



MICROWAVE ASSISTED SYNTHESIS, SPECTRAL AND ANTIBACTERIAL INVESTIGATIONS ON COMPLEXES OF Co (II) WITH HETEROCYCLIC LIGANDS

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Abstract:

The choice of this class of ligands and their complexes for study was influenced by the significance and adaptability of ligands with amide groups. This article presents the synthesis, spectroscopic analysis, and biological studies of amide complexes containing Co (II) ions that are produced from heterocyclic amines. Four ligands, including their complexes with Co (II), generated from 2-(Ethylamino) pyridine have been synthesized. A method of producing complexes by microwave irradiation has been developed in accordance with the green chemistry approach. Elements analysis, infrared, electronic, ESR spectra, and magnetic susceptibility studies have all been used to characterize the complexes. The $n \rightarrow p^*$ transition of the chromophoric C=O group of the amide bond is responsible for the distinctive band seen in the UV spectra of the uncomplexed amide group containing ligands in the 208-220 nm area. In this band, the cobalt complexes with ligands throughout the complete amide group show a bathochromic change. This shift happened because, according to IR research, the carbonyl group is involved in metal complexation. The Co (II) complexes under study have bands that are concentrated at $8000-11010 \text{ cm}^{-1}$, $13100-16800 \text{ cm}^{-1}$, and $20100-23000 \text{ cm}^{-1}$. Elevated spin octahedral compounds are associated with these bands. It was clear from the electronic spectra data that the complexes' octahedral geometry was distorted. The EPR spectra and magnetic moment measurements supported this theory as well. In vitro tests have been performed to assess the antibacterial activity of the generated ligands and their unique metal complexes against Escherichia coli and Staphylococcus aureus. The result shows that all Co (II) complexes are potent antibacterial agents against these microorganisms.

Keywords:

Cobalt (II), Microwave irradiation, Amide, Antibacterial

INTRODUCTION

The amide part is crucial component of various biologically substantial's, and future research in fields like polypeptide in addition with protein chemistry will depend on our ability to comprehend the amides' synthesis, characteristics, and reactions. This is mostly because of the following details:

- (i) A vital component of many biomolecules is the amino group. Furthermore, ligands that include amido groups have been found to be promising chelating agents. These ligands may be analogues of significant complexes that exist in nature, like antimicrobial peptides and metal carrier proteins. (1-2)
- (ii) A major part of amide reactions can be divided into two groups. The first is the nucleophilic attack on positively charged chemicals by oxygen atom, or on occasion through nitrogen atom. The second, less frequent method adds a nucleophile to the carbonyl groups of the amide. Amides function as either very weak acid or weak bases under the right circumstances. Because of this, they can be thought of as weak amphoteric compounds. Their ability to create hydrogen--bound complexes by self-association and with other donors & acceptors serves as evidence for this.
- (iii) The electrons from that nitrogen lone pair delocalizing into the n -system of the carbonyl group accounts enormously to the physical properties of amides. This results in the formation of a 1, 3-dipole, where nitrogen has the partial positive charge and oxygen the partial negative charge, giving the -CO-NH- bond a partial double bond nature.



The environment does not normally contain radioactive isotopes of cobalt; instead, they are released through nuclear power plant operations and accidents. Due to the fact that they are not very hazardous and have short half-lives

Once cobalt has entered the environment, it cannot be removed. It could react with other particles or adsorb on sediments found in water or soil. The majority of cobalt will eventually end up in soils and sediments, although it will only mobilize in acidic environments. Plants deficient in cobalt may grow on soils with extremely low levels of the element. Animals that graze on these areas suffer from a deficiency of cobalt, which is vital to them. However, very high concentrations of cobalt in the soils around mining and smelting facilities may have negative health effects if animals ingest the plants. Plants and animals that consume these plants may acquire cobalt in their bodies. This work reports on the synthesis, spectroscopic characterization, and antibacterial investigations of Co (II) complexes comprising ligands containing amide groups. Elemental studies, infrared spectra, electronic spectra, and magnetic susceptibility tests have all been used to characterize the complexes.

EXPERIMENTAL

Every chemical and solvent that was utilized was of AR grade. The purity of the produced compounds has been verified via TLC. The infrared spectra were recorded using a Bruker optical model alpha (FT-IR) spectrophotometer in KBr disc (Zn-Se optics, ATR) ($4000-500\text{ cm}^{-1}$). FT-NMR with a temperature range of -90 to 80 degrees Celsius. The units used to report the chemical shifts are parts per million, or ppm. Magnetic susceptibility studies using a vibrating sample magnetometer (VSM) model 155 were carried out at a 5500 Gauss field strength. A home microwave oven was used to perform microwave synthesis. DU-64 Beck Man For measuring absorption, a spectrophotometer equipped with a quartz cell with a 10-mm light path was utilized.

Creation of ligands by microwave radiation: N-ethyl-2-nitro-N-(pyridine-2-yl)benzamide (NENP2NB), N-ethyl-2-methyl-N-(pyridine-2-yl)benzamide (NENP2MB), N-ethyl-4-nitro-N-(pyridine-2-yl)benzamide (NENP4NB), and N-ethyl-4-methyl-N-(pyridine-2-yl)benzamide (NENP4MB) were created. The amine solution (0.055 mol in 15 ml ethanol) has been combined with the acid chloride solution to create the amide ligand. Over a heating element (between $60 - 65\text{ }^{\circ}\text{C}$), the reaction mixture was refluxed for around six hours. The crystals were separated, cooled, and then recrystallized with alcohol and vacuum-dried. The TLC method was applied in multiple solvents to evaluate the chemical's purity.

MICROWAVE IRRADIATION SYNTHESIS OF Co (II) COMPLEXES

To synthesise Co (II) complexes with different ligands (NENP2NB, NENP2MB, NENP4NB, and NENP4MB), fill a 250 mL round-bottom flask with 0.002 mol of the respective ligand and constantly agitate it in 30 mL of ethanol and 0.001 mole of cobalt perchlorate. The final mixture involved either exposing the reaction mixture's slurry in a microwave reactor at 600 W for varying periods of time for the sporadic end or conclusive inspection of TLC data, or irradiating the reaction mixture on an alumina bed for two to ten minutes at 600 W in a home microwave oven. The crystals were dried under vacuum, purified, and recrystallized using methanol. Furthermore, the usual approach was employed to create complexes and ligands with satisfactory outcomes.

RESULTS & DISCUSSION

With the exception of DMF and methyl alcohol, it was found that every complex that was produced was a colourful crystalline or powder that was insoluble in the majority of organic solvents and water. Additionally, under typical laboratory conditions, it demonstrated long-term stability. The physical attributes and results of the elemental analysis are shown in Table 1. There is a good correlation between the molecular formula proposed by the complexes and the analytical results. In general, the microwave method took a lot less time and yielded better results than the conventional method.

Table 1: Physical and analytical data of Co (II) complexes



S. No.	Complexes	Color	M.P. (°C)	Reaction period		Yield (%)		R _f value	Elemental analysis % cal. (found)			
				C.M. (h)	M.M. (min.)	C.M.	M.M.		Co	C	H	N
1.	[Co-(NENP2NB) ₂ (H ₂ O) ₂](ClO ₄) ₂	Light brown	147	5.8	2.26	44.77	45	(0.709) ^e	9.24 (9.30)	52.75 (52.72)	4.74 (4.75)	13.18 (13.20)
2.	[Co-(NENP2MB) ₂ (H ₂ O) ₂](ClO ₄) ₂	Pink	229	7	2.01	82.20	87	(0.640) ^f	10.24 (10.30)	62.60 (62.65)	6.30 (6.28)	9.73 (9.75)
3.	[Co-(NENP4NB) ₂ (H ₂ O) ₂](ClO ₄) ₂	Brown	116	6	2.31	45.52	52	(0.748) ^a	9.24 (9.30)	52.75 (52.72)	4.74 (4.75)	13.18 (13.20)
4.	[Co-(NENP4MB) ₂ (H ₂ O) ₂](ClO ₄) ₂	Light Brown	158	6.3	2.41	70.29	78	(0.629) ^a	10.24 (10.30)	62.60 (62.65)	6.30 (6.28)	9.73 (9.75)

b = Ethyl acetate: Carbon tetrachloride (4: 6), g = Acetone: Carbon tetrachloride (6: 4), h = acetone: carbon tetrachloride (7:3)

C.M. = Conventional Method, M.M. = Microwave Method

Vibrational spectra: Tables: 2 provide specific infrared spectral bands, The free amide group including ligands exhibits greater frequency bands due to the amide ν (N-H) mode at 3209-3397 cm^{-1} , while the cobalt complexes show a negative shift in the ν (C=O) (amide -I) frequency, suggesting the participation of the amide group's carbonyl oxygen atom in coordination with the metal ion and the amide nitrogen's absence.

The drop in the double bond character of C = O and the consequent increase in the double bond character of C-N explain this. Put another way, the IR spectra's decrease and increase in frequencies are caused by the lengthening of the C = O bond and the shortening of the C-N bond, respectively. The coordination through carbonyl oxygen is further confirmed by the shift towards higher frequencies of Amide II and III bands resulting from ν (C-N) and δ (N-H) modes (connected to one another).

Because of water's presence, certain vibrational modes are visible in the cobalt complexes of amide groups containing ligands. The complexes exhibit ν (OH) due to H₂O in the 3400-3440 cm^{-1} range, which has been attributed to coordination water. For all the complexes, the 800-350 cm^{-1} region exhibits vibrational bands caused by rocking & wagging owing to water and metal-oxygen stretching modes, which might be explained by coordinated water. Pyridyl nitrogen participates in bonding in complexes, 25-65 cm^{-1} negative shifting of the pyridyl ring peak relative to ligands.

Table 2: IR Spectral data of ligands and its Co (II) complexes

S. No.	Ligands Complexes	ν (C=O) ^p	ν (C - N + δ N - H) ^q	ν (N - H + δ C - N) ^r	ν (N - H) (amide)	Pyridyl ring	ν Co - O	ν Co - N	Miscellaneous band
1.	NENP2NB	1661	1379	1301	3324	1540	-	-	-
	[Co-(NENP2NB) ₂ (H ₂ O) ₂](ClO ₄) ₂	1631	1419	1321	3370	1461	549	489	765 and 628 coordinated water
2.	NENP2MB	1689	1416	1311	3386	1604	-	-	-
	[Co-(NENP2MB) ₂ (H ₂ O) ₂](ClO ₄) ₂	1652	1441	1339	3401	-	540	499	3449, 808 and 630 coordinated water
3.	NENP4NB	1709	1440	1279	3419	1529	-	-	-
	[Co-(NENP4NB) ₂ (H ₂ O) ₂](ClO ₄) ₂	1650	1523	1340	3392	1465	522	498	3455, 809 and 628 coordinated water
4.	NENP4MB	1649	1380	1311	3361	1605	-	-	-
	[Co-(NENP4MB) ₂ (H ₂ O) ₂](ClO ₄) ₂	1619	1420	1340	3391	1561	526	404	3460, 816 and 630 coordinated water

Magnetic moments and electronic spectra: Bivalent cobalt compounds magnetic susceptibility has been investigated at ambient temperature. Table 3 displays the magnetic moments for each complex that were determined using the room temperature magnetic susceptibility data. In these situations, the experimented mag. Moments, that have been documented in the literature fall between 4.4 to 4.7 BM, and there is a significant overlap between these values for different octahedral and tetrahedral complexes. Consequently, it is unlikely that the general stereochemical interaction based solely on UGC CARE Group-1

magnetic data will hold water. The magnetic moment values of the complexes under investigation in this study were greater than the spin-only value (3.87 BM), which may be explained by orbital contribution. By examining the electronic- spectra, the cobalt complexes' octahedral geometry is further determined. The $n \rightarrow p^*$ transition of the chromophoric $C=O$ group of the amide bond is responsible for the distinctive band seen in the UV spectra of the uncomplexed amide group containing ligands in the 208-220 nm area. The cobalt complexes containing ligands throughout the entire amide group exhibit a bathochromic shift in this band. IR investigations suggest that the carbonyl group plays a role in metal complexation, which is why this shift occurred.

The bands in the cobalt (II) complexes under investigation are focused at $8000-11010\text{ cm}^{-1}$, $13100-16800\text{ cm}^{-1}$, and $20100-23000\text{ cm}^{-1}$. These bands are typical of elevated spin octahedral complexes. The electronic spectra data were very helpful in indicating that the complexes octahedral geometry was deformed. This supposition was also confirmed by the magnetic moment measurements. Data from EPR spectra provided additional confirmation of this.

Table 3: Magnetic moment and electronic spectral data of Co (II) complexes

S. No.	Complexes	μ_{eff} (BM)	Electronic spectral bands λ_{max} (cm^{-1})	Tentative assignments	Expected geometry
1.	$[\text{Co}-(\text{NENP2NB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	4.78	19041, 20720, 21049, 21549, 23148, 23419, 23894	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Distorted Octahedral
2.	$[\text{Co}-(\text{NENP2MB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	4.54	16161, 17310, 18101, 18320, 19086, 20982, 21510, 22270, 23949	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Distorted Octahedral
3.	$[\text{Co}-(\text{NENP4NB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	4.70	10131, 16830, 17110, 17311, 17875, 18279, 19051	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$	Distorted Octahedral
4.	$[\text{Co}-(\text{NENP4MB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	4.68	10121, 16809, 16899, 17099, 17670, 18101, 19010	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Distorted Octahedral

Antibacterial activity: Muller Hinton Agar medium was used to test the compound's antibacterial activity against *S. aureus* and *E. coli*. Utilizing the paper disc approach, the activity was completed as shown in Table 4, which demonstrates that all of the Co (II) complexes have modest antibacterial activity against *S. aureus* and *E. coli*.

Table 4: Biological activity of amide group containing ligands and complexes against E. coli & S. aureus

S. No	Ligand/Complexes	Against E. coli		Against S. aureus	
		Zone of inhibition (in mm) at different concentration		Zone of inhibition (in mm) at different concentration	
		100 ppm	200 ppm	100 ppm	200 ppm
1.	NENP2NB	0.0	0.0	7.0	8.0
	$[\text{Co}-(\text{NENP2NB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	0.0	0.0	0.0	0.8
2.	NENP2MB	12.0	10.0	14.0	7.0
	$[\text{Co}-(\text{NENP2MB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	0.0	0.0	4.0	0.5
3.	NENP4NB	4.0	0.0	10.0	5.0
	$[\text{Co}-(\text{NENP4NB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	0.0	0.0	6.0	0.5
4.	NENP4MB	1.0	0.0	5.0	4.0
	$[\text{Co}-(\text{NENP4MB})_2 (\text{H}_2\text{O})_2] (\text{ClO}_4)_2$	0.0	0.0	0.0	0.5

CONCLUSIONS



Changes in the characteristic infrared bands of ligands containing amide groups upon complexation provide information about the coordination mechanism between the pyridyl nitrogen surrounding the metal center and the carbonyl oxygen of the amide group in all of the ligand complexes. The complexes may incorporate an exogenous ligand, and coordination may result from either non-deprotonated or deprotonated nitrogen, according to the infrared spectra. Reiterating the results of the experiment, it is found that these ligands with amide groups have a stoichiometry of two amide ligand molecules and two exogenous ligand molecules per cobalt ion. They act as bidentate ligands in the complexes that take a distorted octahedral geometry. Studies have been conducted on the biological activity of Co (II) complexes that contain ligands with amide groups. The investigation has been conducted using the conventional disc diffusion approach.

The antibacterial qualities of the compounds have been studied using *E. Coli* and *S. Aureus* bacterial subcultures. With a few noteworthy exceptions, the study shows that most ligands have more antibacterial activity than complexes.

References:

1. Garg B S, Bhojak N & Bist. J S, Indian Journal Chemistry, 38 A, (1999), 38
2. Bhojak N, Chachar M, Khaturia S & Soni K P, Asian Journal Chemistry, 15, 2, (2003), 1193
3. Williams D K, Chem. Rev., 72,(1972), 203
4. Barefield E K, Freeman G M, and Van Derveer D G, Chem. Commun., (1983) 1358.
5. Hay W, Govan N, Perotti A and Carugo O, Transition. Met. Chem., 17 (1992) 161.
6. Yan Yu, Neville Anne & Dowson Duncan, *Wear*, 263 (2007) 1105.
7. Mukherjee GN & Dhar P, J. Indian Chem. Soc., 64 (1987) 73.
8. Patel RK & Patel RN, J. Indian Chem. Soc., 66 (1989) 269.
9. Satapathy KC, Dash DC, Pradhan GC & Naik A, J. Indian Chem. Soc., 66 (1989) 291.
10. Mukherjee GN & Sarkar S, J. Indian Chem. Soc., 66 (1989) 293.
11. Vengopal P, Ravinder V & Lingaiah P. Journal of Chemical Science, 104, 1 (1991) 1.
12. Goodgame David ML, Grachvogel David A, Hussain Izhar, White Andrew J P & Williams David J, Inorg. Chem., 38, 9 (1999) 2057.
13. Nelwamondo Aubrey M, Eve Desmond J, Watkins Garesh M & Brown Michael E, *Thermochimica Acta*, 318 (1998) 165.
14. Baran EJ, *Biochemistry (Moscow)*, 65, 7 (2000) 784.
15. Sonmez Mehmet, Turk, J. Chem., 25 (2001) 181.
16. Gubina Kateryna E, Ovchynnikov Vladimir A, Swiatek-Kozlowska Jolanta, Amirkhariov Vladimir M, Sliva Tatyana Yu & Domasevitch Konstantin V, *Polydedron*, 21 (2002) 963.