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Trace electrochemical detection of Ni^{2+} ions with bidentate N, N'-

(ethane-1,2-diyl)bis(3,4-dimethoxybenzenesulfonamide)

[EDBDMBS] as a chelating agent

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Abstract:

The heavy metals are naturally occurring elements and becoming the main source of pollution in our eco-environment due to their commercial applications. So, for the probe of heavy metal cations, bidentate chelating agents N,N-(ethane-1,2-diyl)bis(4-methoxybenzene sulfonamide) [EDBMBS] and *N*,*N*-(ethane-1,2-diyl)bis(3,4-dimethoxybenzenesulfonamide) [EDBDMBS] were synthesized in this study. These chelating agents were characterized by UV/Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (¹H-NMR & ¹³C-NMR), in addition to single crystal x-ray diffraction and x-ray photoelectron spectroscopy (XPS) analysis. After the characterization, I-V technique was executed using electrometer to check the affinity of our synthesized chelating agents against the wide range of heavy metal cations $(Ag^+, Al^{3+}, Au^{3+}, Ba^{2+}, Ce^{4+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+} \& Y^{3+})$. It was found that it has selective affinity with Nickel (Ni²⁺) cations. Ni²⁺ is one of the most toxic heavy metal presents in the environmental contaminants. EDBMBS and EDBDMBS onto flatglassy carbon electrode were fabricated with conducting coating agents to fabricate a sensitive and selective Ni²⁺ ions sensor in short response time in phosphate buffer phase. The comparative study of EDBMBS/Nafion/GCE and EDBDMBS/Nafion/GCE was performed and found that fabricated EDBDMBS/Nafion/GCE cationic-sensor exhibited higher sensitivity, large-dynamic concentration ranges, long-term stability, and improved electrochemical performances towards nickel ions. The calibration plot is linear ($r^2 = 0.9929$) over the large Ni²⁺ concentration ranges (1.0 nM to 1.0 mM). The sensitivity and detection limit is $\sim 2.3417 \text{ }\mu\text{A.}\mu\text{M.}\text{cm}^{-2}$ and $\sim 0.78 \text{ }n\text{M}$ (signal-to-noise ratio, at a SNR of 3) respectively. This novel effort initiated a well-organize way of efficient cationic sensor development with nafion conducting binder deposited on GCE for toxic pollutants in environmental and health-care fields in large scales. Therefore, the proposed EDBDMBS/Nafion/GCE offers a cost-effective compound that can be considered as a viable alternative for effectively detecting and removing toxic Ni²⁺ from water samples.

Key words: Chelating agents; EDBMBS; EDBDMBS; Ni²⁺ ions; I-V method; Sensitivity, Environmental study

1. Introduction

Organic compounds with electron donating functional groups have impressive significance for the scientists for further studies and inventions in chemistry owing to considerable number of applications such as medicinal, biological [1], catalysis [2] and organometallic [3] chemistry. Due to the presence of electron donating functional group such types of molecules have also gained much attention in environmental chemistry [4] and used as an environmental remediation by detection, extraction and estimation of toxic metal ions [5-8]. Sulfonamides or sulfa drugs have been discovered as early as 1939 [9] and well known pharmaceutical agent because of low cost, less toxicity and effective against the bacterial disease [10]. In addition to antibacterial activity this drug also exhibit antifungal [11], anticancer, antiviral [12], anti-inflammatory [13], anticonvulsants [14], diuretic [15], HIV protease inhibitor [16] and carbonic anhydrase activities [17].

Generally, sulfonamides are synthesized by simple reactions of sulfonyl chlorides with primary amine or secondary amine [18]. This reaction is also known as Hinsberg's test for the detection of primary and secondary amine. $-SO_2NH$ - functional group in their structure make them impressive in environmental chemistry and have applications for the detection of toxic metal ions by the capability of donating the unshared pare of electrons from N-H group to metal elements. Recently, for this reason, sulfonamides and its analogue such as N,N'-(ethane-1,2-diyl)bis(2,5-dimethoxybenzenesulfonamide) (EBDMBS) and (E)-4-methyl-N0-(1-(pyridin-2-yl)ethylidene)benzenesulfonohydrazide (MPEBSH) have been used for the detection of Co(II) and Cd(II) in aqueous solution, respectively. [19, 20]. Likewise, N'-[1-(Pyridin-2-yl)ethylidene]benzenesulfonohydrazide (PEBSH) and (E)-N'- Nitrobenzylidene-Benzenesulfonohydrazide (NBBSH) have been reported for Hg(II) [21, 22]. As well as, N, N'-

ethylenebis (ethane sulfonamide) has been employed for the removal of Ni(II), Fe(VI) and Cr(II) in aqueous solution by ICP-OES [23]. Heterocyclic sulfonamides such as sulfadiazine, sulfamerazine, sulfapyridine, sulfisoxazole and many others have been used to make complex with Cu(II) [24]. Acetazolamide and its analog have been used for the probe of Cu(II) and form the dimer complexes [25]. Acetazolamide has also been employed for the determination of Zn(II), Cu(II), Ni(II) and Co(II) by potentiometry both in water system [26]. So, keeping in view the environmental applications of sulfonamides, the plan of the study was to develop the ion selective electrode for the probe of toxic metal ions based on bis-sulfonamide as a bidentate chelating agent. 1,2-diaminoethane & its derivatives act as bidentate ligands and has been used in the formation of many metal complexes [23, 27, 28]. Bis-sulfonamides were synthesized by the reaction of 1,2-diaminoethane with aryl sulfonyl chlorides at 1:2 mole ratio respectively in water, Scheme 1. 4-methoxy benzenesulphonyl chloride is selected to synthesize the bis-sulfonamide and has been reported as an antimicrobial agent [29]. In this work, comparative study of bissulfonamide of 4-methoxy benzenesulfonyl chloride with its analogue was done in terms of sensing the toxic metal ions quantitatively & qualitatively. Both molecules are new in term of crystal structures.

Nickel, one of the most well-known heavy transition metal that existed extensively in different food stuffs of both animal and vegetable origins, is essential for carrying out a number of necessary functions in industrial and healthcare applications [30, 31]. It also constitutes significant constituent to uphold selective and specific activity of numerous enzymes involved in carbohydrate, amino acid as well as lipid metabolism of both bacterium and higher organisms [32]. Nickel ions at low concentrations offer essential trace nutrients, but would exhibit toxic effects under overloading conditions. Nickel,

mostly at higher doses, would result in geno-toxic and mutagenic activity, and its genotoxicity may be aggravated through the generation of DNA-damaging reactive oxygen species (ROS) and the inhibition of DNA repair [33]. Accumulating confirmations recommend that Ni²⁺ is a toxic and carcinogenic element closely linked to several diseases including cancer of nasal lungs, dermatitis, asthma, and disorders of the respiratory and central nervous systems [34, 35]. Therefore, the International Agency for Research on Cancer (IARC) classified nickel compounds as group 1 carcinogenic to humans in 1990 [36], and the American Environmental Protection Agency (EPA) set the maximum contaminant level goal (MCLG) for Ni²⁺ in drinking water to be 0.07 mg/L while the safe-exposure standard for drinking water was set as 20.0 ng/mL by the World Health Organization (WHO) [37].

The identification and measurement of nickel at low concentrations thus became increasingly important [38]. Recently, determination of Ni²⁺ ions can be realized by a number of conventional methods including gravimetry with dimethylglyoxime, voltametric, capillary electrophoresis, and spectrophotometric techniques like flame and graphite furnace atomic absorption spectrophotometry, flow injection spectrophotometry, ICP-AES and flame photometry [39]. However, requirement for complicated sample pretreatment and infrastructure backup greatly limited their application for routine analysis of myriad environmental samples [40]. In view of those problems, the sensory techniques offered an important alternative to meet the drawbacks confronting the large-equipment-dependent detecting methods, and have been extensively applied for reliable and expedient measurement of heavy metal ions [41, 42]. The colorimetric methods, in particular, stand out extremely attractive since they can be easily read out with low-cost and economical portable instruments and even naked eyes. As for nickel

detection, a majority of the sensors depend on electrochemical measurement using dyeencapsulated membranes [43, 44], screen-printed electrodes [45], and adsorptive stripping voltammetry [46]. To date, only limited number of chemosensors have been published to detect nickel ions through indirect or direct colorimetric analysis [47, 48]. Most of those studies involved time-consuming procedures to synthesize and purify specific ionophores, which unavoidably complicates the fabrication and increases cost. And even so, only limited performance has been realized in view of selectivity, sensitivity and stability. Here, we describe a facile, reliable and low-cost electrochemical sensor for trace nickel detection based on the N,N-(ethane-1,2-divl)bis(3,4-dimethoxybenzenesulfonamide) methoxy bi-functional [EDBDMBS]. It is an excellent cationic sensing application to confirm the electrical sensing properties with lab-made bidentate EDBMBS or EDBDMBS compounds. EDBDMBS permits very sensitive transduction of the liquid/surface interactions into modify in the chemical properties. The significant prospect is to appearance a variety of active functional group offers different vision of modification of the toxic nickel ions sensing possessions. EDBDMBS has been used to fabricate a simple and efficient Ni²⁺ sensor and assessed the chemical sensing performance selectively considering nickel ions at room conditions. To the best of our knowledge, this is the first report for detection of Ni²⁺ with EDBDMBS using simple, convenient, and reliable *I-V* technique in short response time.



Scheme 1: Synthesis of chelating agents (EDBDMBS/EDBMBS)

2. Experimental Section

2.1. Materials and Methods

benzenesulphonyl chloride (DMBSC) 3,4-Dimethoxy and 4-methoxy benzenesulphonyl chloride (MBSC) were obtained from Aldrich, USA. 1.2-diaminothane acquired from BDH, Poole, England. Analytical grade solvents (Acetone and Ethanol) were also taken BDH, Poole, England. 5 % Nafion, disodium phosphate, monosodium phosphate, silver nitrate, aluminum chloride, gold chloride, barium sulphate, cerium chloride, cobalt nitrate, nickel nitrate, lead chloride, stannous chloride and yttrium nitrate were purchased from sigma-Aldrich. All these chemicals were used without any further purification. A Stuart Scientific SMP3, version 5.0 melting point apparatus (Bibby Scientific Limited, Staffordshire, UK) was used to record the melting points, and the reported melting points are uncorrected. ¹H-NMR spectra were recorded on an AVANCE-III 600 MHz & 800 MHz instrument (Bruker, Fallanden, Switzerland) at 300 K, and chemical shifts are reported in ppm with reference to the residual solvent signal. FT-IR spectra were recorded as neat on a Thermo Scientific NICOLET iS50 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA). UV-vis. studies were performed by using Evolution 300UV/VIS spectrophotometer (Thermo Scientific). XPS experiment was conducted for the determination of binding energies (eV) of each elements existed in EDBDMBS especially N, O, C element by a K-al spectrometer Thermo scientific $-\alpha 1$ with an e citation rai ation sorce 1 $1 \alpha 1$ e am spot si e m pass 10^{-8} torr). I-V technique was executed by using energ press re e

Electrometer (Kethley, 6517A, Electrometer, USA) for measuring the current responses in two electrode systems for target Ni²⁺ cations based on EDBDMBS in buffer phase at room conditions, where GCE and Pd-wire was used as working and counter electrode respectively.

2.2. General method for the synthesis of 3a & 3b

N,*N*-(ethane-1,2-diyl)bis(4-methoxybenzenesulfonamide) [EDBMBS] (**3a**) and *N*,*N*-(ethane-1,2-diyl)bis(3,4-dimethoxybenzenesulfonamide)[EDBDMBS] (**3b**) were synthesized following literature method [49]. A mixture of 1, 2-diaminoethane and aryl sulfonyl chlorides: {4-methoxy benzene sulfonyl chloride (2a) and 3, 4-dimethoxy benzene sulfonyl chloride (2b)} (at 1:2 mole ratio) in 15 mL of water stirred at room temperature in reaction flask. The progress of reaction mixture was monitored by examining the pH of medium, with equal intervals of times, which kept constant at 8-9 with occasional addition of 1 *N* sodium carbonate. The products (**3a**) & (**3b**) were precipitate out on completion of the reaction which was confirmed by TLC. The precipitates were filtered, washed with plenty of distilled water and dry at room temperature.

2.3. N, N'-(ethane-1,2-diyl)bis(4-methoxybenzenesulfonamide)(3a)

Molecular weight: 400.47 g, Yield 83.79 %; m.p. 153 °C; ¹H-NMR: (850 MHz)(CDCl₃) δ :7.758 (4H, d, 2 x Ar-H, J = 8.5), 6.968 (4H, d, 2 x Ar-H, J = 9.35) 4.940 (2H, s, 2 x -NH-), 3.870 (6H, s, 2 x -OCH₃), 3.046 (4H, s, 2 x -CH₂-); ¹³C-NMR: (850MHz) (CDCl₃) δ : 163.12, 130.89, 129.27, 114.43, 55.67, 42.93; IR (neat) ν_{max} : 3290, 3110, 2979, 2945, 2905, 2844, 1600, 1593, 1497, 1461, 1336, 1262, 1155, 1022, 831, 671 cm⁻¹; λ_{max} : 248 nm

2.4. *N*, *N*'-(ethane-1,2-diyl)bis(3,4-dimethoxybenzenesulfonamide) (3b)

Molecular weight: 460.52176 g, Yield 89.57 %; m.p. 187-189 °C; ¹H-NMR: (600 MHz)(CDCl₃) δ : 7.434 (2H, dd, 2 x Ar-H, J = 2.4, 8.4), 7.296 (2H, d, 2 x Ar-H, J = 1.8),

6.923 (2H, d, 2 x Ar-H, J = 9), 3.939 (6H, s, 2 x –OCH₃), 3.928 (6H, s, 2 x –OCH₃), 3.064 (4H, s, 2 x -CH₂-); ¹³C-NMR: (600MHz) (CDCl₃) δ : 152.85, 149.37, 130.92, 121.11, 110.63, 109.55, 56.31, 56.23, 43.00; IR (neat) ν_{max} : 3245, 3085, 2967, 2938, 2875, 2845, 1592, 1510, 1469, 1442, 1329, 1262, 1237, 1159, 1021, 720 cm⁻¹; λ_{max} : 248 nm, 283 nm

2.5. Fabrication of Ni²⁺ sensor with EDBDMBS/GCE

Phosphate buffer solution (PBS, 0.1 M, pH 7.0) is prepared by mixing 0.2 M Na₂HPO₄ and 0.2 M NaH₂PO₄ solution in 100.0 mL de-ionize water. GCE is made by EDBDMBS with 5 % ethanolic nafion solution as a conducting agent. Subsequently it is moved into the air at room condition for 12 hours until the film is completely uniform, stable, and dry. A chemical cell is mounted with EDBDMBS coated GCE as a working electrode and Pd wire is used as a counter electrode. Nickel solution (0.1 M) is diluted at different concentrations in DI water and used as a target chemical. Amount of 0.1 M PBS (pH 7.0) is kept constant in the small-beaker as 5.0 mL throughout the chemical analysis. Analyte solution is prepared with different concentrations of cadmium from 1.0 nM to 0.1 M. The sensitivity is calculated from the slope of current versus concentration from the calibration plot by considering the active surface area of nickel cationic sensors. Keithley electrometer is used as a voltage sources for *I-V* method in two electrodes system.

2.6. Crystallography

The two new sulfonamide molecules were crystallized. The Molecule **3a** was crystalized in ethyl-acetate under slow evaporation and crystal seeding techniques while molecule **3b** was crystalized in acetone-ethanol (20: 80) under slow evaporation process. Both of the samples were checked under microscope and screened out to collect data for structural characterization. The

selected samples were glued over glass needle fixed on a copper rod with magnetic base. The whole sample assembly was mounted on Agilent SuperNova (Dual source) Agilent Technologies Diffractometer, equipped with microfoc s C/Mo α ratiation for a ta collection. Mo α radiations were used for these samples. The data collection was accomplished using CrysAlisPro software [50] at 9 n e r the C α ratiation. The strict re solition was performe sing SHELXS–97 method [51] and refined by full–matrix least–squares methods on F^2 using SHELXL–97 method [51], in-built with WinGX [52]. All non–hydrogen atoms were refined anisotropically by full–matrix least squares methods [51]. The Figures were generated through PLATON [53] and *ORTEP* [54] in built with WinGX [52].

All the aromatic C-H hydrogen atoms were positioned geometrically and treated as riding atoms with C–H = 0.93 Å and Uiso(H) = 1.2 Ueq(C) carbon atoms. Similarly, the methyl and methylene hydrogen atoms were also positioned geometrically with C_{methyl} -H = 0.96 Å Uiso(H) =1.5 Ueq(C) and $C_{methylene}$ -H = 0.97 Å Uiso(H) = 1.5 Ueq(C). The N-H hydrogen atoms were located through fourier map and refined with N-H = 0.85(1) Å in molecule **3b** and with N-H = 0.84(1)-0.85(1) Å in molecule **3a**. *Uiso* (H) was set to 1.2Ueq for N atoms in both molecules. The Crystal data were deposited at the Cambridge Crystallographic Data Centre and following deposition numbers have been assigned 1520938 and 1520939 which are known as CCDC number for molecules I and II respectively. Crystal data can be received free of charge on application to CCDC 12 Union Road, Cambridge CB21 EZ, UK. (Fax: (+44) 1223 336-033; email: data_request@ccdc.cam. ac.uk).

3. Results and Discussion

3.1. Nuclear Magnetic Resonance (¹H-NMR &¹³C-NMR) chracterization of *N*,*N*'-(ethane-1,2-diyl)bis(4-methoxybenzenesulfonamide) or 3a:

The desired amino ligand 3a for the sensing of heavy metal was synthesized by simple reaction of 1, 2-diaminoethane (0.081 ml, 0.00122 mol) with 4-methoxy benzene sulfonyl chloride (0.5042 g, 0.00244 mole) in water. HCl was produced during the progress of the reaction as a byproduct, which shifts the pH of the reaction from basic to acidic. The HCl was neutralized by the addition of 1 *N* sodium carbonate and solution pH was maintained about 8 to 9. Precipitates of the product were obtained at the end of the reaction which was confirmed by TLC. It was filtered and recrystallized from ethylacetate by seeding method.

In addition to different spectroscopic techniques, single crystal X-ray diffraction studies were also carried out in order to assure and elucidate the structure of our target ligand. The spectra of ¹H-NMR and ¹³C-NMR are shown in Figs. S1 & S2. The six protons of two methoxy (-OCH₃) groups attached to two aromatic rings at *para* position gave one singlets at δ 3,870 ppm. One singlet belongs to four protons of two methylene (-CH₂-) group was observed at δ 3.046 ppm. The two aromatic rings accompanied total eight aromatic protons at *-ortho* and *-meta* position. These eight aromatic protons gave the two doublets at δ 7.758 and 6.968 ppm with coupling constant J = 8.5 & 9.35 respectively, four each, it reveals that two aromatic protons in each ring are of same nature. The two protons of two –NH- groups adjacent to methylene/sulfonyl group were appeared as singlet at δ 4.94 ppm. All this discussion explains the center of symmetry of molecules, Fig. 1a, but x-ray diffraction is against it, Fig. 2.

Similarly, for further confirmation of target ligand ¹³C-NMR spectrum was also collected to observe the number of carbon atoms. The two peaks were appeared at δ 42.93 & 55.67 ppm which belong to two carbon atoms of methylene group attached to amine group & two methoxy carbon atoms attached to aromatic ring respectively. The aromatic C-atoms were appeared in aromatic region with the range values from δ 114.43 to 163.12 ppm.

3.2. ¹H-NMR &¹³C-NMR characterization of *N*,*N*'-(ethane-1,2-diyl)bis(3,4dimethoxybenzenesulfonamide) or 3b:

Same method was adopted, as stipulated above in the discussion of 3a, to synthesize the second 3b molecule using 1, 2-diaminoethane (0.071 ml, 0.001056 mol) with 3,4-dimethoxy benzene sulfonyl chloride (0.500 g, 0.002112 mol) in water. The product was recrystallized from acetone-ethanol (20:80) to carry out single crystal X-ray diffraction studies. The ¹H-NMR and ¹³C-NMR spectra are also shown in Figs. S3 & S4.

The twelve protons of two methoxy groups at *-meta* & *-para* position gave two singlets at δ 3.939 and 3.928 ppm respectively, six each. The one more singlet belong to four protons of two methylene group was also observed at δ 3.064 ppm, which elucidate its center of symmetry (both halves are identical), Fig. 1b. The single crystal X-Ray diffraction also favors the center of symmetry in this molecule, Fig. 3. The six protons in two aromatic rings were of different nature because of substitution of methoxy at *-meta* position. The four protons out of six, two each from two aromatic rings, at position 2 and 5 appeared as doublet at δ 7.296 and 6.923 ppm with coupling constant J = 1.8 & 9 respectively. The remaining two protons at position 6 emerged as doublet of doublet at δ 7.434 ppm with coupling constant J = 2.4 & 8.4, it reveals that these protons have *-ortho*

and *-meta* effect. The protons of –NH- group disappeared in the spectrum but we observed both protons in single crystal determination.

¹³C-NMR spectrum also satisfied the no. of carbon atoms in target ligand **3b**. The four methoxy carbon atoms were appeared at δ 56.31 and 56.23 ppm. The two carbon atoms of methylene group attached to amine observed at δ 43.00 ppm. The aromatic C-atoms peaks s fr were came into view in aromatic region with the range values from δ 109.55 to 152.85



Fig. 1. (a) ¹H-NMR & ¹³C-NMR of EDBMBS (b) ¹H-NMR & ¹³C-NMR of EDBDMBS

3.3. Comparative Optical absorption characteristic (FTIR, UV/VIS) of 3a & 3b:

Optical absorption spectroscopy provides the simple information about the functional group (in FTIR spectroscopy) and conjugation (in UV/VIS spectroscopy) whether it is present or not in organic compounds.

So, FTIR analyses were also performed in order to confirm the functional group for both molecules **3a** & **3b** and spectra are shown in Figs. S5 & S6.

The N-H stretching peaks of **3a** and **3b** were appeared at **3**290 and **3**245 cm⁻¹ respectively. The N-H bending and wagging in **3a** were appeared at 1593 & 671 cm⁻¹ respectively and in **3b** these were observed at 1592 & 720 cm⁻¹. The C-N stretching vibrations were appeared at 1262 and 1022-1021 cm⁻¹ in both molecules. A C-C-N bending in **3b** was also come out at 1237 cm⁻¹. Asymmetric & symmetric stretching vibrations of S=O in **3a** were appeared at 1336 cm⁻¹ and 1155 cm⁻¹ respectively while in **3b** it seemed at 1329 cm⁻¹ and 1159 cm⁻¹ with strong intensity. Asymmetric and symmetric stretching peaks for aliphatic C-H for both molecules come into view in the range of 2844-2979 cm⁻¹. The C-H asymmetric bending of $-OCH_3$ in **3a** at 3110 and in **3b** at 3085 cm⁻¹ were belonged to aromatic C-H stretching. Aromatic C=C stretching were also observed for both molecules in the range of 1442-1600 cm⁻¹. In **3a** C-H bending of *para* substituent benzene appeared at 831 cm⁻¹.

For quantitative UV/VIS spectroscopy, the solutions of 6.24 x 10^{-5} mol/L & 1.08 x 10^{-4} mol/L concentration were prepared for both molecules in chloroform and spectra were recorded on UV/VIS spectrophotometer at room temperature in the range of 200-600 nm. The λ_{max} is 248 nm, for molecule **3a** and Fig. S7. For **3b**, the λ_{max} observed are 248 nm

and 283 nm, Fig. S8. The concentrations, intensities and observed λ_{max} describe that there are π - π * transition in both of molec l es.

3.4. Crystal Structure Description:

Both of these molecules were crystalized in monoclinic crystal system with P21/n and P21/a space groups for 3a and 3b respectively, Figs. 2 & 3, Tables 1, S1 & S2. Molecule 3b has center of symmetry in it. The geometry around the S atoms in both molecules is distorted tetrahedral with $<O1-S1-O2 = 119.41(8)^{\circ}$ in molecule **3b** while $<O1-S1-O2 = 119.60(9)^{\circ}$ and <O4-S1-O5 = 119.75(9)°in molecule **3a** and this is typical behavior of sulfonamide family [55-58] The molecule **3b** has center of symmetry so the planes generated through the fitted atoms of aromatic rings are parallel to each other while the dihedral angle between the two aromatic rings in molecule 3a is 14.39(2)°. Symmetry related N-H...O h rogen boning connects the molecules to form an infinite chain along b axes in compound **3b**. The similar interaction in compound **3a** connects the molecule along a axes to form an infinite long chain in its crystal structure. This interaction in both compounds generates eight membered ring motifs, which can be represented mathematically as R_2^2 (8) [59]. In molecule **3b**, the C-H...O t pe week interaction connects the long chains to produce another infinite chain which goes diagonally along ac plane. In molecule 3a the C-H...O interaction connects the molecule to form two-dimensional framework Table 2 Figs. S9-S11. Overall these interactions give rise to formation of supramolecular systems of these ligands.



Fig. 2: *ORTEP* diagram of molecule **3a** with appropriate labels. Thermal ellipsoids were drawn at 50% probability level.



Fig. 3: *ORTEP* diagram of molecule **3b** with appropriate labels. Thermal ellipsoids were drawn at 50% probability level.

| Identification code | 3a | 3b |
|---|--|--|
| Empirical formula | $C_{16}H_{20}N_2O_6S_2$ | $C_{18}H_{24}N_2O_8S_2$ |
| Formula weight | 400.46 | 460.51 |
| Temperature/K | 296(2) | 296(2) |
| Crystal system | Monoclinic | monoclinic |
| Space group | $P2_1/n$ | P21/a |
| a/Å | 8.0846(4) | 10.1861(5) |
| b/Å | 11.0075(4) | 7.6337(3) |
| c/Å | 20.2421(7) | 14.2058(6) |
| α/° | 90 | 90 |
| β/° | 100.825(4) | 104.403(4) |
| γ/° | 90 | 90 |
| Volume/Å ³ | 1769.31(13) | 1069.89(8) |
| Z | 4 | 2 |
| $\rho_{calc} mg/mm^3$ | 1.503 | 1.429 |
| μ/mm^{-1} | 0.338 | 0.296 |
| F(000) | 840.0 | 484.0 |
| Crystal size/mm ³ | $0.33 \times 0.26 \times 0.06$ | $0.32 \times 0.16 \times 0.07$ |
| θ range for a ta collection | 5.872 to 58.812° | 5.922 to 59.08° |
| Index ranges | $\textbf{-9} \leq \textbf{h} \leq 11 \ \textbf{-8} \leq \textbf{k} \leq 14 \ \textbf{-} \leq 1 \leq 7$ | $\begin{array}{ll} \text{-1} \leq h \leq 1 & \text{-1} \leq k \leq 9 & \text{-19} \leq \\ 1 \leq 15 \end{array}$ |
| Reflections collected | 10717 | 6027 |
| Independent reflections | 4271[R(int) = 0.0233] | 2608[R(int) = 0.0202] |
| Data/restraints/parameters | 4271/2/243 | 2608/0/142 |
| Goodness-of-fit on F ² | 1.034 | 1.058 |
| Final R in e es [I> σ I] | $R_1 = 0.0409, wR_2 = 0.0940$ | R1 = 0.0386, wR2 = 0.0906 |
| Final R indexes [all data] | $R_1 = 0.0545, wR_2 = 0.1029$ | R1 = 0.0502, wR2 = 0.0988 |
| Largest diff. peak/hole / e Å ⁻³ | 0.33/-0.39 | 0.30/-0.33 |

Table 1. Crystal data and structure refinement for 3a and 3b

Table 2

| Mo | lecule | 3a | | | | |
|------------------|----------|-----------------------|--|-----------|----------|---------|
| D | Н | А | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
| C5 | H5A | O4 ¹ | 0.93 | 2.58 | 3.450(2) | 156.0 |
| N1 | H1N | $O4^2$ | 0.847(10) | 2.137(13) | 2.957(2) | 163(3) |
| N2 | H2N | O1 ³ | 0.853(10) | 2.211(13) | 3.026(2) | 160(3) |
| ¹ 3/2 | 2-X,-1/2 | 2+Y,1/2 | -Z; ² -1+X,+Y,+Z; ³ 1+X,+Y | Y,+Z | 9 | |
| Mo | lecule | 3b | | | | |
| D | Н | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
| С9 | H9B | O3 ¹ | 0.96 | 2.51 | 3.464(3) | 176.0 |
| N1 | H1 | $O1^2$ | 0.83(2) | 2.20(2) | 2.992(2) | 158(2) |
| ¹ 2-2 | X,-Y,2- | -Z; ² 1-X, | ,-Y,1-Z | | | |

Hydrogen Bonds for Molecule 3a and 3b

4. Application: Detection of Ni²⁺ ions with EDBDMBS/GCE:

The significant application of EDBDMBS assembled onto GCE as cationic sensors (especially Ni²⁺ ions analyte in buffer system) has been executed for measuring and detecting target chemical in aqueous solution. Enhancement of the EDBDMBS/GCE as cationic sensors is in the initial stage and no other reports are available. The EDBDMBS/GCE sensors have advantages such as stability in air, non-toxicity, chemical inertness, electro-chemical activity, simplicity to assemble, ease in fabrication, and chemo-safe characteristics. As in the case of Ni²⁺ cations sensors, the incident of rationale

is that the current response in *I-V* method of EDBDMBS/GCE considerably changes when aqueous Ni^{2+} analytes are adsorbed. The EDBDMBS/GCE was applied for fabrication of cationic-sensor, where Ni^{2+} ions were measured as target analyte. The fabricated-surface of EDBDMBS sensor was prepared with conducting binders (5 % Nafion) on the GCE surface. The fabricated GCE electrode was put into the oven at low temperature (35.0 °C) for 2.0 hour to make it dry, stable, and uniform the surface totally. The EDBDMBS was employed for the detection of Ni^{2+} ions in liquid phase. *I-V* responses were measured with EDBDMBS coated thin-film (in two electrodes system). In experimental section, it was already outlined the Ni^{2+} ions sensing protocol using the EDBDMBS/GCE modified electrode. The concentration of Ni^{2+} ions was varied from 1.0 nM to 0.1 M by adding de-ionized water at different proportions.

Here, Fig. 4(a) is represented the *I-V* responses for uncoated-GCE (grey-dotted) and EDBDMBS/GCE (red-dotted) electrodes. In PBS system, the EDBDMBS/GCE electrode shows that the reaction is slightly increased owing to the presence of EDBDMBS on bare-GCE surface. A considerable enhancement of current value with applied potential is demonstrated with fabricated EDBDMBS/GCE in presence of target Ni²⁺ ions analyte, which is presented in Fig. 4(b). The blue-dotted and green-dotted curves were indicated the response of the fabricated film before and after injecting 25.0 μ L Ni²⁺ solution in 5.0 mL PBS solution respectively. Significant increases of current are measured after injection of target component in regular interval. *I-V* responses to varying Ni²⁺ ions concentration on thin EDBDMBS/GCE were investigated (time delaying, 1.0 sec; response time, 10 sec) and presented in the Fig. 4(c). Analytical parameters (such as sensitivity, detection limit, linearity, and linear dynamic range etc) were calculated from

the calibration curve (current vs. concentration), which was presented in Fig. 4(d). A wide range of Ni²⁺ ions concentration was selected to study the possible detection limit (from calibration curve), which was examined in 1.0 nM to 0.1 M. The sensitivity was calculated from the calibration curve, which was close to ~2.3417 μ A. μ M⁻¹.cm⁻². The linear dynamic range (calculated from the Fig. 4(e) of the EDBDMBS/GCE sensor was employed from 1.0 nM to 1.0 mM (linearly, r²: 0.9929), where the detection limit was calculated about 0.78 nM (ratio, ^{3N}/_S). The EDBDMBS/GCE was exhibited higher current response, where the electrical resistance decreases under the presence of target Ni²⁺ ions in PBS phase. The film resistance was decreased gradually (increasing the resultant current) upon increasing the Ni²⁺ ions concentration in bulk system.



Fig. 4: Control experiment and optimization of sensor. I-V responses of (a) GCE (without EDBDMBS) and EDBDMBS/GCE (with EDBDMBS); (b) EDBDMBS/GCE (in absence of Ni^{2+} ions) and Ni^{2+} ions/ EDBDMBS/GCE (in presence of Ni^{2+} ions); (c) concentration variations (1.0 nM to 0.1 M) of Ni^{2+} ions, (d) calibration plot of EDBDMBS fabricated GCE (at +1.0 V).

Interference (for selectivity) was studied for Ni²⁺ ions sensor in the presence of other chemicals like Ag⁺, Al³⁺, Au³⁺, Ba²⁺, Ce⁴⁺, Co²⁺, Pb²⁺, Sn²⁺, and Y³⁺ using the EDBDMBS embedded on flat GCE (Fig. 5a). The concentrations of all analytes were kept constant at 0.1 μ M level in PBS system. Here, it is clearly demonstrated that EDBDMBS/GCE sensor is the most selective toward Ni²⁺ ions compared with other cations. The excellent selectivity is ascribed to

the reasons are terminal functional groups have strong and stable interaction with Ni^{2+} resulting in the increase of current response in *I-V* system. To check the reproducibly and storage stabilities, *I-V* response for EDBDMBS/GCE sensor was examined (Fig. 5b). After each experiment, the fabricated EDBDMBS/GCE substrate was washed thoroughly with the phosphate buffer solution and observed that the current response was not significantly decreased. The sensitivity was retained almost same of initial sensitivity up to few days, after that the response of the fabricated EDBDMBS/GCE electrode gradually decreased.

I-V characteristic of the EDBDMBS is activated as a function of Ni^{2+} ions concentration at room conditions, where improved current response is observed. As obtained, the current response of the EDBDMBS/GCE-film is increased (π - π * interaction) with the increasing concentration of Ni²⁺ ions (Scheme 2a), however similar phenomena for toxic chemical detection have also been reported earlier [60-63]. For a low concentration of Ni²⁺ ions in liquid medium, there is a smaller surface coverage of Ni²⁺ ions molecules on EDBDMBS/GCE film and hence the surface reaction proceeds steadily. By increasing the Ni²⁺ ions concentration, the surface reaction is increased significantly (gradually increased the response as well) owing to surface area (assembly of EDBDMBS/GCE; Scheme 2b) contacted with Ni²⁺ ions molecules. Further increase of Ni²⁺ ions concentration on EDBDMBS/GCE surface, it is exhibited a more rapid increased the current responses, due to larger area covered by Ni²⁺ ions an the π - π * interaction of the f nc tional groups of EDBDMBS and Ni²⁺. The π - π * interaction col be approaches as inter-molecular and intra-molecular interactions of the functional compound [64, 65]. Usually, the surface coverage of Ni²⁺ ions on EDBDMBS/binders/GCE surface is reached to saturation, based on the regular enhancement of current responses (Scheme 2c).



Scheme 2. Schematic diagram. Mechanism of the probable interaction of Ni²⁺ with EDBDMBS/GCE. (a) Fabricated GCE electrode b π - π interaction between Ni²⁺ ions and EDBDMBS, and (c) resultant I-V response.

The Ni²⁺ ions sensor based on EDBDMBS/GCE is also displayed good repeatability as well as reproducibility with good stability for over week and no major changes in sensor responses was found. After a week, the cationic sensor response with EDBDMBS/GCE was slowly decreased, which may be due to the weak-interaction between fabricated EDBDMBS active functional sides and Ni²⁺ ions. The significant result was achieved by EDBDMBS/GCE, which can be employed as efficient electron mediators for the development of efficient cationic sensors. Actually, the response time was around 10.0 sec for the fabricated EDBDMBS/GCE to reach the saturated steady-state level. The higher current and sensitivity of the fabricated EDBDMBS/GCE compared to EDBMBS/GCE is attributed to the excellent absorption and adsorption ability with bi-functional methoxy groups, which is presented in Fig. 5(c). Therefore, it was developed the Ni²⁺ sensor based on EDBDMBS/ACE sensor is relatively higher and detection limit is comparatively lower than previously reported Ni²⁺ sensors based on other nano-composite or materials

modified electrodes measured by *I-V* systems [66-69]. Due to EDBDMBS/binders/GCE, it provides a favorable micro-environment for the Ni²⁺ cations detection with good quantity. The high sensitivity of EDBDMBS/GCE provides high electron communication features which enhanced the direct electron transfer between the active sites of EDBDMBS and GCE. The EDBDMBS/GCE system demonstrate a simple and reliable approach for the detection of toxic chemicals. It also reveals the significant access to a large group of ligands/compounds for detection of carcinogenic heavy metallic ions in wide-range of environmental applications. Response time is measured as 13s for the detection of target N²⁺ ions and presented in Fig. 5(d).



Fig. 5: Selectivity studied with various analytes using EDBDMBS/GCE. (a) I-V responses of various analytes, (b) Current responses of analytes at +0.5V (Ni²⁺ ions), (c) comparison of current between EDBDMBS/GCE and EDBMBS/GCE, and (d) response time; Analyte concentration was taken at 0.1 μ M. Potential range: 0 to +1.5 V; Delay time: 1.0 Figure 2. Selectivity studied with various analytes using EDBDMBS/GCE. (a) I-V responses of various analytes, (b) Current responses of analytes at +0.5V (Ni²⁺ ions), and (c) comparison of current between EDBDMBS/GCE and EDBMBS/GCE; Analyte concentration was taken at 0.1 μ M. Potential range: 0 to +1.5 V; Delay time: 1.0 Figure 2. Selectivity studied with various analytes using EDBDMBS/GCE. (a) I-V responses of various analytes, (b) Current responses of analytes at +0.5V (Ni²⁺ ions), and (c) comparison of current between EDBDMBS/GCE and EDBMBS/GCE; Analyte concentration was taken at 0.1 μ M. Potential range: 0 to +1.5 V; Delay time: 1.0 s.

5. Interference Effect:

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Interference study is the impressive statistical approach in the field of analytical applied science to study the effect of other cations $(Ag^+, Al^{3+}, Au^{3+}, Ba^{2+}, Ce^{4+}, Co^{2+}, Pb^{2+}, Sn^{2+}, Y^{3+})$ in the presence of Ni²⁺ on EDBDMBS/GCE for the development of selective electrochemical Ni²⁺ sensor [22]. The *I-V* response of EDBDMBS/GCE towards all cations in the presence of Ni²⁺ (at .1 M an 5.0 L in P S pH 7. were e amine an their interference effect in comparison with Ni²⁺ were also investigated at the calibrated potential (+ 1.0 V). From the interference study, it was found that designed EDBDMBS/GCE is very sensitive, selective and reliable only for Ni²⁺ detection and it does not reveals any significant change in current response towards the other interfering toxic metal cations (Fig. 6 and Table S3).



Fig. 6. Interference study. Analytes concentration were taken at 0.1 μ M. Potential: +1.0 V; Delay time: 1.0 s.

The Ni²⁺ interaction with EDBDMBS was also examined by the UV-Vis and FTIR spectroscopy in addition to the X-ray photoelectron spectroscopy (XPS analysis). The results are given the supporting information section. In UV-Vis spectrum, hyperchromic shift was observed because intensity of absorbance increased in the presence of Ni²⁺, Fig. S12. As well as in FTIR spectrum, intensities of the peaks in fingerprint regions decreased with the addition of Ni²⁺. The two new peaks, one at 3512 cm⁻¹ and second at 3425 cm⁻¹ adjacent to N-H stretching at 3245 cm⁻¹ were also appeared. In addition to these, little distortion of two N-H peaks as a shoulder like appearance, one N-H stretching at 3245 cm⁻¹ and second N-H bending at 1592 cm⁻¹, were also observed which corroborate the interaction Ni²⁺ with the newly synthesized EDBDMBS, Fig. S13. From the XPS study, it is revealed that the shifting the N1s peak due to the interaction between EDBDMBS and Ni²⁺. The total XPS study is presented in supporting information section (Figure S14).

6. Conclusions

Two new chelating agents EDBDMBS and EDBMBS were synthesized with the aim to probe the heavy metal ions and their comparison study with specific heavy metal cation. Classical

spectroscopic techniques like UV/Vis, FTIR, ¹H-NMR & ¹³C-NMR were used for their structure elucidation in addition to single crystal X-Ray diffraction analysis. The dihedral angles between the different planes of molecules were measured. Inter and intra-molecular hydrogen bonding interactions has been discussed on the basis of results obtained from single crystal data. This extensive research is performed in terms of preparation and characterization of EDBDMBS and EDBMBS and applied for the Ni²⁺ ions sensor using *I-V* method. The analytical performance of Ni²⁺ ion sensor using EDBDMBS/GCE was higher and fascinated rather than EDBMBS/GCE by reliable *I-V* method in terms of sensitivity, detection limit in short response time as well as reproducibility. This novel idea imparts high selectivity and fast detection for nickel-ion to the EDBDMBS fabricated GCE-probe. Potentially, the same concept might be applied to the creation of new sensors for monitoring other cationic ions. Hence, this approach is introduced a new route for efficient toxic cationic sensor development in environmental and healthcare fields.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/.....

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Graphial Abstract



Research highlights

- 1. Bidentate, EBBMBS and EDBDMBS were synthesized
- 2. Sensor application as heavy metallic ions
- Single crystal X-Ray diffraction studies were proved the EDBDMBS structures
 Selective and sensitive potential Ni²⁺ sensor by reliable I-V method
- 5. Efficient cationic sensor for environmental toxins
- 6. Environmental safety

[71]