SYNTHESIS, SPECTRAL STUDY OF NOVEL 4-[(E)-(2-NITROPHENYL)DIAZENYL]-1,3-THIAZOL-AMINE (NTA/$C_9H_7N_5O_2S$) AND ITS COORDINATED METAL [$CO(NTA)_2.(H_2O)_2$] AND [$NI(NTA)_2.(H_2O)_2$] COMPLEXES; ANTIOXIDANT ACTIVITY STUDY

Vasantakumarnaik N.K[1], Bindu Pavan.V[2], Krishnamurthy. G*[1], Malathesh Pari[1], Venughopal. N[1], Sunil Kumar. N[1], Prabhakar Walmik[1], Manjuraj .T[3]

Abstract
In this study, the novel azo-dye 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$) and its coordinated metal salts [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] were synthesized. Further, geometry and its physico-chemical character of the compounds characterised via FT-IR, elemental analysis, UV-Vis, mass spectra, ^{1}HNMR and thermogravimetric spectral analysis; the all spectral data suggested tetrahedral geometry for synthesised Co (II) and Ni (II) complexes along with PXRD evidence. Ligand and its [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] compounds were tested against in-vitro antioxidant properties. The [$Co(NTA)_2.(H_2O)_2$] act as a good antioxidant agent. In this connection, we designed a new efficient drug performance in biological properties and actively participates against foreign diseases in body.

Key word: Azo-dye, Metal complexes, TGA, Antimicrobial, Antioxidant.

[1*]Department of Chemistry, Sahyadri Science College, Kuvempu University, Shivamogga, Karnataka, India-577203. email:gkmnaiksahyadri@gmail.com,vasanthnaiknk77@gmail.com,malathshpari@gmail.com, venuchavan9@gmail.com, sunil.nbas@gmail.com, prabhakarchavan7@gmail.com
[2]Department of Chemistry, JNN College of Engineering, (VTU) Shivamogga, Karnataka, India. bindupavan.v@gmail.com
[3]Department of Chemistry, Bapuji Educational Association's DRM Science College, Davanagere University, Davanagere, Karnataka, India. manjuraj877@gmail.com

***Corresponding Author:** Krishnamurthy .G
*Department of Chemistry, Sahyadri Science College, Kuvempu University, Shivamogga, Karnataka, India-577203. email:gkmnaiksahyadri@gmail.com

Accepted: 23 August 2023

DOI: 10.48047/ecb/2023.12.11.36

1. INTRODUCTION

Azo dyes are the great interest among the nitrogen containing synthetic compounds which have greater tendency to coordinate with transition metals to form coordination complexes [1]. The reaction of primary amine with a coupling compound is one of the most widely used methods to prepare azo dye. Azo dyes are important class of organic colorants consists of at least a conjugated chromophore (R-N=N-R). The azo group are largest and most versatile class of dyes. In which R and R′ are usually aryl. This chromophoric system is associated with two or more heterocyclic rings. The colour properties of organic dye depend on both the presence of chromophore group and crystallographic arrangement of the molecule in the solid state [2]. These ligands can be easily prepared by daizonium and coupling reactions. The complexes of transition metal ions contribute a diverse and rich field of research. These complexes received much attention because of their applications in biology, medicine and industry [3]. Coordination compounds of azo received much importance due to their ability to mimic complex molecules involved in vital biological process such as oxygen transport, electron transfer, catalysis etc., This is because metal chelation is involved in many important biological process [4]. This chelation is taking place between a variety of metal ions and a wide range of ligands in biology. The 2-niroaniline and 2-aminothiazole moiety have recognised these compounds are now in good demands as optical and conducting organic

materials. Also, Fabrics dyed using metal complex dyes show good light fastness [5, 6].They have a variety of applications like wood stains, in leather finishing, stationery printing inks and colouring for metals, plastics, etc. Significant interest due to the presence of donor atom like nitrogen and oxygen has achieved dazzling coordination capacity and diverse pharmacological activities and perform a class of molecule which show a comprehensive biological property. Azo dyes derived from heterocyclic amines containing nitrogen in the aromatic rings and their metal complexes have been receiving the attention of research groups due to number of Co (II) and Ni (II) complexes of azo-dye have been extensively studied their diverse antifungal, antibacterial, anti-tuberculosis, anticonvulsant and anticancer activities. Thus, the design of new chemotherapeutic drug is now engaging the consideration of medicinal chemists which reduce the toxicity [7, 8].

In our lab focused on synthesis of transition metal complexes, evolution of on drug resistance properties on synthesised bioactive molecules. In continuation of our research work here-in we report the synthesis and characterisation of azo dye ligand (NTA) and its [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] complexes screening by anti-oxidant activities have been evaluated

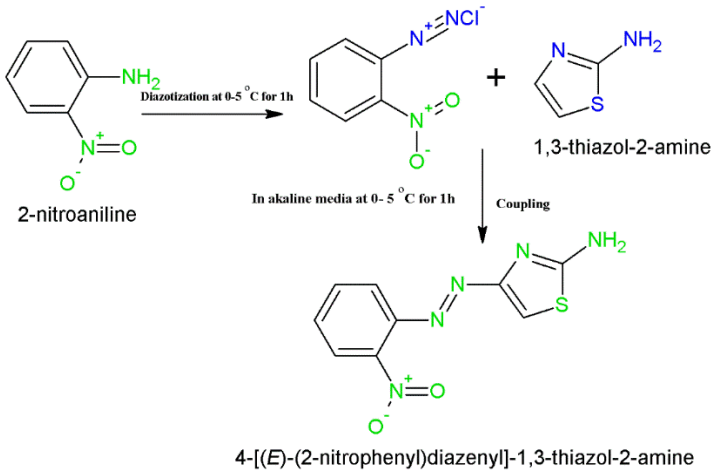
2. MATERIALS AND MEASUREMENTS

2.1 Source and Instrumentations

All the chemicals used were of analytical grade and purchased from himedia chemical company which were used without further purification. The melting point is determined by the digital melting point apparatus, electrothermal IA9100. The synthesized compounds were characterized by UV-Vis spectrophotometer in the range 200-800 nm using systronics 119 model in DMF solvent. The percentage composition of the elements was recorded using CHN analyser carlo erba 1108 analyser. The IR spectra were recorded using a KBr pellet in a Shimadzu FT-IR spectrophotometer in the range 4000–400 cm^{-1}. ^1H NMR spectrum from JEOL JNM-ECZ400S/L spectrometer of the ligand was recorded with an internal standard tetramethylsilane. The molar conductance measurement was conducted using an ELICO-CM82 conductivity meter. The magnetic moment of the complexes was noted at 28 °C by Gouy balance version 7550 using $Hg[Co(NCS)_4]$ as a calibrant. The TGA of complexes was carried out on SII Exstar TG/DTA 6300 instrument from the laboratory temperature to 1000 °C with a scan rate of 10 °C/ min. Melting points of the synthesized azo compounds were recorded in an open capillary on the electrothermal melting point apparatus.

2.2.1 Synthesis of the ligand [NTA]

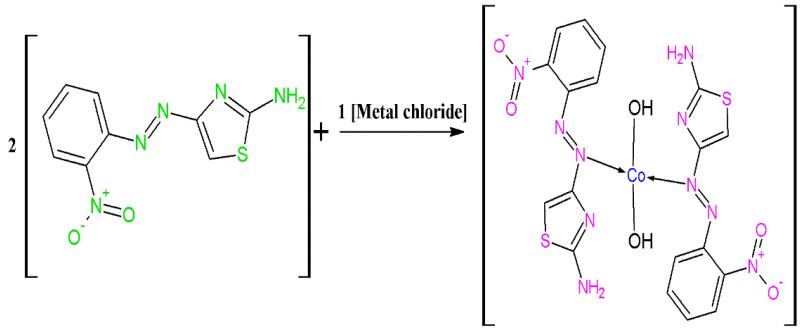
The azo 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$) was synthesized as following literature [1, 7 and 8]. Initially 2-nitro aniline (5 mM/0.69g) is dissolved in a mixture of (5.5 mL strong hydrochloric acid plus 5.5 mL distilled water). Moreover the reaction condition of mixture was maintained at 0-4 °C. The 5 mM/0.34g of sodium nitrite compound in 6 mL of water is added to above hydrochloric 2-nitro aniline mixture. Then, it was maintained for 1.5 h to complete diazotization salt process. After, 2 h 2-nitro aniline diazoniumsalt obtained. Further final step the 2-nitroaniline-diazoniumsalt solution was added drop wise to a coupling solution of 1,3-thiazol-2-amine (5 mM/0.5g) which was dissolved in water under KOH basic media. After the complete the reaction quenched with ice cold water observed pH at 4-6 pink red solid precipitate (NTA/$C_9H_7N_5O_2S$) is form and separated by filtration. However, dried compound for next continued step, recrystallization from methanol and cooled in lab temperature finally kept in desiccator the yield is obataine 81.3 %. [8, 9] The route of scheme 1 is represented in below.



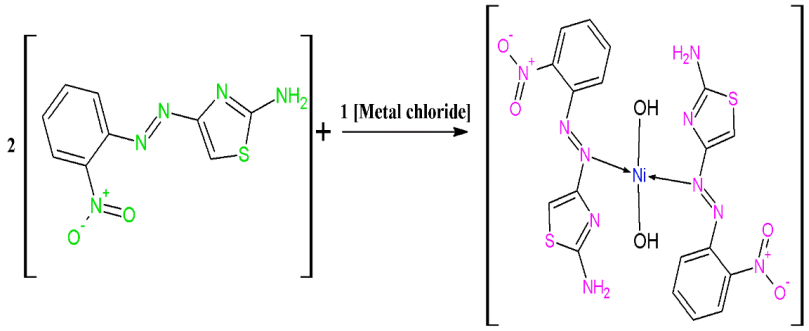
Scheme 1: 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$)

2.2.2 Preparation of Co(II) and Cu(II)

The Co(II) and Ni(II) complexes have been prepared according to the following literature in the form of 1:2 stoichiometric ratio like as [Co(II) (1.6 mM/0.35g) : 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$) (3 mM)/0.8g] was dissolved in warm 23 mL of ETOH under reflux on water bath at 63 °C for 3.8 h. Moreover complete the reaction the wine dregs red colour precipitate for Co and Cabernet red for nickel ppt collected via filtration and washed with methanol, the ppt dried over in a desiccator [8, 9]. The synthetic route is depicted in scheme 2a and 2b the yield obtained is 85–89%.



Scheme 2a Synthesis of [$Co(NTA)_2.(H_2O)_2$]



Scheme 2b Synthesis of [$Ni(NTA)_2.(H_2O)_2$]

2.4 BIOLOGICAL STUDIES

2.4.1 Antioxidant Studies

The antioxidant studies carrying used of (DPPH) 2,2-diphenyl-1-picrylhydrazyl radical is extensively for the screening of synthesised NTA ligand and its complexes by spectrophotometrically. The 24 mg of DPPH with 100 mL of methanol solution is storing at 20 °C until needed. In our research group was made the working solution by diluting DPPH solution and added synthesised substances, were produced in DMSO solvent at various concentration of 25, 50,

100 and 200 µg/mL under stirring and measuring through electronic absorbance at 517 nm [10, 11] and maintained at lab temperature for 35 min in the dark room. The percentage of inhibition was evaluated using the formula and given at below.

$$\mathbf{A} = [\frac{[\text{Abs control} - \text{Abs sample}]}{\text{Abs control}}] \times 100$$

Where: $Abs_{control}$ = Absorbance of the DPPH radical+ methanol.
Abs_{sample}= Absorbance of DPPH + sample (tested sample/standard).

3. RESULT AND DISCUSSION

3.1. Characterization

The NTA ligand is coordinate with Co(II) and Ni(II) metal salts and this were good agreement with formulated structure like as $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$. The prepared compounds were characterized by various spectroscopic techniques. The complexes are soluble in DMF solvents. The molar conductance values of the complexes recorded in DMF (1×10^{-3}M) solution and reported 13-19 $cm^2\ \Omega^{-1}mol^{-1}$ indicate non-electrolytic behaviour [12, 13]. The analytical data are saved in Table 1

Table 1 Physical properties and analytical data of NTA and its complexes

Compounds	Colour	Mol.Wt	M.P °c	Elemental analysis (%) (Cal)				Λm ($cm^2\Omega^{-1}mol^{-1}$)
				C	H	N	M	
NTA	Pink red	249.25	142-149	43.37 (43.23)	2.83 (2.79)	28.10(28.12)	-	-
$[Co(NTA)_2.(H_2O)_2$	Wine dregs red	591.40	166-168	38.92 (36.55)	2.18 (2.73)	23.74 (23.68)	9.97(9.96)	19
$[Ni(NTA)_2.(H_2O)_2]$	Cabernet red	591.20	140-143	37.94 (36.57)	2.78 (2.73)	23.70(23.69)	9.98(9.93)	11

3.2 ^{1}H NMR Spectral Data

The newly symphonized NTA has been signalized by way of ^{1}H NMR in DMSO-d_6 at laboratory condition and reperesnt in Figure 1. The Ar-H four protons assigned at 8.40 to 8.27 ppm (m, 4H, Ar-H) and the 2-aminothiazole proton resonance showed singlet with respect to 7.88 to 7.86 ppm (s, 1H, Ar-H). The thiozole amine protons reveal as a singlet on 7.229 ppm (s, 2H, Ar-NH_2) [10-13].

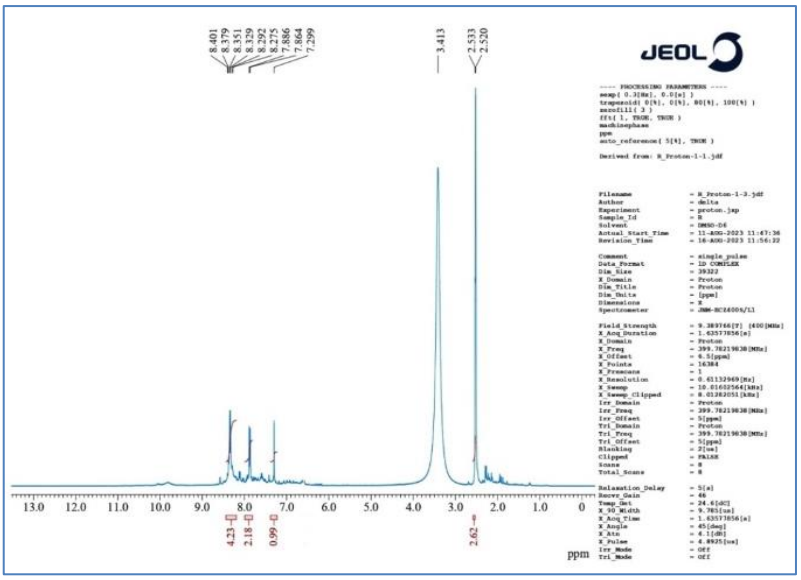


Figure 1 ^{1}H NMR spectrum of NTA

3.3 IR spectral studies

Functional groups are finding by Infrared spectroscopy for synthesised NTA and its coordinated complexes and data are noted in Table 2. The NTA ligands band raised due to its group of amine ν(NH_2) at 2960 cm^{-1} while its $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$ appeared at 2953 and 2952 cm^{-1} respectively. The (-N=N-) functional group of synthesised NTA shows 1370 cm^{-1} but its complexes shows various wavelength ranges between 1440-1499 cm^{-1} is attributed and new ν(OH) peaks appeared at 3441

to 3430 in complexes. These shifted and newly appeared wavelength regions indicate formation of coordinated bond for complexes. In addition, the spectral peaks appeared at 509-535 cm^{-1} is due to (M-N) and (M-O) stretching at 663- 655 cm^{-1} confirms the respectively, for bond formation. The spectra are shown in Figure 2 [10-13]

Table 2 FT-IR spectral data of azo dye NTA ligand and its metal complexes

Compound	$\nu_{(-OH)}$	$\nu_{(-NH2)}$	$\nu_{(N=N)}$	$\nu_{(M-O)}$	$\nu_{(M-N)}$
NTA	-	2960	1370		
$[Co(NTA)_2.(H_2O)_2]$	3441	2953	1441	663	509
$[Ni(NTA)_2.(H_2O)_2]$	3430	2952	1499	655	531

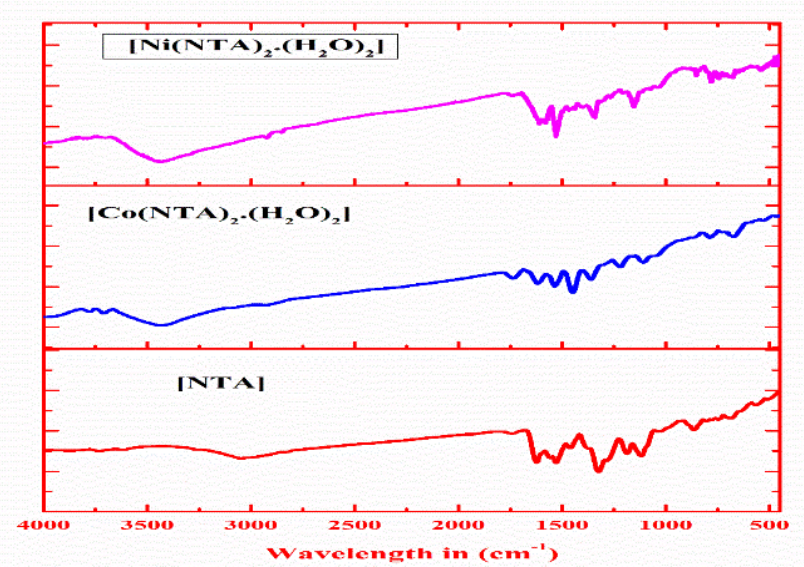


Figure 2 FT-IR spectral data of azo dye NTA ligand and its metal complexes

3.4 UV Studies

The novel NTA and its coordinated complexes were investigated by electronic spectral studies between 200-800 nm at the concentration 10^{-6} M in DMF solvent. The NTA revealed two distinct absorption bands exhibits at 36,101 and 25,641 cm^{-1} attributed to the corresponding $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions assigned and this indicates due to the interaction of azo-aromatic chromophore due to intermolecular charge transfer. In $[Co(NTA)_2.(H_2O)_2]$ exhibited $^4T_{1g}\rightarrow\ ^1A_{2g}(P)$ transition assignment due to at 24,390 cm^{-1} and along with its magnetic moment is 3.872 BM shows tetrahedral geometry [10-13]. The [Ni $(NTA)_2.(H_2O)_2$] is attributed absorption peak at 25,000 its transition assignments is $^2B_{1g}\rightarrow{}^2E_g$ its magnetic moment is 2.828 BM, it is also revealed tetrahedral geometry. The wavelength is shifted various regions in complexes compared to ligand due to charge transfer from ligand to metal, while all transition appeared in bathochromic shift. The spectral results of the electronic spectral studies were noted in Table 3 and Figure 3 [10-14].

Table 3 The electronic spectral data of NTA and its metal complexes

Compounds	Absorptions in (cm^{-1})	Transitions assignment	Magnetic moment μ_{eff}(BM)
NTA	36,101 25,641	$n\rightarrow\pi^*$ $n\rightarrow\pi^*$	

[$Co(NTA)_2.(H_2O)_2$]	24,390	$^4T_{1g} \rightarrow {}^4A_{2g}(P)$	3.872
[$Ni(NTA)_2.(H_2O)_2$]	25,000	$^2B_{1g} \rightarrow {}^2E_g$	2.828

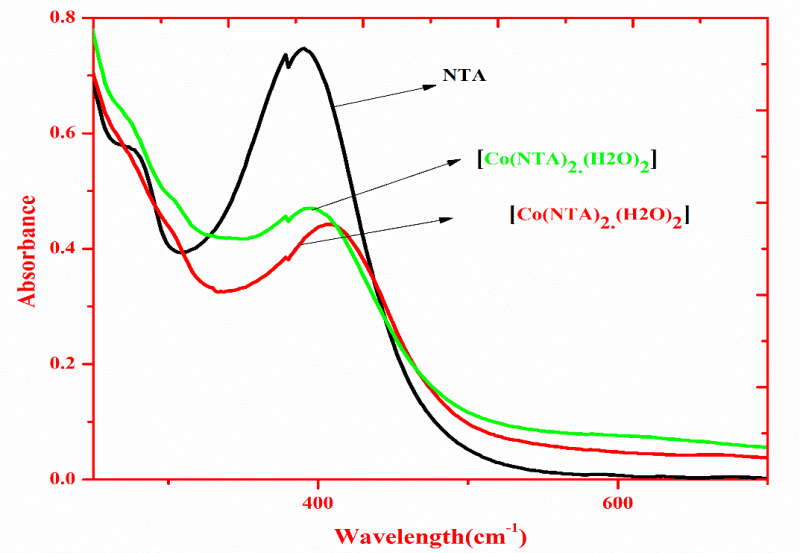


Figure 3 Electronic spectra of NTA, $[Co(NTA)_2.(H_2O)_2]$and $[Ni(NTA)_2.(H_2O)_2]$

3.5 XRD Studies

The crystallinity of prepared $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$ complexes was determined by PXRD pattern in this order to scan at 10°/min and constant a wavelength (λ) 1.54 Å in the region between 5–100°. The inter-planar space was determined using Bragg's formulae $n\lambda = 2dSin\theta$. However, (d) is inter-planar distance recorded data are given in Table 4. The diffractogram 2θ peak of $[Co(NTA)_2.(H_2O)_2]$ shows 5 reflections and it's $h^2+k^2+l^2$ values are good agreements with 1, 5, 7, 8 and 4 hence it represents tetrahedral/octahedral nature. The $[Ni(NTA)_2.(H_2O)_2]$ also $h^2+k^2+l^2$ values noted as 1, 5, 6, 7, 8 and 11 forbidden diffractions, these diffractions indicate tetrahedral/octahedral structure of complex [10-13, 15]. Further, the lattice parameter of Co and Ni complexes provide a=b=c = 11.64 and 11.63 Å respectively. All novel synthesised metal complexes data relived the molecules are arranged in crystalline nature as shown in Figure 4.

Table 4 XRD data of NTA ligand and its metal (II) complexes

Compound	Point	2θ	Sinθ	$Sin^2\theta$	$Sin^2\theta \times 1000$	$h^2+k^2+l^2$	h k l	D		a in A°
								Obs	Cal	
[$Co(NTA)_2.(H_2O)_2$]	1	7.6	0.066	0.0043	4.356	1	1 0 0	11.69	11.66	11.66
	2	17.17	0.147	0.0216	21.609	5	2 1 0	5.33	5.23	11.7
	3	20.11	0.174	0.0302	30.276	7	-	4.43	4.42	117
	4	21.82	0.189	0.0357	35.721	8	2 2 0	4.17	4.07	11.5
	5	28.7	0.247	0.0610	61.009	14	3 2 1	3.23	3.11	11.66
[$Ni(NTA)_2.(H_2O)_2$]	1	7.7	0.067	0.0044	4.489	1	1 0 0	11.5	11.48	11.48
	2	17.3	0.145	0.0210	21.025	5	2 1 0	5.36	5.30	11.87
	3	18.5	0.16	0.0256	25.6	6	2 1 1	4.89	4.81	11.78
	4	20.25	0.175	0.0306	30.625	7	-	4.4	4.39	11.63
	5	21.71	0.188	0.0353	35.344	8	2 2 0	4.1	4.09	11.58
	6	25.68	0.222	0.0492	49.284	11	3 1 1	3.51	3.46	11.49

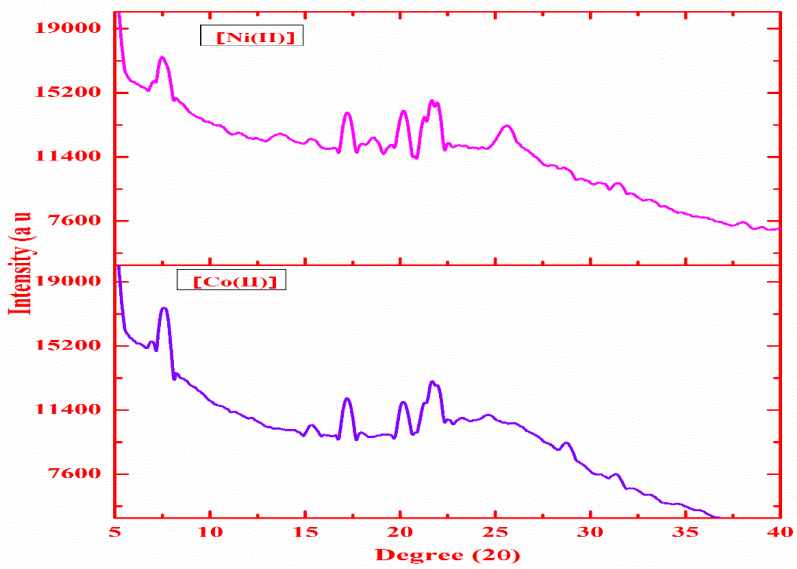


Figure 4 XRD patterns of $[Co(NTA)_2.(H_2O)_2]$and $[Ni(NTA)_2.(H_2O)_2]$

3.6 Mass Spectra Of Syntheses Compounds

The mass spectra of the novel NTA ligand peak attributable to the given molecular ions peak m/z 250.07 (Cal: 249.23) represents in Figure 5 and its $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$ complexes m/z ion peak showed at (Cal:592.44) and (Cal: 591.20) respectively, as data shown in elemental analysis Table 1

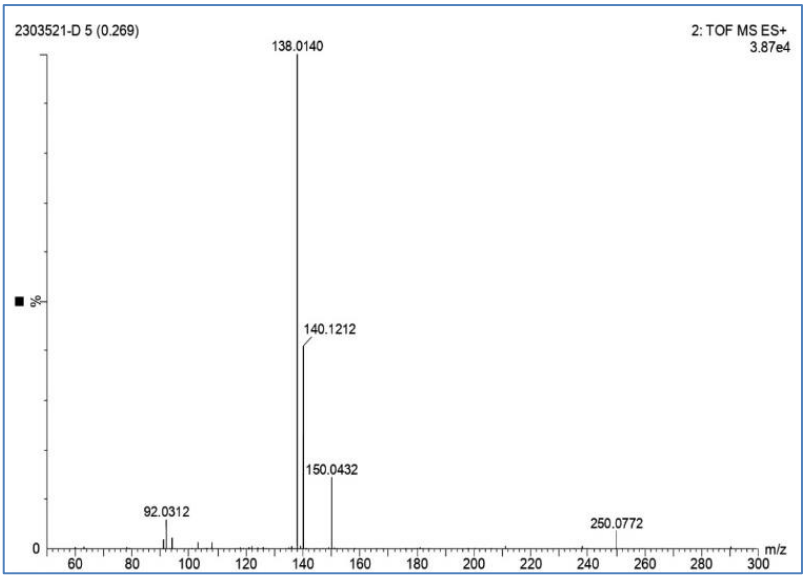


Figure 5 Mass of the NTA ligand

3.7 Thermal Studies of Compounds

The metal complexes were examined by thermo gravimetric analysis in the temperature range 25 to 1000 °C at a heating rate 10 °C/min under nitrogen atmosphere. Thermograms of $[Co(NTA)_2.(H_2O)_2]$ exhibited two steps of degradations. The first step being at 20.05 to 332.25 °C, which corresponds to the mass loss of 67.5 % due to one coordinated water, 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-2-amine and nitro aniline molecules. In the second step 19.6 % weight loss between 332.25 to 796.3 °C is due to 1,3-thiazole-2,4-diamine and at the end Co oxide residue formed. The $[Ni(NTA)_2.(H_2O)_2]$ exhibits three degradation steps, in the first step 52.5 % of mass loss is due to the dissociation of two oxygen, one amine, one coordinated water and NTA molecules at temperature between 24.01-295.5 °C. The second degradation step, has occurred from 295.5-528.03 °C showed the weight loss of 19.1 % benzene-1,2-diamine molecules and the third degradation step at 528.03- 751.2 by 2-aminothiazole molecules of 16.9 % weight loss the end left over residue is NiO [25-29] as shown Table 5 and Figure 6 [10-13, 15-16].

Table 5 Thermal degradation data of complexes

Complex	Step	Decomposition Temp (°C)	Assignment Moiety left	Loss of mass (%)	Residue
$[Co(NTA)_2.(H_2O)_2]$	1	20.05-332.25	One coordinated water, NTA and nitro aniline	67.5	CoO
	2	332.25-796.3	1,3-thiazole-2,4-diamine	19.6	
$[Ni(NTA)_2.(H_2O)_2]$	1	24.01-295.5	Two oxygen one amine One Coordinated water molecule and NTA	52.5	NiO
	2	295.5-528.03	benzene-1,2-diamine	19.1	
	3	528.03-751.2	2-aminothiazole	16.9	

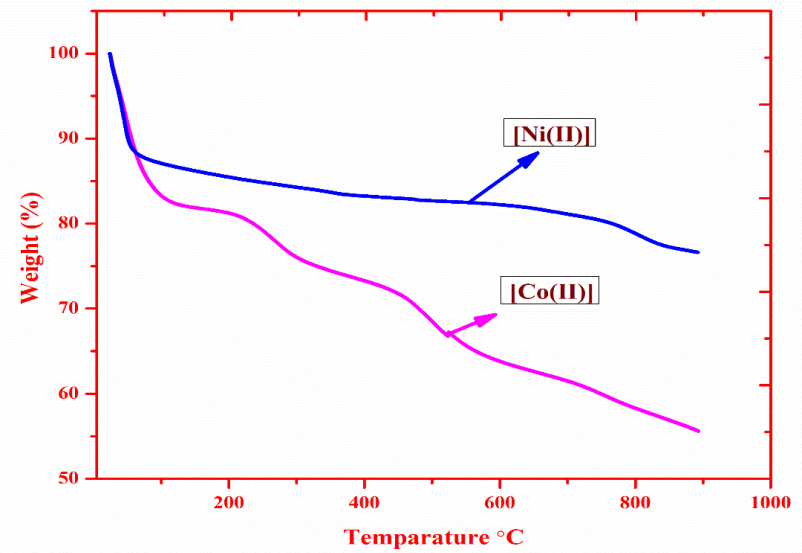


Figure 6 TGA curves for $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$

3.8 BIOLOGICAL STUDIES

3.8.1 Antioxidant Studies

The synthesised NTA and its metal (II) complexes $[Co(NTA)_2.(H_2O)_2]$ and $[Ni(NTA)_2.(H_2O)_2]$ are evaluated by DPPH scavenging activity in different concentrations. The metal (II) complexes shows positive results towards DPPH free radical which presented in Figure 7. Whereas the [Co(II)] complex explore more potential activity result compered by other complexes. Briefly at 200 µg/mL, the $[Co(NTA)_2.(H_2O)_2]$and $[Ni(NTA)_2.(H_2O)_2]$ percentage inhibited DPPH free radical till 74.93 and 53.83 % respectively results are entered in Table 6 and comparatively results suggest they act as good prevention against oxidation caused diseases [17-21].

Table 6 Antioxidant activity of NTA and its metal (II) complexes

Compounds	% Scavenging activity (Concentration in µg/mL)			
	25	**50**	**100**	**200**
NTA	37.55	39.16	41.35	46.64
$[Co(NTA)_2.(H_2O)_2]$	59.98	62.18	67.23	74.93
$[Ni(NTA)_2.(H_2O)_2]$	41.19	48.14	49.98	53.83
Ascorbic acid	82.33	88.77	91.42	94.78

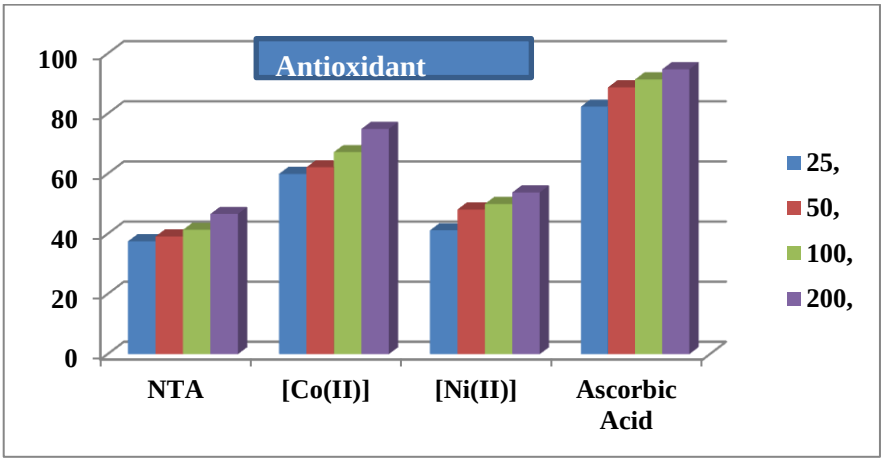


Figure 7 DPPH free radical scavenging activity of NTA and their complexes

4. CONCLUSIONS

A novel NTA and its metal (II) complexes [$Co(NTA)_2.(H_2O)_2$]and [$Ni(NTA)_2.(H_2O)_2$] synthesised and the structure of the prepared compounds was elucidated by various spectra-chemical studies. The non-electrolytic nature of [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] was confirmed by the molar conductivity method. Infrared spectral data suggested the mode of bonding between the metal ions with NTA. Antioxidant examine on synthesized compounds, however, [$Co(NTA)_2.(H_2O)_2$] shows best significant antioxidant agent. In addition, the biocompatibility and synergistic effect of compounds enhanced results in medical purpose. The spectrochemical, pharmaceutically results suggest that the synthesised compound act as drug.

5. Acknowledgment

The authors thank the sahyadri science college Kuvempu University, Shimoga. The University of Mysore and Mangalore university, mangala gangotri DST lab, Mangalore, SAIF Dharwad for providing spectral facilities. The authors also thankful to Protein Design Private Limited Mathikere Bangalore, Karnataka, India for biological studies.

COMPLIANCE WITH ETHICAL STANDARDS

Conflicts of interest there is no conflicts interest this work.

REFERENCES

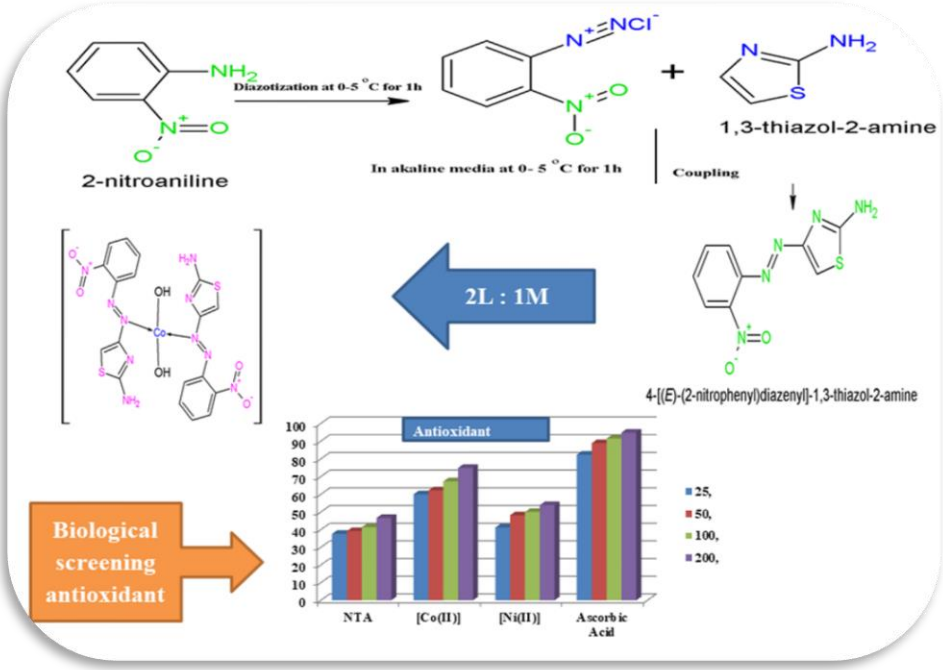
1. N. Venugopal, G. Krishnamurthy, H.S. Bhojya Naik, J.D. Manohara, DNA Binding, Molecular Docking and Antimicrobial Evaluation of Novel Azo Dye Ligand and Their Metal Complexes. J. Inorg. Organoment. Polym. **30**, 2608-2625 (2019). https://doi.org/10.1007/s10904-019-01394-8.
2. F.A. Saad, H.A. El- Ghamry, M.A. Kassem, Synthesis, structural characterizationand DNA binding affinity of new bioactive nano- sized transitionmetal complexes with sulfathiazole azo dye for therapeutic applications. Appl Organometal. Chem. **33**, 4965 (2019). https://doi.org/10.1002/aoc.4965.
3. Mohamed Gaber, S.K. Fathalla, H.A. El-Ghamry, 2,4- Dihydroxy- 5- [(5- mercapto- 1H- 1,2,4- triazole- 3- yl)diazenyl] benzaldehyde acetato, chloro and nitrato Cu(II) complexes: Synthesis, structural characterization, DNA binding and anticancer and antimicrobial activity. Appl Organometal Chem. **33**, 4707 (2019). https://doi.org/10.1002/aoc.4707.
4. N. Ranjitha, G. Krishnamurthy, M.N. Manjunatha, H.S. Bhojya Naik, Malathesh Pari, Vasantakumarnaik. N.K, J. Laxshmikantha, K. Pradeepa, Electrochemical determination of glucose and H_2O_2 using Co(II), Ni(II), Cu(II) complexes of novel 2-(1,3-benzothiazole-2ylamino)-N-(5-choro-2hydroxyphenyl) acetamide: Synthesis, Structural Characterisation, antimicrobial, anticancer activity and docking studies. J. Mol. Struct.
5. **1274**, 134483 (2022). https://doi.org/10.1016/j.molstruc.2022.134483
6. S.H. Alotaibi, A.S. Radwan, Y.K. Abdel-Monem, M.M. Makhlouf, Synthesis, thermal behavior and optical characterizations of thin films of a novel thiazole azo dye and its copper complexes. *Spectrochim. Acta A Mol.* **205**, 364–375 (2018). https://doi.org/10.1016/j.saa.2018.07.043.

7. Murugaiyan Manimohan, Sivashanmugam Pugalmani, Mohamed-Aboobucker Sithique, Synthesis, Spectral Characterisation and Biological Activities of Novel Biomaterial/N, N, O Donor Tridentate Co (II), Ni (II) and Zn (II) Complexes of Hydrazide Based Biopolymer Schiff Base Ligand. J. Inorg. Organomet. Polym. **30**, 4481-4495 (2020). https://doi.org/10.1007/s10904-020-01578-7.
8. N. Venugopal, G. Krishnamurthy, H.S. Bhojya Naik, M. Girdhar, Novel bioactive azo-azomethine based Cu (II), Co (II) and Ni(II) complexes, structural determination and biological activity. J. Mol. Struct, **1191** 85-94 (2019). https://doi.org/10.1016/j.molstruc.2019.04.022.
9. N. Venugopal, G. Krishnamurthy, H.S. Bhojya Naik, Madhukar Naik, N. Sunilkumar, Synthesis, characterization, and biological activity of Cu(II) and Co(II) complexes of novel N1 , N2 -bis(4-methyl quinolin-2-yl)benzene-1,2-diamine: CuO and CoO nanoparticles derived from their metal complexes for photocatalytic activity. Inorg. Nano-Met. Chem. **51,** 1117-1126 (2021). https://doi.org/10.1080/24701556.2020.1814337.
10. Athulya Das, Anjana Rajeev, Sarmistha Bhunia, Manivel Arunkumar, Nithya Chari, Muniyandi Sankaralingam, Synthesis, characterization an antimicrobial activity of nickel(II) complexes of tridentate N_3 ligands, Inorganica Chim. Acta. **526,** 120515 (2021). https://doi.org/10.1016/j.ica.2021.120515.
11. Murugaiyan Manimohan, Sivashanmugam Pugalmani, K. Ravichandran, Mohamed Aboobucker Sithique, Synthesis and characterisation of novel Cu(II)-anchoredbiopolymer complexes as reusable materials for the photocatalytic degradation of methylene blue. RSC Advances. **10**, 18259–18279 (2020). https://doi.org/10.1039/d0ra01724h.
12. N. Venugopal, G. Krishnamurthy, H.S. Bhojya Naik, P. Murali, Krishna, Synthesis, spectral characterization and biological studies of Cu (II), Co (II) and Ni (II) complexes of azo dye ligand containing 4–amino antipyrine moiety. J. Mol. Struct. **1183**, 37-51 (2019). https://doi.org/10.1016/j.molstruc.2019.01.031.
13. N.M. Mallikarjuna, J. Keshavayya, M.R. Maliyappa, R.A. Shoukat Ali, Talwara, Venkatesh, Synthesis, characterization, thermal and biological evaluation of Cu (II), Co (II) and Ni (II) complexes of azo dye ligand containing sulfamethaxazole moiety. J. Mol. Struct. **1165**, 28-36 (2018). https://doi.org/10.1016/j.molstruc.2018.03.094.
14. Vasantakumarnaik, Narayanapura, krishnanaik., Ganganaik, Krishnamurthy., Malathesh, Pari., Nagaraju, Venugopal., Nanjundaswamy, Ranjitha., Nagaraja, Naik**.:** Synthesis, spectral characterisation of novel Azo–dye 4-((E)-(2-hydroxy-3-methoxy-5-((E)-thiazol-2-yldiazenyl)benzylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one and its transition metal complexes; Differential pulse voltammetric detection of nitrite and its biological activities, Biointrrface Res. Appl. Chem. **13**, 513 (2023), https://doi.org/10.3363/BRIAC136.531**.**
15. D.N. Sathyanarayana, Electronic Absorption Spectroscopy and Related Technique (University Press (India) 2001.
16. Abrar Ul Hassan, Sajjad Hussain Sumrra, Muhammad Nadeem Zafar, Muhammad Faizan Nazar, hsan Ullah Mughal, Muhammad Naveed Zafar, Mazhar Iqbal , New organosulfur metallic compounds as potent drugs: synthesis, molecular modeling, spectral, antimicrobial, drug likeness and DFT analysis. Mol. Divers. **26**, 51-72 (2022). https://doi.org/10.1007/s11030-020-10157-4
17. Abdul Kareem, Laxmi, Mohammad Arshad, Shahab A.A. Nami, Nahid Nishat, Herbo-mineral based Schiff base ligand and its metal complexes: Synthesis, characterization, catalytic potential and biological applications. J. Photochem. Photobiol. B. Biol. **160**, 163-171 (2016). https://doi//10.1016/j.jphotobiol.2016.03.030.
18. Nirmal Joshi, Vishnu Gore, Sunil Tekale, Rajesh Nawale, Dhanaji Rajani, Bembalkar, Rajendra Pawar, Synthesis and Biological Evalution Study of New Bis-imine Ligand ans Metal complexes. Lett. Appl. Nano. Bio. Science. **10**, 2207-2214 (2021). https://doi.org/10.33263/LIANBS102.22072214.
19. Vasantakumarnaik, N. K.; Krishnamurthy, G.; Malathesh Pari. Synthesis of novel 2-chloro-6-{[(E)-{2-hydroxy-3-methoxy-5-[(E)-1,3-thiazol-2-yldiazenyl]phenyl}methylidene]amino}-4-nitrophenol and its Co(II) Cu(II) complexes : biological studies and Detection of Hg by

[$Co(CEN)_2$]/GCE. J. Surv Fish Sci. **10(4S)**, 2403-2419 (2023), https://doi.org/10.17762/sfs.v10i4s.1568

20. O.A. El-Gammal, D.A. Saad, A.F. Al-Hossainy, Synthesis, spectral characterization,optical properties and X-ray structural studies of centrosymmetri N_2S_2 or $N_2S_2O_2$ donor Schiff base ligand and its binuclear transition metal complexes. J. Mol. Struct. **1124,** 130974 (2021). https://doi.org/10.1016/j.molstruc.2021.130974 .
21. N. Saikumari, Synthesis and characterization of amino acid Schiff base and its copper (II) and its antimicrobial studies. Mater. Today: Proc. **47**, 1777-1781 (2021). https://doi.org/10.1016/j.matpr.2021.02.607.
22. N.K Vasantakumarnaik, G. Krishnamurthy, Malathesh Pari, N. Ranjitha, H.A. Anilkumara, G.Y Akarsh, M.N Manjunatha. Synthesis, characterization of 4-{[(E)-{2-hydroxy-3-[(Z)-1,3-thiazol-2-yldiazeneyl]napthalen-1-yl}methylidene]amino}benzoic acid and its transition metal complexes ; biopharmaceutical activities and electrochemical detection of ciplactin. J. Mol. Struct. **136405,** 1294 (2023). https://doi.org/10.1016/j.molstruc.2023.136405

Graphical Abstract



Bibliography of Authors

Synthesis, Spectral study of novel 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$) and its coordinated metal [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] complexes; Antioxidant activity study

Vasantakumarnaik N.K[1], Bindu Pavan. V[2], Krishnamurthy. G*[1], Malathesh Pari[1], Venughopal. N[1], Sunil kumar. N[1], Prabhakar Walmik[1], Manjuraj .T[3]

Author Contribution:
Vasantakumarnaik N.K[1]: Writing- Reviewing, Writing- Original draft preparation and Main 1st Author.
Bindu Pavan. V[2]: Supervision and Software validation
Krishnamurthy .G*[1]: Supervision, Writing - Review & Editing and Corresponding author
Malathesh Pari: Supervision, Data correction.
Venughopal. N[1]: Software validation
Sunil kumar. N[1]: Software validation
Prabhakar Walmik[1]: Supervision
Manjuraj. T[3]: Software validation

KUVEMPU UNIVERSITY

SAHYADRI SCIENCE COLLEGE
Dr. G. Krishnamurthy **M.Sc., M.Phil., Ph.D.**
Professor
Department of Chemistry
Sahyadri Science College
Kuvempu University
Shimoga – 577 203
Karnataka, INDIA.
E-mail: gkmnaiksahyadri@yahoo.co.in Phone No: 08182-240435(O)
gkmnaiksahyadri@gmail.com Cell: +919448774649

To
Editor-in-Chief
Prof. Dr. K. Krishna
Department of Chemistry, India

Sir,

Subject: Submission of manuscript for publications.

With reference to the subject I am here with submitting the paper entitled "**Synthesis, Spectral study of novel 4-[(*E*)-(2-nitrophenyl)diazenyl]-1,3-thiazol-amine (NTA/$C_9H_7N_5O_2S$) and its coordinated metal [$Co(NTA)_2.(H_2O)_2$] and [$Ni(NTA)_2.(H_2O)_2$] complexes; Antioxidant activity study"** I request to consider for Publications in your esteemed **"European Chemical Bulletin (ISSN 2063-5346)"** and oblige.

Yours sincerely,
Dr. G Krishnamurthy
(Research Guide)