

**INVESTIGATION OF THE METAL COMPLEXES OF
ISOMERIC NAPHTHOIC ACID WITH BASE: SYNTHESIS,
CRYSTAL STRUCTURE, AND ITS ENERGY APPLICATIONS**

THESIS

Submitted to Bharathiar University

in partial fulfillment of the requirements for the award of the Degree of

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

Submitted by

M.SWATHIKA

Under the guidance of

Dr. N. ARUNADEVI, M.Sc., M.Phil., Ph.D.

Assistant Professor



DEPARTMENT OF CHEMISTRY

PSGR KRISHNAMMAL COLLEGE FOR WOMEN

(Autonomous Institution – Affiliated to Bharathiar University)

Coimbatore – 641004

Tamil Nadu, India

SEPTEMBER 2023

Chapter XI

CHAPTER XI

SUMMARY AND CONCLUSIONS

Higher analogs of naphthoic acid and substituted naphthoic acid were of greater attention among researchers because they possess a larger range of biological and chemical applications like medicine, photo-chemical, organic pigments, pesticides, photosensitive materials, dyes, cosmetic preparations, etc. Naphthoic acid was synthesized and assembled from a planar dimer unit. It was mainly used for the synthesis of highly economical and effective herbicides as well as plant growth regulators, thermal testimony materials, and photosensitive objects. Some materials prepared from 1-naphthoic acid have plasticizer resistivity and solvent resistivity. It was one of the best examples of the naphthalene derivative which has been often used as a chelating agent. These significant features lead to the detailed analysis of complexes of naphthoic acid. Further due to the increase in sustainable energy sources and environmental remediation, the attention towards metal and mixed metal oxide has markedly increased nowadays and it has a promising role in electrochemical energy storing devices.

The present research work concentrates mainly on the synthesis and spectral characterization of 1-naphthoic and 2-naphthoic acid with guanidine and aminoguanidine with alkali and alkaline transition metals. The physiochemical characterization we carried out includes elemental analysis, IR, UV, TG-DTA, PXRD, Single crystal XRD, antimicrobial, antifungal, and catalytic activity. With the interest of finding out the application of material towards corrosion behavior, nano metal oxide/mixed metal oxides are synthesized from complex and used as corrosion inhibitors. Further, to enhance the production of hydrogen, the targeted complexes are used as electrocatalysts for Hydrogen Evolution Reaction. The results obtained are concluded as follows:

Initially, the ligands were prepared from 1-naphthoic and 2-naphthoic acid with aminoguanidine/ guanidine. The acid and base moieties are stabilized by employing intermolecular bonds between OH, COOH, CH_5N_4^+ , and CH_4N_3^+ . The presence of FT-IR peaks around νNH , $\nu\text{N-N}$, and $\nu\text{C-N}$ evidence for the formation of salts. The bandgap energy for all the salts exhibits a range of 2.5-3.5 eV and confirms the semiconducting nature of the adducts. All salts are thermally stable and show a uniform pattern of degradation.

Further, we tried to synthesize the compounds in the form of crystals and succeeded in developing two crystals, one is from ligands with 2-naphthoic acid and guanidine. The crystal system is monoclinic, and it has $P121/c 1$ symmetry. Theoretical crystal morphology exhibits the eight sets of facets that are (0,0,1), (0,0,-1), (0,1,0), (0,-1,0), (1,0,0) (-1,0,0), (1,0,-1) and (-1,0,1) and the distance between the planes is found to be 13.75° angle. In IR spectra, the region around $3195-3300\text{ cm}^{-1}$ is due to the presence of N-H frequencies. The carbonyl stretching frequency was seen around 1679 cm^{-1} to 1671 cm^{-1} . The optical properties of the adduct were illustrated in the UV-visible spectroscopy, in which fundamental absorption was noticed at 4.7 e V. From Tauc's plot, the energy band gap was determined, and the value of the 4.6 eV which confirms the semi-conducting nature of the compounds. The higher refractive indexes were detected at 234 nm and lower wavelengths due to fundamental absorption. The extinction coefficient increases, after 200 nm they are gradually reduced and the skin depth of the sample, is indicated by increasing the photon energy by decreasing the skin depth value. XRD data confirms the synthesized adduct is highly crystalline. In the thermal analysis, the stability of the crystal was confirmed and the thermodynamic parameters were determined at 543K, 793K, and 953 K. The negative value of ΔS represents that the reaction is slower, the positive ΔH specifies the endothermic nature of the reaction, and the positive ΔG value proves they are non-spontaneous. The acid, base, and adduct slope values were correlated with the linear fit in which the R^2 value produced 0.99. Density function theory and frontier molecular orbital are used to estimate the possible reactivity tendency. Hirshfeld surface analysis was used to confirm the contributions of the dissimilar intermolecular interactions in the development of crystal packing.

We developed another crystal with strontium metal ions in the form of a metal-organic framework. The space group of the crystal is monoclinic, and it has $C2/c$ symmetry. Theoretical crystal morphology exhibits eight sets of facets, and the distance between the planes is denoted by a 52.85° angle. In FTIR spectra, the peaks at 1686 cm^{-1} are due to the COOH group of naphthoic acid, Sr-MOF peak appears at 690 cm^{-1} which confirms the formation of a metal-organic framework. XRD data confirms the synthesis of MOFs is highly crystalline. The UV data represents the E_g value, which is calculated to be 3.9 eV, which confirms the semi-conducting nature. DFT and FMO demonstrate optimized

geometry, energy gap (ΔE), chemical stability, and global reactivity descriptors. The Hirshfeld surface represented the 2D fingerprint plot, and crystal voids deliver data about the molecular interaction, electronic density, and intermolecular assets of close contacts.

Further metal complexes are synthesized from aminoguanidinium-1-naphthoate with metal ions like Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Li^+ , Na^+ , and K^+ .

Systematic synthesis and characterization through analytical, spectral, thermal, and structural methods of complexes were carried out. FT-IR spectral study reveals the nature of the functional groups and vibrational modes of the metal complexes. In UV-visible spectra, the peak at 250-350 nm corresponds to $\pi \rightarrow \pi^*$ transition and the peak at 362-400 nm is due to the aminoguanidine group with band gap energy of 3.5-4.7 eV. TG-DTA result shows a majority of decomposition occurs around 230-395°C and confirms the stability of the metal complexes. Powder XRD indicates the isomorphism among the metal complexes. Zn (II) complex shows better antibacterial activity against *Escherichia coli*. Further complexes show good cytotoxic effects towards MCF-7 (breast cancer) and A-549 (lung cancer). The role of complexes in the form of electrocatalysts for hydrogen evolution reactions was verified by carrying out a series of analysis.

Linear sweep voltammetry (LSV) curves display excellent activity and the Tafel slope was found in the range of 6.38 to 40 $mVdec^{-1}$ in 0.5 M H_2SO_4 . The electrochemical impedance spectroscopy (EIS) test was accomplished to recognize the mechanism of HER, and charge transfer resistance was less which indicates that composites are favorable for the hydrogen evolution. The electrochemical surface area (ECSA) was figured by studying the electric double-layer capacitance (C_{dl}) and it was found to be $0.377 \mu Fcm^2 - 0.143 \mu Fcm^2$. More prominent ECSA values imply the target complexes have enhanced electrochemically active/dynamic sites and better hydrogen evolution performance. According to the results, high-performing catalytically active sites are found to be Li[1NA-AMG] metal ions. Furthermore, in a volcano plot, the position of the Li[1NA-AMG] metal ions is found to be close to the near thermoneutral catalytic activity. Based on the results, we successfully designed an electrocatalyst as a prospective candidate for hydrogen evolution reaction. In addition, nano oxide of ligand and Ni-Co composites were performed. Powder XRD

diffraction was employed to characterize the ligand and metal composite, confirming the linkage of acid and base moiety with the metal ions. In the FT-IR analysis, the two different bands of M–O showed the linkage of the two metal ions in the composite. Further, the decomposition of the metal composite resulted in the formation of NiCo₂O₄ as the end product. Epoxy-ligand/NiCo₂O₄ was examined for its anticorrosive property using mild steel in three different types of acids including HCl, H₂SO₄, and H₃PO₄ at different concentrations. Langmuir adsorption isotherm evidenced the excellent link between epoxy-NiCo₂O₄ and the exterior surface of the chosen mild steel specimen with a physisorption process. The Tafel plot result confirmed the mixed-mode corrosion protection behavior. The protection efficiency showed that epoxy-NiCo₂O₄ was a better inhibitor than epoxy-L in 3M hydrochloric acid. The anti-corrosion layer formed by the inhibitors had outstanding barrier potential by hindering the exchange of H₂O, O₂, and corrosive particles. The surface morphology of NiO, CoO, and NiCo₂O₄ was investigated using SEM (50nm) and TEM (138nm) and shows noteworthy anticorrosive properties. Thus, the synthesized mixed metal complex can be utilized in numerous industries for corrosion protection, which will be beneficial for achieving sustainability.

In addition, new metal complexes with 1-naphthoic acid and guanidine were synthesized and characterized by CHNS analysis, TG-TA analysis, and P-XRD analysis. The spectral studies deliberate the coordination of ligands with metal ions through oxygen and nitrogen. The formation of nanoparticles was confirmed by the stretching frequency of M-O. Electronic spectral complexes revealed that all the complexes possess octahedral geometry. The optical band gap (E_g) values for metal complexes were found to be 3.2-4.6 eV. The average crystalline sizes were found to be in the range of 29-36 nm. Cu (II) metal complexes illustrate better antimicrobial activity against *Escherichia coli* than the other microbes and show more antioxidant activity. The application towards metal complexes as an electrocatalyst with high activity in HER. The final product formed from thermal degradation was metal oxides. The redox nature of the electrocatalysts ranged from -0.15 to +2.0 V vs. RHE. It exhibits a reversible oxidation–reduction peak. Cu (II) LSV produces 98 mV and current density -3.0 V vs. RHE, respectively. The DFT data exposes an apparent synergistic effect on the compound, creating activated complexes and promoting electron allocation in hydrogen evolution. Furthermore, the metal oxide prepared from complexes

was found to be an efficient inhibitor for the treatment of wastewater effluents from industries. Further, in this study, a series of NiO, MnO, and Ni-MnO₃ oxides was confirmed by the stretching frequency of M-O. The optical band gap (E_g) values for the nano metal oxides of NiO, MnO, and NiMnO₃ range from 0.1-2.30 eV. The theoretical DFT band gap energy was correlated with the UV band gap energy value. XRD patterns of metal oxide were matched well with the JCPDS and DFT structural framework thereby substantiating nano metal oxide formation. Environmental application of synthesized metal oxides has been remarkably registered as pronounced sorbents for sequestering the toxic Pb(II) ions from aqueous media by Batch mode registered 97% sequestering ability. Further extension through upscaling the lab result to field samples to Batch (96%) and column method (98%), prove the promising sorption nature of the mixed metal oxides.

A series of novel $[M(C_2H_7N_4O_3)_2\{C_{10}H_7(COO)\}_2 \cdot 2H_2O]$ complexes with naphthoic acid and aminoguanidine have been synthesized, and characterized. FT-IR confirms the presence of functional groups and monodentate linkage of the ligands. P-X-ray diffraction was well-defined, and sharp peaks indicate the crystalline nature of the complexes. UV-visible spectra indicate the $\pi-\pi^*$ and the $n-\pi^*$ transition at a longer wavelength and authenticate the presence of distorted octahedral geometry around the metal ion. TG-DTA confirms the thermal stability and shows dehydration and decomposition are the major mechanistic processes. The final decomposition was concerned as metal oxides arise from the 500° C – 800 °. Antimicrobial activity shows good inhibition for the Zn (II) complex. The metal complexes are found to be promising aspirants as phosphorescent materials for OLED applications. In photoluminescence spectra, cobalt moiety shows enhanced spectra due to the MLCT process. The decay lifetime was in the range of 525 μ s which establishes the luminescence character of the title compound. In correlated color temperature, the Cu(II) complex shows positive values with bluish green tinge while others have negative values with a slightly pinkish shade. The tolerance level of Cu (II) ion is much greater than white light compared with American National Standards Institute standard values. The color rendering index and TLCI for the copper complex are high with a 90 %CRI value, proving this complex's promising application in workplace lighting and television. The photometric properties of synthesized complexes have been examined in a substantial range owing to their thermal stability, cost-effective synthetic procedure, and progressive applications as white phosphors.

The metal oxides synthesized from complexes were characterized by FT-IR, UV-visible spectra, TG-DTA, and P-XRD. The FT-IR signifies the formation of M-O around 610-705 cm^{-1} . The optical energy was predicted from Tauc's plot and the energy gap was estimated as 2.9 eV for NiO and 3.2 eV for CoO. Powder-XRD observes the phase structure and purity of the metal oxide. There are no additional peaks that denote the high degrees of phase purity. The average crystallization size is 10 nm. In TG-DTA the initial loss was found between 200-400 ° C, due to the removal of water. DTA curve signifies an exothermic peak around 392-406° C due to the formation of pure NiO and CoO. FESEM resembled a flower-like structure and elemental mapping proves the dispersal between nickel, cobalt, and oxide. The corrosion resistance of metal oxide was studied in bore water, and soil. Based on the result epoxy-CoO shows good anticorrosive properties than epoxy-NiO due to the hydrophobicity on the metal substrate whereas epoxy-blank exhibits poor protection due to the diffusion pathway in the corrosive metal substrate.

Finally, we examine the complexing ability of a series of divalent metal ions like Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} in terms of synthesis and characterization with 1- naphthoic acid and guanidine in a methanolic medium. The prepared complexes were characterized by element analysis, FTIR, electronic spectra, thermal analysis, and PXRD. The complexes reveal good antimicrobial and antioxidant activity against Zn (II) ions. The photometric properties of the complexes were studied by PL analysis. The cobalt shows a high excitation peak comparable with the other two compounds due to metal-to-ligand charge transfer. The fluorescence lifetime can be calculated from the metal complexes is 441,530 μs and 450 μs in which R^2 values were calculated. The CIE value was closely related to the NTSC of standard which results in the blue phosphors emitted which gather in the near Understanding *Ultraviolet LED*-based White-LEDs. The metal complex's Duv values occur around -0.0049 to -0.175 in which the negative Duv value is closely related to the white light emission. Ni (II) complexes in $\text{TLCI}=100$ which requires the light source observed in television as the Co (II) and Cu (II) produce $\text{TLCI}=1$ they are not suitable for applications in the broadcast area. ΔE^* value always produces the positive it understood they are considered in commercial production. The evidence established the newly exposed efficient metal complexes show have great application towards the blue-light-excited w-LEDs found to be suitable phosphors for

OLED. To study the corrosion behavior, the nanometal and mixed metal oxide namely CeMnO_3 , CeO , and MnO was synthesized and coated with epoxy resin on the steel substrate. The structural parameters and surface morphology were determined from XRD, SEM, and TEM analysis. We have successfully analyzed the anti-corrosion behavior of epoxy- $\text{CeMnO}_3/\text{CeO}_2/\text{Mn}_3\text{O}_4$ in different mediums like salt spray and marine water. The encapsulated nanocomposite material prevents the steel plate for 120 days by forming an insoluble protective layer. In electrochemical corrosion studies, CeMnO_3 possesses a higher E_{corr} value demonstrating its enhanced protection ability. CeO_2 shows minimum anti-corrosion behavior due to higher affinity and lower diffusivity of trivalent ion than divalent manganese oxide. Thus, effectiveness in mitigating membrane degradation will be poor in cerium oxide, so this can be concluded that all the synthesized epoxy metal oxides have suitable barrier properties against corrosive environments.

Future prospects

Many guanidine/aminoguanidine naphthoate systems, are only microcrystalline solids. Single crystals may be formed by modifying the method of preparation. Hydrothermal synthesis is suggested for the preparation of single crystals to confirm their structures. Further, this method may be useful in preparing the complexes of naphthoate with lanthanides series which could be prepared by the solution method. Electrochemical synthesis can also be attempted to prepare the complexes. Photocatalytic and biomedical applications of the synthesized metal oxides will be studied. Progressing efficient and low-cost catalysts to reduce overpotential within the hydrogen evolution reaction (HER) in large-scale production is highly desirable in the present era. The catalysts are accustomed to initiating an excellent approach to optimizing the electronic characteristics employed to boost their electrocatalytic production. Based on the results, we can design and fabricate more electrocatalysts as prospective candidates for hydrogen evolution reactions.