

Synthesis and Characterization of Binuclear Metal Complexes of Cu(II), Ni(II) and Co(II) with 3,6-Dimethyl-2,7-Dioxo-4,5-Diazaocta-3,5-Diene-2,7-Dihydrazone (BAAD)

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Abstract - The synthesis and characterization of a series of homo binuclear metal complexes of Cu(II), Ni(II) and Co(II) with the titled ligand 3,6-Dimethyl-2,7-Dioxo-4,5-diazaocta-3,5-Diene-2,7-Dihydrazone(BAAD) have been reported. The complexes were synthesized by treating an ethanolic solution of the ligand with equimolar amount of appropriate metal salts in ethanol by a direct route. The ligand and its metal complexes have been characterized on the basis of analytical and spectral data, thermal analysis, magnetic and conductivity measurements. Based on the results, tentative structures of the complexes have been proposed. The ligand as well as the metal complexes exhibited antimicrobial activities against the pathogenic fungus *T. viridae*, *Aspergillus flavus*, and *Aspergillus niger*. The fungicidal activities of the complexes have been compared with a standard fungicide Fluconazole.

Keywords - Macrocyclic complex, Thermal analysis, Antimicrobial activity, Fluconazole.

I. INTRODUCTION

Transition metal complexes with vicinal dihydrazones have assumed importance [1]-[7]. The bis and tris-(2,3-butanedionedihydrazone) metal complexes have been used to prepare mononuclear macrocyclic and the three dimensional clathrochelate [8] metal complexes by the reaction of aldehyde and ketones. Amongst the dihydrazone ligands, 3, 6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone (BAAD) possesses unique structural characteristics in relation to the position of nitrogen atoms and conjugated π -electron systems. It can act as a tetra functional ligand coordinating with metal ions in a bi-bidentate manner. As a matter of fact this ligand has been used to give binuclear complexes, $[\text{Fe}_2(\text{BAAD})_3]\text{I}_4$ and $[\text{Ni}_2(\text{BAAD})_3]\text{I}_4$. A bi-bidentate coordination of the ligand with metal ions has been proposed in analogy with similar ligands such as pyridylaldazine [4].

The present work relates to the investigation on the preparation of dinuclear acyclic complexes by the action of BAAD on the metal ions. The open chain acetyldihydrazone

metal complexes have been prepared as precursors for the preparation of macrocyclic complexes. They have been characterized on the basis of their spectral, magnetic and thermo chemical properties which have been used as valuable tools in the elucidation of the structure. In the present chapter, we describe some bis-chelate complexes of BAAD with the metal ions Co(II), Ni(II) and Cu(II).

II. EXPERIMENTAL

All the chemicals and solvents used are either of Glaxo or Merck grade. The solvents were purified before use in the reaction. The metal contents of all the complexes were estimated by standard methods [9]. The percentage of nitrogen was calculated by combustion method. The values obtained were also supported by semi micro Kjeldahl's method. Carbon and hydrogen were estimated with CHN micro analyzer. Infrared spectra of the complexes were recorded in KBr phase using Shimadzu-FTIR-121 Spectrophotometer. The electronic spectra of the compounds were recorded in a Shimadzu-2450 UV-Visible Spectrophotometer. Magnetic susceptibility of the compounds were measured by Gouy balance using $\text{Hg}_2[\text{Co}(\text{CNS})_4]$ as the calibrant. Thethermoanalytical measurements TG and DTA were done with a NETZSCH Geratebau. GmbH thermal analyzer.

III. MATERIALS AND METHODS

2, 3 - butanedione, hydrazinehydrate, dimethylformamide (DMF) and DMSO were of BDH quality and used as supplied. Perchloric acid was of Fluka make. Bromide salts of copper(II), nickel(II) and cobalt(II) were prepared by dissolving the respective metal carbonates in minimum volume of hydrobromic acid followed by crystallization. For the preparation of cupric bromide it was essential to add a few drops of bromine to get the pure product [10]

i) *Preparation of 3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone(BAAD)-(C₈H₁₆N₆):* The ligand BAAD was synthesized with a slight modification of the literature method⁴. To an alcoholic solution of 2,3-butanedione (17.2 g, 0.2 mol) at 0°C was added an alcoholic solution of hydrazine hydrate (5 g, 0.1 mol) with stirring over a period of 30 mins. The resulting solution was kept at 0°C for 12-20 hrs. and was again added slowly to a solution of hydrazine hydrate (10 g, 0.2 mol). The yellow solution was allowed to crystallize by slow evaporation at room temperature and finally recrystallized from ethanol. The product was obtained as a bright yellow solid. Yield 60% [melting point 130⁰ - 135⁰C (lit. melting point 127⁰ - 141⁰ C) found N, 42.2%, calc.N, 42.855].

ii) *Preparation of tetrachloro- bis (3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone)dnicobalt(II) [Co₂(C₈H₁₆N₆)Cl₄]:* About 4 g of BAAD (0.02 mol) was dissolved in 25 ml of absolute ethyl alcohol by gently warming below 70⁰ C. To this warm solution an alcoholic solution of CoCl₂ .6H₂O (4.5 g, 0.03 mol) was added drop wise with stirring. A pink red product was formed after few minutes. It was stirred for thirty minutes, allowed to settle and quickly filtered. It was repeatedly washed with absolute alcohol, ether and dried in vacuo.

Bis-bromo, nitrate and perchlorato Co(II) complexes were prepared following similar procedures.

Copper(II) and Nickel(II) complexes were synthesized following similar method as the Cobalt (II) complexes.

The analytical data of the metal complexes are presented in Table 1

TABLE I
ANALYTICAL DATA AND COLOUR OF BAAD COMPLEXES.

| Complexes | Colour | Found(Calculated)%. | | | Λ in ohm ⁻¹ cm ² mol ⁻¹ |
|---|-----------------|---------------------|------------------|------------------|--|
| | | Metal | Anion | Nitrogen* | |
| [Ni ₂ (BAAD) ₂ Cl ₄] | Green | 17.95 (18.09) | 21.65 (21.77) | 25.29 (25.76) | 134 |
| [Ni ₂ (BAAD) ₂ Br ₄] | Pale green | 14.16 (14.21) | 38.45 (38.55) | 19.91 (20.24) | 135 |
| [Ni ₂ (BAAD) ₂ (NO ₃) ₄] | Brownish green | 15.32 (15.46) | - - | 29.23 (29.55) | 136 |
| [Ni ₂ (BAAD) ₂ (ClO ₄) ₄] | Light green | 19.01 (19.09) | - - | 18.02 (18.50) | 136 |
| [Co ₂ (BAAD) ₂ Cl ₄] | Orange | 17.93 (18.09) | 21.7 (21.8) | 25.6 (26.70) | 138 |
| [Co ₂ (BAAD) ₂ Br ₄] | Reddishbrown | 14.1 (14.21) | 39.2 (38.5) | 19.9 (20.03) | 139 |
| [Co ₂ (BAAD) ₂ (NO ₃) ₄] | Orange red | 15.28 (15.56) | - - | 29.4 (29.55) | 139 |
| [Cu ₂ (BAAD) ₂ Cl ₄] | Dull green | 18.97 (19.21) | 21.21 (21.48) | 25.23 (25.41) | 142 |
| [Cu ₂ (BAAD) ₂ Br ₄] | Dark brown | 14.92 (15.13) | 38.98 (39.14) | 19.87 (20.02) | 143 |
| [Cu ₂ (BAAD) ₂ (ClO ₄) ₄] | Yellowish green | 13.62 (13.84) | - - | 18.21 (18.32) | 145 |

BAAD = C₈H₁₆N₆, *Including nitrate nitrogen

IV. RESULTS AND DISCUSSION

The complexes are highly coloured and have melting point greater than 250°C. The complexes are insoluble in most of the organic solvents but are moderately soluble in water, DMF and DMSO. They are stable under normal conditions and are slowly attacked by alkalis and acids. The perchlorate complexes are sensitive to moisture and get decomposed when exposed to air. They are explosive in nature. The molar conductance of binuclear Schiff base complexes were recorded in DMF (10^{-3} M) at room temperature. The complexes showed high molar conductance values ($134 - 145 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) which indicated that the complexes were electrolytic in nature with the presence of anions outside the coordination sphere. The analytical data of the complexes are recorded in Table 1. The ligand and its complexes have been characterized on the basis of different physico-chemical studies like IR, UV – VIS spectral properties, TGA and magnetic properties and a tentative structure for the complexes have been proposed. They have been tested as possible fungicides against some fungal pathogens.

i) *Infrared spectra*: The IR spectra of metal complexes have been studied by comparing the ligands 3,6- dimethyl-2,7-dioxo- 4,5-diazaocta-3,5-diene-2,7-dihydrazone and other related compounds in the region 4000- 400 cm^{-1} . Some of the important and significant bands have been presented in Table 2. All the spectra show similar characteristics suggesting their iso structural nature. Many of the important bands in these spectra indicate the mode of bonding of the ligand with the metal ion. The spectral bands are in accordance with the structures of the complexes displayed in Fig. 1 and Fig. 2. The ligand exhibits two characteristic bands at around 3330 cm^{-1} and 3125 cm^{-1} with medium intensity arising out of $\nu_{\text{asymm}}(-\text{NH}_2)$, $\nu_{\text{sym}}(-\text{NH}_2)$ arising out of the terminal $-\text{NH}_2$ groups [11]. The position of these bands is lowered to some extent than normal $\nu(\text{NH}_2)$. They occupy an intermediate position compared to 1,2- diphenylethane-1,2- dione dihydrazone [5] and 2,3- butanedione dihydrazone [6]. Such a shifting is attributed to the change in vibrational energy for $-\text{NH}_2$ group due to the high degree of conjugation. The concerted shifting of the two bands to lower frequency region in all the metal complexes is in accordance with already reported dihydrazone complexes [7].

Apart from these structurally important bands, a series of three to four bands are observed in the region 3100-2700 cm^{-1} which are weak in intensity and can be assigned unequivocally to $\nu\text{C-H}$ vibrations [12].

In the finger print region, two bands which are of considerable structural significance are observed $\sim 1645 \text{ cm}^{-1}$ and $\sim 1565 \text{ cm}^{-1}$ for the free ligand. The former is relatively broad and of medium intensity whereas the later appears as a sharp and strong band. The high frequency band is least

perturbed in almost all the metal complexes, while the low energy band moves towards a higher frequency region by 15 to 30 cm^{-1} with increased intensity. Taking into consideration their behaviour and relative intensities, the former band is attributed to δNH_2 vibrations and the latter to $\nu(\text{C}=\text{N})$. There is no other band comparable in sharpness and intensity than the $\nu(\text{C}=\text{N})$ in this region implying that all the azomethine linkages have similar vibration energies. The shift of $\nu(\text{C}=\text{N})$ to a higher frequency region in the metal complexes clearly demonstrates that the linkage of the ligand with the metal ions occurs in a bi-bidentate manner with coordination taking place through azomethine nitrogen atoms. Far I.R. spectra, electronic spectra, magnetic susceptibility and thermochemical data corroborate these structures.

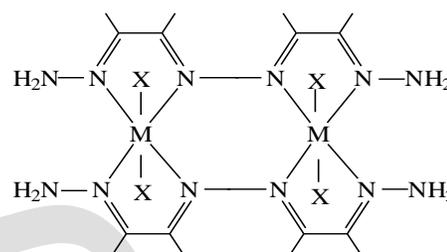


Fig.1 M= Co(II) and Ni(II), X= Cl^- , Br^- , NO_3^-

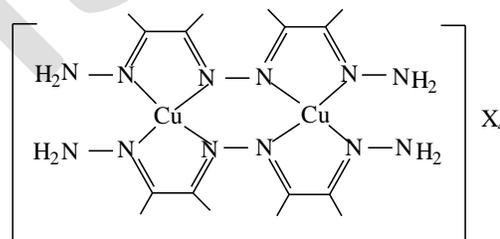


Fig. 2 X= Cl^- , Br^- , NO_3^- , ClO_4^-

All the complexes exhibit $\nu(\text{M-N})$ in the range 530-570 cm^{-1} . For the Ni(II) and Co(II) perchlorate complexes a broad band of strong intensity is observed at $\sim 1050-1120 \text{ cm}^{-1}$ which is characteristics of uncoordinated ClO_4^- ion [13] and confirm them to be present in the outer-sphere of the complex ions. The nitrate complexes of Co(II) show three distinct bands around 1080, 1260 and 1415 cm^{-1} and suggest the nitrate groups to be coordinated in a unidentate manner [14]. Absence of these bands and higher molar conductance value of Copper(II) complexes suggest them to be of ionic character. A series of bands for the metal complexes as well as the ligand are observed around 1460, 1400, 1310, 1215, 915 and 755 cm^{-1} . They show closely similar features and positions in all the complexes and originate due to deformation vibrations.

TABLE 2
STRUCTURALLY IMPORTANT INFRARED BANDS OF BAAD AND ITS METAL COMPLEXES (IN CM^{-1})

| Complexes | $\nu_{\text{as}}(\text{NH}_2)$ $\nu_{\text{s}}(\text{NH}_2)$ | $\nu(\text{C-H})$ | $\nu(\text{C=N})$ | δNH_2 | $\nu(\text{M-N})$ | $\nu(\text{N-O})$ (NO_3) | δCH_3 |
|--|---|-------------------|-------------------|---------------------|-------------------|--|-------------------------|
| BAAD | 3330s* 3125s | 2850w | 1565s | 1645m | - | - | 1370m 1300m |
| $[\text{Ni}_2(\text{BAAD})_2\text{Cl}_4]$ | 3300s 3135s | 2980w 2910w | 1580s | 1650m | 538s | - | 1455m 1400m 1390m |
| $[\text{Ni}_2(\text{BAAD})_2\text{Br}_4]$ | 3259s 3145s | 2020w 2970w | 1585s | 1645m | 535s | - | 1445m 1415m 1375m |
| $[\text{Ni}_2(\text{BAAD})_2(\text{NO}_3)_4]$ | 3310s 3162s | 2960w 3000w | 1580vs | 1645m | 530s | 1390s | 1405m 1380m |
| $[\text{Ni}_2(\text{BAAD})_2(\text{ClO}_4)_4]$ | 3310s 3130s | 2900w | 1590s | 1640m | 535s | - | 1455m 1400m |
| $[\text{Co}_2(\text{BAAD})_2\text{Cl}_4]$ | 3335s 3170s | 3000w 2930w | 1595s | 1650m | 542s | - | 1445m 1420m 1385m |
| $[\text{Co}_2(\text{BAAD})_2\text{Br}_4]$ | 3320s 3170s | 3030w 2980w | 1575s | 1645m | 554s | - | 1445m 1400m 1385m |
| $[\text{Co}_2(\text{BAAD})_2(\text{NO}_3)_4]$ | 3320s 3162s | 2965w | 1570s | 1640m | 534s | 1415s 1260s 1080s | 1395m 1305m |
| $[\text{Co}_2(\text{BAAD})_2(\text{ClO}_4)_4]$ | 3330s 3178s | 2925w | 1580s | 1645m | 535s | - | 1455m 1422m 1395m |
| $[\text{Cu}_2(\text{BAAD})_2\text{Br}_4]$ | 3300s 3160s | 2915w | 1585s | 1635m | 537s | - | 1460m 1420m 1380m |
| $[\text{Cu}_2(\text{BAAD})_2\text{Cl}_4]$ | 3260s 3170s | 2910w | 1575s | 1645m | 558s | - | 1445m 1430m 1380m |
| $[\text{Cu}_2(\text{BAAD})_2(\text{ClO}_4)_4]$ | 3300s 3190s | 292w | 1586s | 1645m | 536s | - | 1460m 1405m 1350m |

BAAD= $\text{C}_8\text{H}_{16}\text{N}_6$, s= strong, vs = very strong, m = medium, w = weak

ii) *Thermal analysis*: Thermogravimetric and differential thermal analyses of the complexes have been carried out from the ambient temperature of the furnace to 1000^o C. Thermal behaviour of the complexes follows a complex pattern and varies from compound to compound showing thermal stability in varying degrees. Almost all the complexes show three major decomposition temperature ranges 400-500^oC, 500-600^oC and 700-800^oC and are marked with exothermic peaks in DTA curves implying dissociation of the ligand with synchronous oxidation to simpler products. The complexes containing nitrate ions on the other hand are found to be thermally least stable and begin to decompose at a relatively low temperature. For all the compounds the final products are found to be of the respective metal oxide. Attempts to correlate stepwise ligand dissociation with temperature were unsuccessful. CAUTION: The perchlorate complexes are explosive in nature and violently decompose above 320-330^oC.

iii) Electronic spectra and magnetic properties

a) *Nickel(II) complexes*: The electronic spectra for the present series of complexes have been studied in the region 6000 to 30000 cm⁻¹. The possible assignments and spectral bands are recorded in Table 3 and two representative spectra are shown in Fig. 3.

The spectra show three distinct bands and clearly approach the spectral features of octahedral Nickel(II) complexes. The broad band in the range 9000 to 11,000 cm⁻¹ and two intense bands around 21,000 and 29,000 cm⁻¹ are assigned under octahedral micro asymmetry to ³A_{2g}→³T_{2g}(F), ³A_{2g}→³T_{1g}(F) and ³A_{2g}→³T_{1g}(P) transitions respectively. The high intense third band arises due to charge transfer contributions. The width of the first band manifests distortion of the complex most probably along the trigonal axis. Trigonal distortion is uncommon for Nickel(II) complexes. However some trigonal molecules are known [15] , [16] and their electronic spectra have been characterized [17]. They closely resemble spectral features of octahedral complexes.

Apart from the aforementioned transitions all of these complexes show a shoulder near 14,000 cm⁻¹ which is attributed to ³A_{2g}→¹T_{2g}(¹D) spin forbidden transition.

TABLE 3
ELECTRONIC SPECTRAL BANDS (IN CM⁻¹) OF NICKEL(II)
COMPLEXES WITH BAAD.

| Complexes | μ_{eff} in B.M | ³ A _{2g} → ³ T _{2g} (F) (cm ⁻¹) | ³ A _{2g} → ¹ T _{2g} (¹ D) (cm ⁻¹) | ³ A _{2g} → ³ T _{1g} (F) (cm ⁻¹) | ³ A _{2g} → ³ T _{1g} (P)) +CT (cm ⁻¹) |
|--|---------------------------------|--|---|---|---|
| [Ni ₂ (BAAD) ₂ Cl ₄] | 2.72 | 9,820 | 14,100sh | 23,500 | 29,400 |
| [Ni ₂ (BAAD) ₂ Br ₄] | 2.93 | 9,700 | 14,300 | 21,000 | 29,550 |
| [Ni ₂ (BAAD) ₂ (NO ₃) ₄] | 2.99 | - | 14,400 | 22,000 | 28,870 |

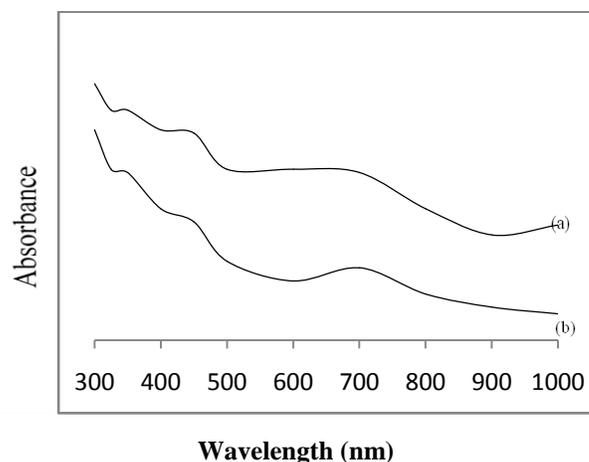


Fig. 3 Electronic spectra of a) [Ni₂(BAAD)₂Br₄] (b) [Ni₂(BAAD)₂(NO₃)₄]

b) *Copper(II) complexes* : The Copper(II) complexes show subnormal magnetic moments in the range 1.30 to 1.61 B.M. per copper atom having the ground term ²D. The low magnetic moments are attributable to possible intermolecular or intramolecular magnetic interactions between Copper(II) ions. The band positions and assignments are recorded in Table 4 and a representative spectrum is shown in Fig. 4. They show an unsymmetric and broad ligand field band around 15,100 cm⁻¹ except the perchlorate complex for which the ligand field band is located ~19,200 cm⁻¹. The width and asymmetry manifest two or three superimposed bands comparable both in magnitude and width with established Cu(II) complexes having similar low symmetry ligand fields with CuN₄ chromophores [18] , [19].

TABLE 4
ELECTRONIC SPECTRA OF COPPER (II) COMPLEXES WITH BAAD.

| Complexes | μ_{eff} in B.M. | Ligand field band (in cm ⁻¹) | Remarks |
|---|-------------------------------|---|----------------------|
| [Cu ₂ (BAAD) ₂ Cl ₄] | 1.60 | 15,200 | |
| [Cu ₂ (BAAD) ₂ Br ₄] | 1.31 | 15,150 | Broad and asymmetric |
| [Cu ₂ (BAAD) ₂ (ClO ₄) ₄] | 1.39 | 19,200 | |

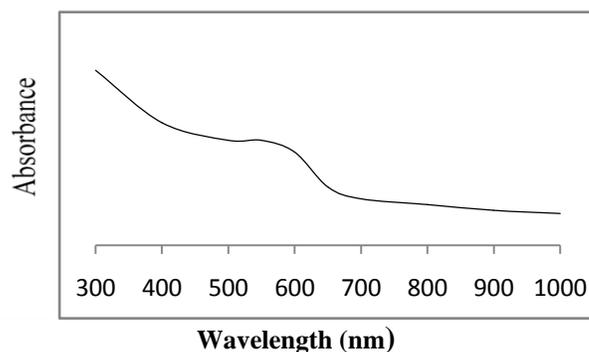


Fig. 4 Electronic Spectra of [Cu₂(BAAD)₂](ClO₄)₄

c) *Cobalt(II) complexes* : The Cobalt(II) complexes are all paramagnetic and their magnetic moments lie in the range 4.1 to 4.7 B.M. per cobalt atom. The electronic spectra of the complexes have been measured in the range 6500 to 30,500 cm^{-1} .

The electronic spectra (Table 5 and Fig. 5) show ligand field transition for chloro, bromo complexes at $\sim 16,200 \text{ cm}^{-1}$ attributable to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition. However this band is not observed in case of the nitrate complex due to the overlapping of the $20,900 \text{ cm}^{-1}$ band. The next important band for all the complexes is located in the region $19,000\text{--}21,000 \text{ cm}^{-1}$ which arises due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. These two important bands generally characterize octahedral or more appropriately to tetragonal ligand field about the metal ions [20]. In addition to the above bands all the cobalt complexes exhibit a strong CT band beyond $25,500 \text{ cm}^{-1}$.

TABLE 1
ELECTRONIC SPECTRA OF COBALT (II) COMPLEXES WITH
BAAD(CM^{-1}).

| Complexes | μ_{eff} in B.M | ${}^4T_{1g}(F) \rightarrow$ ${}^4A_{2g}(F)$ | ${}^4T_{1g}(F) \rightarrow$ ${}^4T_{1g}(P)$ | C.T. Band |
|--|---------------------------------|--|--|--------------|
| $[\text{Co}_2(\text{BAAD})_2\text{Cl}_4]$ | 4.7 | 16,300 | 19,100 | 27,500 |
| $[\text{Co}_2(\text{BAAD})_2\text{Br}_4]$ | 4.2 | 16,000 | 20,000 | 28,900 |
| $[\text{Co}_2(\text{BAAD})_2(\text{NO}_3)_4]$ | 4.1 | - | 20,900 | 31,000 |
| $[\text{Co}_2(\text{BAAD})_2(\text{ClO}_4)_4]$ | 4.3 | 15,900 | 21,200 | 28,700 |

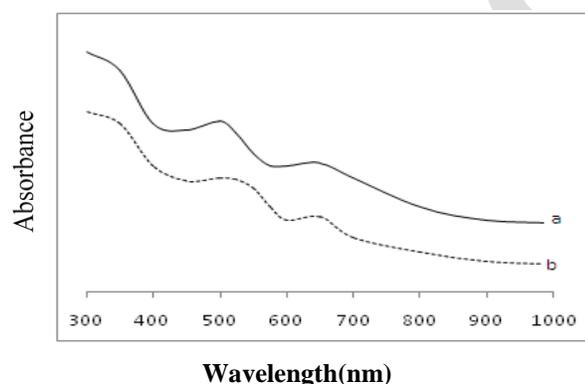


Fig. 5 Electronic Spectra of a) $[\text{Co}_2(\text{BAAD})_2\text{Cl}_4]$, b) $[\text{Co}_2(\text{BAAD})_2\text{Br}_4]$

V. ANTIFUNGAL ACTIVITY

i) *Microorganisms tested*: The microbial strains (*T. viridae*, *Aspergillus flavus*, and *Aspergillus niger*) were obtained from National Chemical Laboratory (NCL), Pune. The fungi were maintained on nutrient agar at 4°C and sub cultured before use. The microorganisms studied are clinically important ones causing several infections, food borne diseases, spoilages, skin infection and it is essential to overcome them through some active therapeutic agents

ii) *Method*: In the present investigation standard potato dextrose agar medium was used for antifungal activity by well diffusion method [21]. DMSO was used as the solvent and

Fluconazole (antifungal agent) as control. The PDA (potato dextrose agar) medium was prepared and inoculation was done inside the Laminar Air Flow. A well was made on the agar medium inoculated with microorganisms. The well was filled with the $50 \mu\text{l}$ test solution, covered with petri plates and they were incubated at 35°C for 72 hrs. During the incubation period, the solution was diffused and affected the growth of the inoculated microorganisms. The inhibition zone was developed and values of the compounds against the growth of microorganisms are recorded (Table 6)

iii) *Statistical Analysis*: Antifungal data were analyzed by one-way Analysis of Variance (ANOVA) followed by Dennett's t test with equal sample size ($n = 3$). The difference was considered significant when p value < 0.05 . All the values were expressed as mean \pm standard error mean (S.E.M.)

iv) *Results and Discussion*: The inhibitory activity of metal complex was observed in fungal pathogens. A comparative study of the ligand and its complexes (Zone of inhibition) indicates that all of the metal chelates show higher antibacterial activity than the free ligand. The increased activity of the metal chelates is due to increased lipophilicity of the metal ions. Among the three metal complexes, Cu metal complex was highly susceptible than others complexes. They showed activity in $\text{Co} < \text{Ni} < \text{Cu}$ manner. Such increased activity of the complexes can be explained on the basis of Overtone's concept [22] and Tweedy's Chelation theory [23]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only the lipid-soluble materials due to which liposolubility is an important factor, which controls the antifungal activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. The increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism. The antifungal activities of the complexes are recorded in Table 6.

TABLE 2
ANTIFUNGAL ACTIVITY OF SYNTHESIZED COMPLEXES

| Sl.No | Compound | <i>A.niger</i> | <i>A.flavus</i> | <i>T.viridae</i> |
|-------|---|------------------|------------------|------------------|
| 1 | BAAD | 1.15 ± 0.067 | 1.09 ± 0.173 | 1.10 ± 0.231 |
| 2 | $[\text{Co}_2(\text{BAAD})_2\text{Cl}_4]$ | 1.28 ± 0.133 | 1.21 ± 0.219 | 1.25 ± 0.252 |
| 3 | $[\text{Ni}_2(\text{BAAD})_2\text{Cl}_4]$ | 1.50 ± 0.120 | 1.40 ± 0.176 | 1.43 ± 0.153 |
| 4 | $[\text{Cu}_2(\text{BAAD})_2\text{Cl}_4]$ | 2.09 ± 0.088 | 2.01 ± 0.260 | 2.05 ± 0.346 |
| 5 | Fluconazole | 2.80 ± 0.346 | 2.70 ± 0.176 | 2.73 ± 0.153 |

Values are expressed as Mean \pm S.E.M. $n=3$

The fungicidal activities of the binuclear metal complexes and the ligand (BAAD) are presented in the following bar diagram [Fig. 6] taking the chloride complexes at concentration level of 50 μ l compared with standard drug Fluconazole which follows the activity order as calculated i.e Fluconazole > Cu₂ > Ni₂ > Co₂ > BAAD.

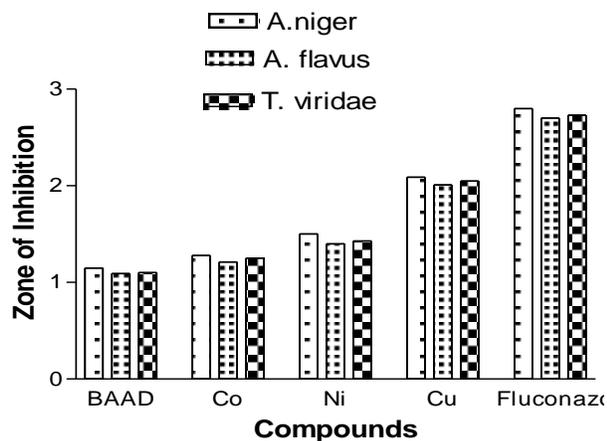


Fig. 6 Antifungal activities of synthesized compounds against selected fungus.

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