695w	463Sh,S 409w	542w

Key: br=broad, Sh=Sharp, S=Strong, m=medium, w=weak

Table 3: Selected FT-IR absorption bands for Pyrazine-2-carboxylic acid, its derivatives and complexes.

Compound	Absorbance Maximum	Wavelength λ_{max} (nm)	Assignment
PYPC1	2.184	296	n → π*
	0.772	240	n → π*
Co(II) complex (A3)	3.000	324	C-T band
	0.150	960	⁴ T _{1g} → ⁴ T _{1g} (p)
Cu(II) complex (A5)	3.000	295	C-T band
	0.114	650	² e _g (D) → ² b _{1g} (D)

C-T=Charge transition

Table 4: Electronic spectra data on UV/vis spectrophotometry.

Conclusion

The proposed compound anticipated for by method of functional group transformation was achieved by refluxing method, from the interpretation of the UV/Visible spectroscopy and FT-IR spectrum of the final product PYPC1 and PYPC2 ligand predicted to be a novel compound with the name N-(pyridine-2-yl)pyrazine-2-carboxamide. The analyses indicate coordination of the amide nitrogen to the metal ion, coordination of the oxygen of the carbonyl to the metal ion and the also the oxygen of the sulphate ion to the metal ion showed coordination.

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