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Synthesis, Cyclic Voltammetric and Biological Studies of 2-Acetyl-1-Naphthol Sulfadiazine and its Cu(II) Complex

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ABSTRACT

Schiff base ligand 2-acetyl-1-naphthol sulfadiazine (2-Ac-1-NapSD) and its new Cu(II) complex were synthesized. The nature of bonding and structural features of the 2-Ac-1-NapSD and Cu(II) complex were characterized by the elemental analysis, IR spectra and ¹HNMR spectra. Electrochemical properties of the 2-Ac-1-NapSD and Cu(II) complex were investigated at glassy carbon electrode in dimethylformamide (DMF) and methanol solvent using cyclic voltammetry at different scan rates. The effect of change in pH, solvent and sweep rates is evaluated. Kinetic parameters are calculated from cyclic voltammetric measurements and biological studies of the ligand and copper complex were carried out against various bacteria and fungi.

Graphical Abstract:



Copper(II) complex of 2-Ac-1-NapSD Schiff base.

Keywords: 2-Acetyl-1-Naphthol Sulfadiazine, Cu(II) Complex, Cyclic Voltammetry, Biological Studies.

INTRODUCTION

Schiff bases named after Hugo Schiff who described the condensation between aldehydes and amines. Schiff bases are good ligands as they are able to coordinate with metals through imine nitrogen and another group usually linked with aldehydes. They are important class of ligands in coordination chemistry [1-3]. In recent years, researchers show much interest in synthesis and characterization of Schiff base metal complexes due to their importance as catalysts in many reactions [4-6]. Many

important sulfa drugs are therapeutically important due to possessing $-SO_2NH$ - moiety. The products obtained from condensation of sulfa drugs with aldehydes or ketones are biologically active and also have good complexing ability with metals. It is also noted that their activity is enhanced by complexation with transition metals. The enhanced activity of metal complexes of Schiff base derived from sulfa drug has led to considerable interest in coordination chemistry [7-8]. It was also established that the biological activity of Schiff bases has altered many folds on coordination with metal ions [9-10].

MATERIALS AND METHODS

Synthesis of Schiff base ligand: All chemicals used in this work were of analytical grade. Schiff base 2-acetyl-1-naphthol sulfadiazine was synthesized by refluxing methanolic solution of 2-acetyl-1-naphthol with sulfadiazine in methanol on a water bath for 8 hours at 70°C. The condensation product separated on cooling, was filtered off and purified by repeated recrystallization from appropriate solvent (yield 76%).



Figure 1. Scheme of 2-Ac-1-NapSD Schiff base synthesis.

Synthesis of copper(II) complex: A stirred solution of the synthesized 2-Ac-1-NapSD in methanol were mixed with a methanolic solution of $(CH_3CO_2)_2Cu$. H₂O for synthesis of Cu(II) complex. The reaction mixture was refluxed for 3 hours at 80° C; then, the solution was evaporated to 1/3 volume and cooled. The green solid complex was filtered, washed with methanol and dried in vacuum over anhydrous calcium chloride (Yield 68%).



Figure. 2. Copper(II) complex of 2-Ac-1-NapSD Schiff base.

RESULTS AND DISCUSSION

Elemental analysis: Elemental analysis was carried out using micro analytical technique on C, H, N, S, O elemental analyzer. Melting points were recorded using melting point apparatus and found 176° C for 2-Ac-1-NapSD and 198° C for Cu(II) complex.

Table 1. Elemental analysis

C No	Composition of ligand/	Color	Yield	Elemental analysis (%): found (cal.)					
3.INU	Complex (M. Wt.)		(%)	С	Η	Ν	0	S	Cu
1	C ₂₂ H ₁₈ N ₄ O ₃ S (418.47)	Pale Yellow	76	63.09 (63.14)	4.65 (4.34)	13.42 (13.39)	11.56 (11.47)	7.28 (7.66)	-
2	$\begin{array}{c} C_{44}H_{34}CuN_8O_6S_2\\ (898.47)\end{array}$	Green	68	58.77 (58.82)	3.96 (3.81)	12.55 (12.47)	10.52 (10.68)	7.12 (7.14)	7.06 (7.07)

Infrared spectral studies: The infrared spectra of 2-Ac-1-NapSD and Cu(II) complex were recorded on KBr pellets in the range 4000-450 cm⁻¹ on PerkinElmer FT-IR spectrometer. The IR spectra of the Cu(II) complex indicates that the ligand behaves as bidentate and copper coordinates via azomethine nitrogen and phenolic oxygen atoms. The shift of $v_{C=N}$ to lower wave number by 30-40 cm⁻¹ in the complex indicates that nitrogen of imine group involved in complexation. The ligand shows strong band at 3430 cm⁻¹ due to phenolic -OH group. This band disappears in Cu(II) complex, that indicates the involvement of this group in complex formation. Moreover, the shift of the v_{C-O} phenolic band from 1282 cm⁻¹ to 1292-1327 cm⁻¹ in the spectra of Cu(II) complex supports the chelation of phenolic oxygen atom to the Cu(II) ion. The presence of sharp band in the region 514-521 cm⁻¹ in the spectra of the complex assigned to v_{Cu-N} mode, further supports the involvement of nitrogen atom in coordination.

NMR spectral studies: The ¹HNMR spectra were recorded in DMSO using TMS as an internal standard. The ¹HNMR spectra of the 2-Ac-1-NapSD have expected characteristic signals. The methyl protons show singlet at δ 2.43 (3H, s), diazine ring protons at δ 6.62 (1H, t), 8.53 (2H, m), naphthol ring protons at δ 7.62 (1H, m), 8.01 (1H, m), 8.66 (1H, m), 7.63 (2H, m), 8.35 (1H, m) and benzene ring protons at δ 7.29 (2H, m), 7.92 (2H, m). The hydroxyl proton resonates as a singlet at δ 12.10 ppm in case of ligand and disappears in the Cu(II) complex which indicates the involvement of phenolic oxygen in the coordination via deprotonation. Signals observed in the ligand at region of δ 8.15 ppm due to azomethine proton show downfield shift of 0.06 ppm and appear at δ 8.08 ppm which indicates the coordination of azomethine nitrogen with copper(II) ions. These observations support the following assigned structure of 2-Ac-1-NapSD as well as Cu(II) complex.

Cyclic voltammetric studies of 2-acetyl-1-naphthol sulfadiazine ligand: The cyclic voltammograms of 1mM 2-acetyl-1-naphthol sulfadiazine (2-Ac-1-NapSD) ligand were recorded at glassy carbon electrode in methanol and DMF solvents using phosphate buffer at 50, 100, 150, 200 and 250 mV/s sweep rates and on pH 5, 7 and 9. For studying the redox behavior, potential was applied in the range of +400 mV to -1200 mV in methanol-phosphate buffer medium and in the range of +1000 mV to -1400 mV in DMF-phosphate buffer medium. The compound exhibits one irreversible reduction peak in the cathodic direction. The cyclic voltammograms are shown in figure 3 to 8. The shape of the reduction wave clearly shows the irreversible nature of electrode process [11-14]. Thus, kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{V_2}$) and rate constant ($k^{\circ}_{f,h}$) have been evaluated for irreversible and diffusion controlled reduction using following equations (1 to 3) and are reported in tables 2 to 3.







Figure 4. Cyclic voltammograms of 2-Ac-1-NapSD in methanol-phosphate buffer at pH 7.



Figure 5. Cyclic voltammograms of 2-Ac-1-NapSD in methanol-phosphate buffer at pH 9.











Figure 8. Cyclic voltammograms of 2-Ac-1-NapSD in DMF-phosphate buffer at pH 9

$$\left|E_{p} - E_{p/2}\right| = \frac{1.857 RT}{\alpha_{n} F} = \left(\frac{47.7}{\alpha_{n}}\right) mV \qquad (1)$$

$$I_{p} = 3.01 \times 10^{5} n (\alpha_{n})^{1/2} A C D_{0}^{-1/2} v^{1/2} \qquad (2)$$

$$E_{P} = -\frac{RT}{\alpha_{n}F} \left[0.78 + \ln\left(\frac{D_{0}^{1/2}}{k^{\circ}_{f,h}}\right) + \ln\left(\frac{\alpha_{n}Fv}{RT}\right)^{1/2} \right] \quad (3)$$

 Table 2. Effect of sweep rate on voltammetric parameters of 1 mM 2-Ac-1-NapSD in methanol-phosphate buffer at different pH (Figure 3 to 5)

pН	v (mVs ⁻¹)	<i>E_{pc}</i> (mV)	<i>I_{pc}</i> (μA)	<i>E</i> _{<i>p</i>/2} (mV)	$I_{pc} / v^{1/2}$	a _n	$D_o^{1/2}$ (cm ² s ⁻¹)	$k^{\bullet}_{f,h}$ (cm.s ⁻¹)
	50	-942	2.12	-831	0.2998	0.4297	2.8789	8.18×10^{-10}
	100	-956	2.92	-845	0.2920	0.4286	2.8038	8.92×10^{-10}
5	150	-964	3.34	-856	0.2727	0.4416	2.5830	5.70×10 ⁻¹⁰
	200	-974	3.72	-867	0.2630	0.4457	2.4799	4.57×10^{-10}
	250	-988	4.15	-888	0.2624	0.4770	2.3921	1.20×10^{-10}
	50	-950	4.56	-845	0.6448	0.4542	6.0227	6.21×10 ⁻¹⁰
	100	-965	4.91	-855	0.4910	0.4336	4.6934	1.11×10 ⁻⁹
7	150	-978	5.62	-867	0.4588	0.4297	4.4062	1.19×10 ⁻⁹
	200	-985	5.93	-892	0.4193	0.5129	3.6855	4.59×10 ⁻¹¹
	250	-1002	6.65	-905	0.4205	0.4917	3.7753	8.36×10 ⁻¹¹
	50	-964	5.23	-856	0.7396	0.4416	7.0056	8.92×10^{-10}
	100	-978	6.52	-869	0.6520	0.4376	6.2041	1.02×10^{-9}
9	150	-997	8.29	-878	0.6768	0.4008	6.7297	3.91×10 ⁻⁹
	200	-1012	9.56	-899	0.6759	0.4221	6.5493	1.54×10 ⁻⁹
	250	-1025	10.24	-912	0.6476	0.4221	6.2746	1.33×10 ⁻⁹

pН	ν (mVs ⁻¹)	<i>E_{pc}</i> (mV)	<i>I_{pc}</i> (μΑ)	<i>E</i> _{<i>p</i>/2} (mV)	$I_{pc}/v^{1/2}$	an	$D_0^{1/2}$ (cm ² s ⁻¹)	$k^{\bullet}_{f,h}$ (cm.s ⁻¹)
5	50	-952	5.03	-845	0.7113	0.5482	6.0472	3.11×10 ⁻¹¹
	100	-961	6.74	-867	0.6740	0.5074	5.9558	1.03×10^{-10}
	150	-994	8.65	-898	0.7062	0.4968	6.3070	1.04×10^{-10}
	200	-1032	9.81	-916	0.6936	0.4112	6.8092	1.77×10^{-9}
	250	-1075	11.02	-934	0.6969	0.3382	7.5429	2.11×10 ⁻⁸
	50	-989	5.61	-856	0.7933	0.3586	8.3391	1.52×10 ⁻⁸
	100	-1009	7.95	-879	0.7950	0.3669	8.2614	1.18×10 ⁻⁸
7	150	-1052	9.25	-904	0.7552	0.3222	8.3742	4.62×10 ⁻⁸
	200	-1093	10.52	-922	0.7438	0.2789	8.8657	1.99×10 ⁻⁷
	250	-1128	12.13	-945	0.7671	0.2606	9.4587	3.50×10 ⁻⁷
	50	-1026	6.31	-875	0.8923	0.3158	9.9942	5.64×10 ⁻⁸
	100	-1078	8.94	-891	0.8940	0.2550	11.1423	5.42×10 ⁻⁷
9	150	-1102	10.56	-905	0.8622	0.2421	11.0298	8.78×10 ⁻⁷
	200	-1124	11.78	-935	0.8329	0.2523	10.4370	5.08×10 ⁻⁷
	250	-1174	14.02	-956	0.8867	0.2188	11.9323	1.72×10 ⁻⁶

Table 3. Effect of sweep rate on voltammetric parameters of 1 mM 2-Ac-1-NapSD inDMF-phosphate buffer at different pH (Figure 6 to 8)

Effect of change of scan rate: The effect of scan rate on voltammetric parameters of 2-Ac-1-NapSD ligand is observed by varying the scan rate 50, 100, 150, 200 and 250 mV/s at pH 5, 7 and 9. Single irreversible reduction peak at all scan rates has been observed. The peak potential values shifted in the more negative direction with an increase in the scan rate indicates the electrochemical process was irreversible. The irreversibility of the reduction process is confirmed from the linear dependence of the cathodic peak potential (E_{pc}) with $\ln v$ (Figure 9 to 10). Peak current was also found to be increased as the scan rate increased for all the compounds. Data obtained from cyclic voltammograms were used in the plotting of cathodic peak current (I_{pc}) and the square root of scan rate ($v^{1/2}$). The linear relationship between the square root of scan rate ($v^{1/2}$) and cathodic peak current (I_{pc}) (Figure 11 to 12) shows the irreversible nature of charge transfer process. The current function ($I_{pc}/v^{1/2}$) has been found to be fairly constant with respect to sweep rate showing that the electrode process is diffusion controlled [11-13].

Effect of pH: The effect of pH upon the reduction of 2-Ac-1-NapSD was investigated (tables 2 and 3). Peak potential values of the compound are found to be changed with the pH values of the solution. This dependence of the peak potential on pH suggests that proton transfer also takes place in the electrode reaction [14]. The peak potential shifts in more negative value depends upon the pH of the solution. This means that the reduction is easier in acidic media and difficult in the media where the proton concentration is low. The reduction is found to be easier in acidic pH than in alkaline pH which may be because of the formation of easily reducible protonated intermediate.

Effect of solvent: The effect of solvent on electrochemical properties can't be explained by any single chemical or physical property of the solvent or by a single unified theory. It can be explained by viscosity, dielectric constant, steric factor and polarity of the solvent [15, 16]. In the present research cyclic voltammograms of 2-Ac-1-NapSD were recorded in DMF and methanol solvents with phosphate buffer. It was observed that the peak potential shifts to more negative potential in the presence of DMF. This trend is parallel to the trend in viscosity (for DMF is 0.796 and methanol is 0.544), dielectric constant (for DMF is 36.7 and methanol is 32.7) and polarity of solvent (dipole moment of DMF is 3.86 and methanol is 1.47)[17-18].

Cyclic voltammetric studies of Cu(II) complex of 2-Ac-1-NapSD: The cyclic voltammograms of 1 mM Cu(II) Complex of 2-Ac-1-NapSD were recorded in DMF solvent using NaClO₄ as supporting electrolyte at glassy carbon electrode in a wide range of scan rates from 100 to 300 mVs⁻¹. The obtained cyclic voltammograms consisted of a single cathodic peak at potential ranging from -0.45 V



Figure 9. $E_{pc}vs \ln v$ for 1 mM 2-Ac-1-NapSD in methanolphosphate buffer



Figure 11. I_{pc} vs $v^{1/2}$ for 1 mM 2-Ac-1-NapSD in methanolphosphate buffer at pH 7



Figure 10. E_{pc} vs lnv for 1 mM 2-Ac-1-NapSD in DMFphosphate buffer at pH 9



Figure 12. I_{pc} vs $v^{1/2}$ for 1 mM 2-Ac-1-NapSD in DMFphosphate buffer at pH 5

to -0.55 V, and in reverse scan a corresponding anodic wave occurs in the range of -0.085 V to -0.037 V and the peak separation (ΔE_p) varies from 0.37 V to 0.52 V. Since 2-Ac-1-NapSD is not reduced or oxidized in the above applied potential range in experimental conditions, the redox process is assigned to the copper centre only. The cathodic wave corresponding to the irreversible two electron reduction of the imino group present in the ligand is no longer observed in Cu(II) complex. On the other hand, the separation between the anodic and cathodic peak potentials (ΔE_p) indicates a degree of reversibility of electrochemical reaction [19-20]. ΔE_p values listed in the table 4 is considerably greater (0.37 V to 0.52 V) than the theoretical Nernstian values (0.059 V) for an electrochemically reversible one electron process. It suggests that the reduction of copper(II) complex corresponds to a one electron charge transfer. The quasi-reversible nature of the reduction peak is confirmed by the large difference in the potential ($\Delta E_p > 0.1$ V). The exceedingly large ΔE_p values for copper(II) in the complex suggest a quasi-reversible behavior of the $Cu(II) + e^{-} \rightarrow Cu(I)$ couple under the experimental conditions here adopted and the non-aqueous nature of the system. The ratio between the anodic and cathodic peak currents suggests simple one electron transfer quasi-reversible process. The ratio of anodic peak current to cathodic peak current is less than unity $(I_{pa}/I_{pc} < 1)$ which further confirms the quasi reversible nature of the redox couple [21-22]. A linear relationship between cathodic peak current (I_{pc}) and the square root of the scan rate ($v^{1/2}$) have also been observed (Figure 14). This fact implies that these electrochemical processes are mainly diffusion controlled.

 Table 4. Effect of sweep rates on voltammetric parameters of 1 mM Cu(II) Complex of 2-Ac-1-NapSD in DMF- NaClO₄ solvent (Figure 14)

v (mVs ⁻¹)	E _{pc} (mV)	$E_{p,a}$ (mV)	$\frac{\Delta E_p}{(\mathrm{mV})}$	<i>E</i> _{1/2} (mV)	$I_{p,c}$ (μ A)	<i>I</i> _{p,a} (μA)	$I_{p,a}/I_{p,c}$	$I_{p,c}/v^{1/2}$
100	-458	-85	373	-314	26.45	22.14	0.8370	2.6450
150	-491	-74	417	-329	32.42	26.49	0.8170	2.6470
200	-516	-62	454	-341	36.92	30.15	0.8166	2.6106
250	-538	-51	487	-354	41.48	33.84	0.8158	2.6234
300	-557	-37	520	-372	45.61	38.92	0.8533	2.6332

50

45

40

25

20

8

10

(MA) 35

 \mathbf{I}_{pc} 30



Figure 13. Cyclic voltammogram of Cu(II) complex of 2-Ac-1-NapSD in DMF-NaClO₄at different scan rates.



12

14

 $v^{1/2} \,(\mathrm{mV/s})^{1/2}$

16

18

APPLICATION

Biological screening studies: The *in-vitro* biological screening effects of the 2-Ac-1-NapSD and its Cu(II) complex were tested against the various bacteria such as *Escherichia coli*, *Salmonella typhi*, Staphylococcus aureus, Starptococci and fungi Candida albicans, Aspergillus niger by disc diffusion method. The minimum inhibition concentration (MIC) value of the compounds against the growth microorganisms are summarized in the table 5. A comparison of the MIC values of 2-Ac-1-NapSD with its Cu(II) complex indicates that the Cu(II) complex exhibited higher antimicrobial activity than 2-Ac-1-NapSD. Such increased activity of the Cu(II) complex can be explained on the Overtone's concept and the Tweedy chelation theory [23]. According to the Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials, due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion will be reduced due to the partial sharing of positive charges with donor groups. Furthermore, it increases the delocalization of π -electrons over the whole chelate ring that enhances the lipophilicity of the Cu(II) complex. This increased lipophilicity enhances the penetration of the complex into lipid membranes and the blocking of the metal binding sites in the enzymes of microorganisms [24]. The presence of hydroxyl and azomethine groups, which forms hydrogen bonding with proteins present in the cell wall of the microorganisms, results in interference with the normal cell process [25-27].

		B	Fungi			
Compound	Escherichia coli	Salmonella Typhi	Staphylococcus aureus	Starptococci	Candida albicans	Aspergillus niger
2-Ac-1-NapSD	65	60	60	85	100	65
Cu(II) Complex	55	45	50	60	65	50

Table 5. Biological activities of 2-Ac-1-NapSD ligand and its Cu(II) complex (MIC values in µmg)

CONCLUSION

Schiff base ligand 2-acetyl-1-naphthol sulfadiazine (2-Ac-1-NapSD) and its Cu(II) complex were synthesized and characterized by elemental analysis, IR spectra, and ¹HNMR spectra. Electrochemical properties of these compounds were investigated by cyclic voltammetry using glassy carbon electrode. The effect of pH, solvent and scan rates is evaluated. It was observed that single irreversible reduction wave observed for 2-Ac-1-NapSD while quasi-reversible wave was observed for copper(II) complex under all applied experimental conditions. Biological screening studies shows that Cu(II) complex have higher antimicrobial activity than 2-Ac-1-NapSDdue to higher lipophilicity of Cu(II) complex.

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