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SYNTHESIS AND STRUCTURAL PROPERTIES OF MIXED LIGAND METAL COMPLEXES OF TRANSITION METALS WITH AZO DERIVATIVES OF COUMARIN-3-CARBOXYLIC ACID AND PHENANTHROLINE

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ABSTRACT

This research article consists of synthesis of mixed ligand metal complexes of azo derivatives of coumarin-3-carboxylic acid and phenanthroline. The transitions metals like Cobalt, Nickel, Copper and Zinc and Silver, these metals are having biological importance and have good tendency to form coordinate bond with ligand. The mixed ligand with transition metals which are then characterized using techniques, FTIR, UV-Visible, elemental analysis, XRD, conductivity measurements, TGA analysis. The synthesized ligand azo derivatives of coumarin-3-carboxylic acid acts as a bidentate ligand and coordinated through carboxylic acid oxygen and carbonyl oxygen from coumarin ring and phenanthroline is also a bidentate ligand and coordinated through both the nitrogen to the transition metal forming a hexadentate complex with 2 water molecules coordinated.

KEYWORDS: Azo-coumarin derivatives, Mixed-ligand complexes, Phenanthroline, Coumarin-3-carboxylic acid, azo derivatives.

INTRODUCTION

It has been observed in many research articles that mixed ligand complexes are having interesting chemical and physical properties. It is of great interest in synthesizing and characterizing metal complexes of azo derivatives of coumarin-3-carboxylic acid and 1,10-phenanthroline. There are wide range of coumarin and its derivatives, obtained from nature and synthesized in laboratory and studied to show excellent potential in pharmaceutical chemistry. The naturally occurring coumarin and its derivatives shows wide range of biological and pharmacological activities viz., anticoagulant,[1,2] antitumor,[3,4,5] clatogenic,[6] cytotoxic,[6] anti-proliferative,[7] Sunscreen, a fluorescent indicator, a dye indicator,[8,9,10] Some of these coumarin derivatives show enhanced biological activities with transition metals. The complexes of transition metals have significant biological functions including antibacterial, antifungal and anticancer activities.[11]

The azo group containing heterocyclic compound have been widely studied because of their excellent thermal, optical and medicinal properties, such as antibacterial, antiviral, anti-fungal and antioxidant activities.[11-16] Assimilation of hydrazine and azo group has been studied and found to improve the pharmacological activity of heterocyclic compounds.[17] In the view of excellent chemical, physical and pharmacological characteristics of the azo compounds, the authors have incorporated the phenylazo group to the coumarin moiety and are expecting the resulting compound to show enhanced properties. It is also revealed from studies that the metal coordinated coumarin-3-caboxylic acids and its derivatives shows excellent anti-proliferative activity against several kinds of cancerous cells individually or in incorporation with other derivatives.[7]

Coumarin and its derivatives can be efficiently studied for their biological and pharmacological activities if these are used with a molecule which have affinity to bind with different active sites and help in effective drug delivery. One of such molecules which shows excellent DNA binding characteristics is 1,10-phenanthroline and its derivatives in coordination metal ions.[18] It is found in research articles that among heterocycles containing nitrogen, phenanthroline shows good legating properties and binds to the central metal with nitrogen at positions 1 and 10. Mixed ligand complexes Phenanthroline and its derivatives with transition metal shows DNA binding characteristics.[19]

Transition metals are easily accessible in their salts and show low toxicity which even can be minimized by incorporating them as a central metal atom / ion in the form of coordination complexes.[20] The complexes of transition metals have significant biological functions including antibacterial, antifungal and anticancer activities.[11] Significant transition metals have essential chemistry in living system. Metals such as Iron, Cobalt, Copper, Zinc etc. have many biological functions in the living systems forming centre of the biologically essential macromolecules without which the biological functions can be incomplete and collapse.

Proteins containing Iron which helps to transport oxygen and electron transport which are main functions in living systems.

Intending to study of the enhanced characteristics of the coumarin-3-carboxylic acid, in the present article, the synthesis and characterization of mixed ligand complexes of azo derivatives of Coumarin-3-carboxylic acid and 1,10-phenanthroline with transition metals such as Cobalt, Nickel, Copper, zinc and silver are reported. These complexes are characterized and studied for physical and chemical properties.

EXPERIMENTAL

MATERIALS AND METHODS

All the reagents and solvents which are used of AR grade and chemically pure. The chemicals and solvents were purchased from Spectrochem and Loba chemicals. The reagents and solvents were used without further purification but checked using TLC. The melting points were measured using Thieles' apparatus showing a sharp melting of some of the crystals. The completion of reaction was checked using ALUGRAM® SXtra Aluminum Sheet, SILGUR UV254 with visualization in UV light using 7:3 mixture of n-hexane/petroleum ether and ethyl acetate to run the spot.

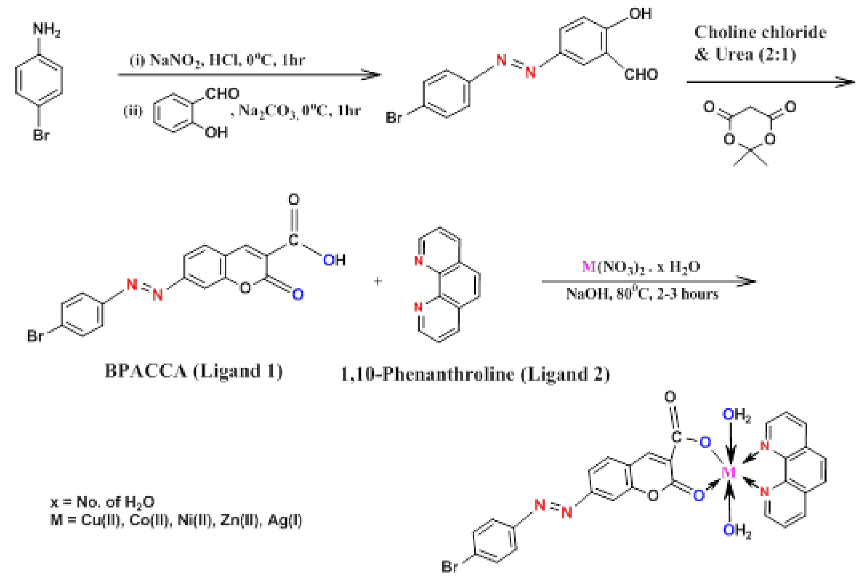
The IR spectra was measured by PerkinElmer Spectrum Version 10.5.2. Mass spectra were measured using methanol and water solvent (3:1). Further characterization was also done using XRD and TGA techniques. The physical properties electrolytic conductance and magnetic moment were also studied for metal complexes and depicted in the present article.

Synthesis of Ligand 1 – BPACCA

The synthesis of ligand 1 was carried out by adding 5(4-bromo phenylazo) salicylaldehyde (0.005mol) and meldrum's acid (0.005mol) to hot DES at 80^0C (5 mole equivalent of homogeneous liquid)[21] The temperature was maintained 140^0C for 1-2 hours. The completion of reaction was checked by using TLC. When the reaction was completed, the crystallization of the product was done in ice cold water. It was filtered. The crystals, obtained, washed with water several times and recrystallized in ethanol and ethyl acetate (1:1) to yield turmeric yellow solids of *2-oxo-6-(4-bromo phenyldiazenyl)-2H-chromene-3-carboxylic acid.* The compound was insoluble in water, ethanol, methanol, partially soluble in ethyl acetate and completely soluble in DMF and DMSO.

Preparation of metal complexes

The method of preparation of mixed ligand complexes was taken from previous research articles with slight modifications.[22] *2-oxo-6-(4-bromo phenyldiazenyl)-2H-chromene-3-carboxylic acid* (0.001M) (Ligand 1) was added to a solution of NaOH (0.8 g, 0.02M) and stirred. An aqueous solution of $M(NO_3)_2 \cdot xH_2O$ (0.001M) was added followed by 1, 10-phenanthroline (0.001M) (Ligand 2) in alcohol with continuous stirring. The mixture was heated and stirred on a water bath for 2 h with continuous stirring. The hot solution is then filtered in a crucible and allowed to stand at room temperature. The crystals/precipitate was obtained in 2-3 days on standing the solution. The precipitate was recrystallized using ethanol, washed, filtered, and dried in a vacuum oven to give coloured mixed ligand metal complexes (Table-1) of *2-oxo-6-(4-bromo phenyldiazenyl)-2H-chromene-3-carboxylic acid and 1,10-phenanthroline*. The complexes were completely soluble in water and sparingly to completely insoluble in ethanol, acetone and other organic solvents. The scheme 1 indicates schematic reaction to obtain the metal complexes of Cu(II), Co(II), Ni(II), Zn(II) and Ag(I).



Scheme 1: Schematic representation for the route of synthesis of Mixed Ligand metal complexes.

RESULTS AND DISCUSSIONS

The physical properties of complexes such as molecular weight, colour, percentage of metals and melting point of transition metals Cu(II), Co(II), Ni(II), Zn(II) and Ag(I) are depicted in the Table 1. The percentage of the metals for each complex was determined by volumetric analysis as per standard procedure and found that the calculated and obtained weight are matching.

Table 1: Physical properties and percentage yield of synthesized complexes.

Compound/ Metal Complexes	**Molecular weight (g/mol)**	**Colour**	**M Obtained (%)**	**M Calculated (%)**	**Yield (%)**	**Melting point/ decomposition temp. (^{0}C)**
BPACCA(2c)	-	Turmeric Yellow	-	-	85	158-160
Phen	-	White	-	-	-	117
Cu-Phen-BPACCA	652.94	Deep green	9.59	9.7323	58	205-207
Co-Phen-BPACCA	648.32	Brown	8.98	9.0901	50	>310
Ni-Phen-BPACCA	648.08	Brick red	9.08	9.0564	45	250-252
Zn-Phen-BPACCA	654.77	Orange	9.88	9.9852	65	228-230
Ag-Phen-BPACCA	697.26	Yellow	15.35	15.4703	60	>300

IR data

The Infrared spectral study of *2-oxo-6-(4-bromo phenyldiazenyl)-2H-chromene-3-carboxylic acid* (BPACCA) *and 1,10-phenanthroline* along with their metal complexes of Cu(II), Co(II), Ni(II), Zn(II) and Ag(I) were done in the range of 4000-400 cm^{-1} to determine characteristics vibrations of the different functional groups linked with the molecules. The characteristic broad band at 3197cm^{-1} is due to -O-H stretching of BPACCA ligand. A week stretch at 3098 cm^{-1} is due to aromatic C-H in the BPACCA. The carbonyl stretching is observed at 1730cm^{-1} of lactone ring from BPACCA ligand. A stretching at 1688cm^{-1} is due to carbonyl present at COOH group of BPACCA ligand. The stretch at 1600-1550 cm^{-1} corresponds to -N=N- group present in the ligand. At 1300 cm^{-1} the stretch is due to C-N stretch. The stretch at 1005 cm^{-1} and 1095 cm^{-1} due to aromatic C-H bend present in BPACCA. At 516 cm^{-1} the stretch is due to C-Br bond in BPACCA ligand.

The ligand 2 1,10- phenanthroline showed its characteristics vibrational frequencies. The stretching vibrational frequencies of C=N and C=C double bonds appears at 1639 cm^{-1} and 1590 cm^{-1}. The skeleton vibration peak of ligand 2 appears a 1560 cm^{-1} and bending appeared at 735 cm^{-1} (23). The Mixed Ligand complexes showed vibrational frequencies to the lower than that of the ligands individually. In regards to Cu (II) complexes, the carbonyl frequencies shifted to lower band 1656 cm^{-1} and the carbonyl at lactone ring of BPACCA ligand seems to be disappeared due to Coordinate bond formation with Cu (II). The stretching at 3454 cm^{-1} and 3053 cm^{-1} are due to $-OH_2$ and aromatic C-H vibrations. 1171 cm^{-1} and 1065 cm^{-1} are due to aromatic C-H bend vibration from both the ligands in the Cu(II) metal complex.

In the region 500 to 400 cm^{-1}, the spectra of all complexes have detected bands which indicates to υ(M-O) and υ(M-N) stretching vibrations (24). For Cu(II) complexes, vibrations at 560 cm^{-1} and 497 cm^{-1} are due to υ(Cu-O) and υ(Cu-N) stretching vibrations respectively. For Co(II) complexes of 563 cm^{-1} and 429 cm^{-1} are due to υ(Cu-O) and υ(Cu-N) stretching vibrations respectively. For Ni(II) complexes the bands at 562 cm^{-1} and 498 cm^{-1} are due to υ(Cu-O) and υ(Cu-N) stretching vibrations respectively. For Zn(II) complexes of 557 cm^{-1} and 497 cm^{-1} are due to υ(Cu-O) and υ(Cu-N) stretching vibrations respectively. For Ag(II) complexes of 483 cm^{-1} and 415 cm^{-1} are due to υ(Cu-O) and υ(Cu-N) stretching vibrations respectively.

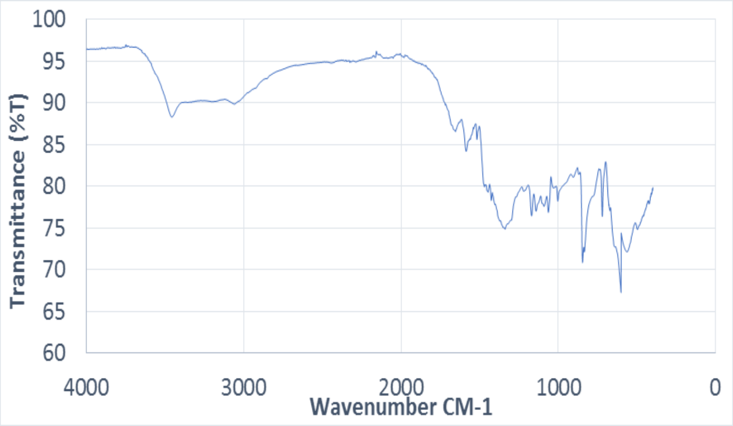


Figure 1: FT-IR Spectrum of metal complex Cu-Phen-BPACCA.

TGA analysis

The thermogravimetric analysis of ligands and their metal complexes were done using PerkinElmer thermogravimetric analyzer TGA 4000 in an inert atmosphere of nitrogen at 20-800^{o}C temperature range. The ligands BPACCA and phenanthroline started to decompose at above 150^{o}C and continued to decompose till 350-400^{o}C. From thermogram, it was observed that the metal complexes of Cu(II), Co(II), Ni(II), Zn(II) and Ag(I) have more thermal stability than the free ligands. In metal complexes, the peak at 100-150^{o}C indicates removal of two water molecules coordinated with the metal complex in the thermogram. The percentage loss of the molecules matched with the theoretical value of the H_2O molecules in all the metal complexes.

At 151-250^{o}C, the ligand BPACCA started degrading with elimination of N_2 and Br. At 251-600^{o}C, the ligand BPACCA degraded completely which matched with theoretical value of ligand BPACCA. At 601-750^{o}C, the loss of ligand 2 phenanthroline was observed. At 800^{o}C, the compound left with only CuO which matched with the theoretical percentage weight in the complex and verified using IR spectra.

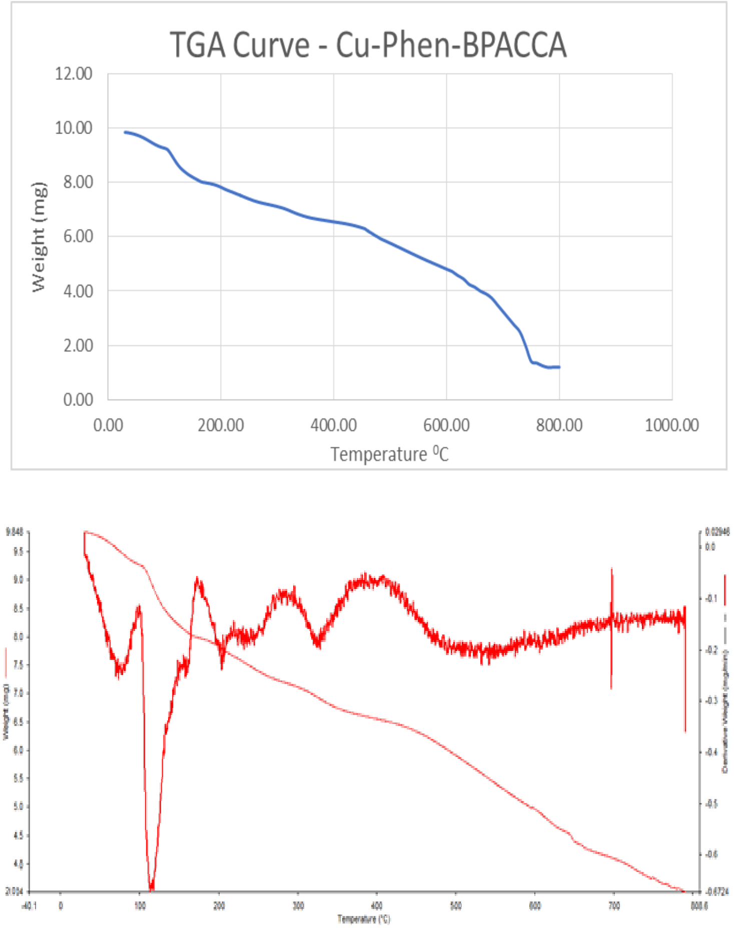


Figure 2: Thermogram of metal complex Cu-Phen-BPACCA.

Mass spectra

The mass spectra of complexes were measured and found the base peaks matching with m/z = M+2. Figure 3. shows mass spectra of Cu(II) metal complex of BPACCA and 1,10-phenanthroline and depicts base peak at m/z = 650.9 which matches with M+2 of the molecular weight 652.9 g/mol of the complex Cu-phen-BPACCA. The rest of the complexes also showed m/z at 647.9, 646.2, 652.7 and 695.3 for Co(II), Ni(II), Zn(II) and Ag(I) respectively and matched with the molecular weights of the complexes in Table 1.

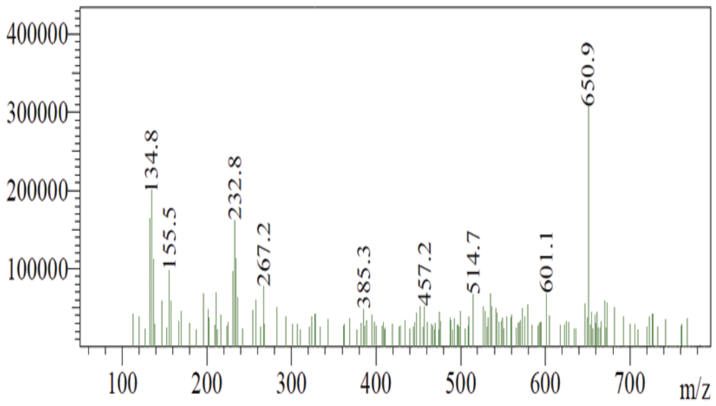


Figure 3: Mass spectrum of metal complex Cu-Phen-BPACCA (M+2).

UV-Visible study

The UV-visible spectra of all metal complexes were measured in water solvent due to their good water solubility. The absorbance band at 375-475 nm was seen for all metal complexes due to presence of azo group (25) in the ligand BPACCA which corresponds to π – π* transitions. The sharp absorption bands in the range of 270-275 nm were due to conjugated bonds present in the ligand phenanthroline and carbonyls which corresponds to π – π* transitions. The complexes were seeming to be associated with n – π* and π – π* transitions where n – π* is a forbidden transition due to non-bonded lone pair of electrons.

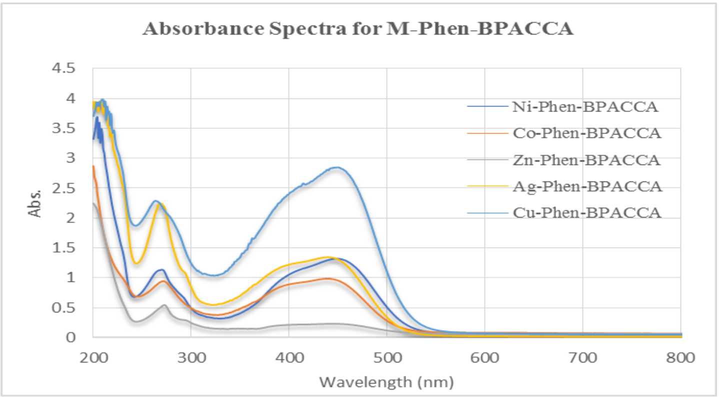


Figure 4: Comparative absorbance spectra of all metal complexes M-Phen-BPACCA.

Molar conductivity

Molar conductivity of all metal complexes were checked in distilled water as a solvent using a conductivity meter to check whether the complexes are electrolytic or non-electrolytic in nature. The conductivity of metal complexes at 20µS was measured for 10^{-3} M solutions and found that it was in the range of 25 to 80 Ω^{-1} cm^2 mol^{-1} as shown in the table 2. This proves that the metal complexes are non-electrolyte due to absence of acetate ion in the solution (26-27).

Magnetic Properties and XRD studies

The observed magnetic moment of Cu(II), Ni(II) and Co(II) metal complexes are 1.82 B.M, 2.79 B.M and 4.30 B.M. respectively indicating presence of 1, 2 and 3 unpaired electrons are corresponding to paramagnetic nature of the metal complexes. This also means that the complexes have octahedral geometry. The metal complexes of Zn(II) and Ag(I) are found to be diamagnetic due to absence of unpaired electrons. The magnetic moment of synthesized metal complexes is mentioned in the table 2.

Table 2: Molar conductivity of all synthesized metal complexes in deionized water at 10^{-3} M concentration and

Sr. No.	Metal complexes	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Magnetic moment (B.M.)
1	D.W.	3.6	--
2	Cu-Phen-BPACCA	67.8	1.82
3	Co-Phen-BPACCA	50.8	4.30
4	Ni-Phen-BPACCA	25.4	2.79
5	Zn-Phen-BPACCA	80.8	--
6	Ag-Phen-BPACCA	46.4	--

X-ray diffraction studies have revealed that the synthesized Cu(II), Co(II), Ni(II), Zn(II) and Ag(I) complexes are crystalline in nature which is indicated by sharp characteristics peaks obtained with respect to the metals present in the complex. Figure 5. depicts and pattern of peaks for Cu-Phen-BPACCA complex.

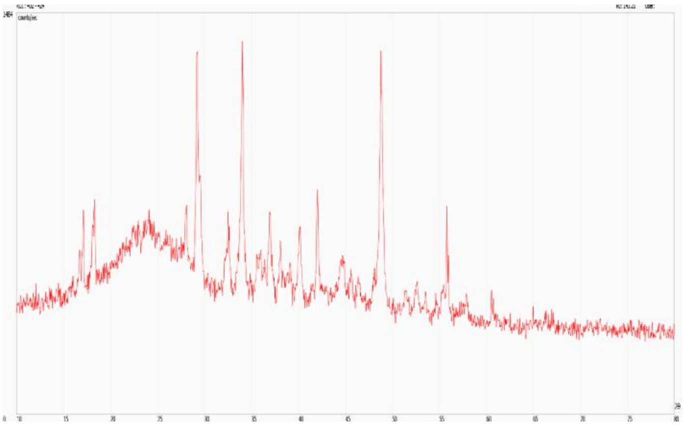


Figure 5: XRD pattern of Cu-Phen-BPACCA.

CONCLUSIONS

Mixed ligand complexes of *2-oxo-6-(4-bromo phenyldiazenyl)-2H-chromene-3-carboxylic acid* (BPACCA) *and 1,10-phenanthroline* with transition metals Cu(II), Co(II), Ni(II), Zn(II) and Ag(I) are synthesized successfully. The synthesized metal complexes were then characterized by IR, Mass, UV-visible, TGA, XRD and found up to the correct. The physical parameters like melting point, molar conductance and magnetic properties were also recorded for the synthesized complexes and compared with standards. The synthesized metal complexes can further be studied for biological applications.

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