Research Article

Synthesis, Electrochemical, Spectroscopic, Antimicrobial, and Superoxide Dismutase Activity of Nickel (II) Complexes with Bidentate Schiff Bases

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Five new nickel (II) complexes, namely, [Ni(L 1 ) 2 ][ClO 4 ] 2 (1); [Ni(L 2 ) 2 ][ClO 4 ] 2 (2); [Ni(L 3 ) 2 ][ClO 4 ] 2 (3); [Ni(L 4 ) 2 ][ClO 4 ] 2 (4); [Ni(L 5 ) 2 ][ClO 4 ] 2 (5), where L 1 = benzoylhydrazide; L 2 = N-[(1)-1-(2-methylphenyl)ethylidene]benzohydrazide; L 3 = N-[(1)-1-(4-methylphenyl)ethylidene]benzohydrazide; L 4 = N-[(1)-1-(2-methoxyphenyl)ethylidene]benzohydrazide; L 5 = N-[(1)-1-(4-methoxyphenyl)ethylidene]benzohydrazide, have been synthesized and characterized by various physicochemical and spectroscopic techniques. The synthesized complexes are stable powders, insoluble in common organic solvents such as ethanol, benzene, carbon tetrachloride, chloroform, and diethyl ether, and are nonelectrolytes. The magnetic and spectroscopic data indicate a distorted square planar geometry for all complexes. The superoxide dismutase activity of these complexes has been measured and discussed. Antibacterial and antifungal properties of these complexes were also tested.

1. Introduction

The synthesis of low molecular weight nickel (II) complexes mimicking superoxide dismutase (SOD) activity has been challenging for bioinorganic chemists and recently some complexes with high catalytic activity have been reported [1–3]. Nickel-containing superoxide dismutase (Ni-SOD) has been isolated from several Streptomyces species [4]. The enzymatic activity of Ni-SOD [5] is as high as that of Cu-Zn SOD at about 10 9 M −1 S −1 per metal center. Oberley and Buettner [6] have reported that cancer cells had less superoxide dismutase (SOD) activity than normal cells. Superoxide ion is toxic to cells; a defense mechanism must have been initiated by nature. All organisms, which use dioxygen and many that have to survive an oxygenated environment, contain at least one SOD. The superoxide radical (O 2− ) is an inevitable byproduct of aerobic metabolism which if not eliminated may cause significant cellular damage and has been implicated in numerous medical disorders [7]. To avoid such harmful consequences, all oxygen metabolizing organisms possess metalloenzymes known as superoxide dismutases (SODs). These SODs disproportionate the toxic O 2− radical to molecular oxygen and hydrogen peroxide [8, 9]. All SODs employ the two-step Ping-Pong mechanism shown in

\[ M^{\text{ox}} + O_2^- \rightarrow M_{\text{red}} + O_2 \]  
\[ M_{\text{red}} + O_2^- + 2H^+ \rightarrow M^{\text{ox}} + H_2O_2 \]

where M is a redox active metal center capable of both oxidizing and reducing superoxide.

Metal complexes of bidentate Schiff bases have been extensively studied [10, 11], because such ligands can bind with one, two, or more metal centers involving various coordination modes and allow synthesis of homo- and heteronuclear metal complexes with interesting stereochemistry [12, 13]. A number of papers [14, 15] highlight the flexible nature of bidentate ligands, their analytical, and biological properties. Recently, we have studied [16–18] various Schiff bases and their metal (II) complexes. This paper describes synthesis, electrochemical, spectroscopic, antimicrobial,
and superoxide dismutase (SOD) activity of nickel (II) complexes namely \([\text{Ni}(L^1)_2](\text{ClO}_4)_2(1), [\text{Ni}(L^2)_2](\text{ClO}_4)_2(2), [\text{Ni}(L^3)_2](\text{ClO}_4)_2(3), [\text{Ni}(L^4)_2](\text{ClO}_4)_2(4), \) and \([\text{Ni}(L^5)_2](\text{ClO}_4)_2(5)\). All the Schiff bases \(L^2, L^3, L^4, \) and \(L^5\) are bidentate ligand having donor site nitrogen and oxygen atom (Scheme 1). Superoxide dismutase activity of all these complexes has been revealed to catalyze the dismutation of superoxide \((O_2^-)\), and IC_{50} values were evaluated and discussed.

2. Experimental

2.1. Physical Measurements. Nickel (II) chloride hexahydrate was purchased from S. D. Fine-Chem Limited, India. All other chemicals used were of synthetic grade and used without further purification. Elemental analyses were performed on an Elementar Vario EL III Carlo Erba 1108 analyzer. Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer data system using xenon (6kV, 10mA) as the FAB gas. The accelerating voltage was 10kV and the spectra were recorded at room temperature. UV-Vis spectra were recorded at 25°C on a Shimadzu UV-Vis recording spectrophotometer UV-1601 in quartz cells. IR spectra were recorded in KBr medium on a Perkin-Elmer 783 spectrophotometer in the 4000–600 cm\(^{-1}\) region. Cyclic voltammetry was carried out with a BAS-100 Epsilon electrochemical analyzer having an electrochemical cell with a three-electrode system. Ag/AgCl was used as a reference electrode, glassy carbon as working electrode, and platinum wire as an auxiliary electrode. 0.1M NaClO\(_4\) was used as supporting electrolyte and DMSO as solvent. Molar conductivities of freshly prepared \(2 \times 10^{-3}\) M of acetonitrile solutions were measured on a Systronics conductivity TDS meter 308. The \textit{in vitro} SOD activity was measured using alkaline DMSO as a source of superoxide radical \((O_2^-)\) and nitroblue tetrazolium chloride (NBT) as \(O_2^-\) scavenger [19]. In general, 400\(\mu\)L sample to be assayed was added to a solution containing 2.1mL of 0.2 mol L\(^{-1}\) potassium phosphate buffer (pH 8.6) and 1mL of 56 \(\mu\)mol L\(^{-1}\) alkaline DMSO solution prepared under similar condition in DMSO (except NaOH). A unit of SOD activity is the concentration of complex, which causes 50% inhibition of alkaline DMSO-mediated reduction of NBT. The \textit{in vitro} antimicrobial (antibacterial) activities of these complexes were tested using paper disc diffusion method [20]; the chosen strains were \textit{Streptococcus aureus} and \textit{Escherichia coli}. The liquid medium containing the bacterial subcultures was autoclaved for 20min at 121°C and at 15lb pressure before inoculation. The bacteria were then cultured for 24h at 36°C in an incubator. The antifungal activity of the present complexes has been evaluated against \textit{Aspergillus} sp. and \textit{Penicillium} sp. by the Radial Growth Method [21] using Czapek’s agar medium. The compounds were added directly with the medium in 5, 10 and 15 mM concentrations.

2.2. Synthesis of \(L^2, L^3, L^4, \) and \(L^5\). The Schiff bases \(L^2, L^3, L^4, \) and \(L^5\) were prepared by general condensation reaction and recrystallized from ethanol or methanol. A methanol solution of benzoilhydrazide (10 mmol, 1.36 g) was stirred with (10 mL) of 2-methyl acetophenone (10 mmol, 1.34 g), 4-methyl acetophenone (10 mmol, 1.34 g), 2-methoxy acetophenone (10 mmol, 1.50 g), and 4-methoxy acetophenone (10 mmol, 1.50 g), respectively. The precipitate was obtained, washed with cold methanol, dried in air, and stored in a CaCl\(_2\) desiccator. Yield varied at the range 80–90%. Anal. Calc. for \(C_{16}H_{16}N_2O\) \((L^2)\) Found: (%): C, 76.09; H, 6.74; N, 11.09. Calc. (%): C, 76.07; H, 6.32; N, 11.07. FAB-mass (m/z) = Calc. 252.33, Found: 252. Anal. Calc. for \(C_{16}H_{16}N_2O\) \((L^3)\) Calc. (%): C, 76.07; H, 6.32; N, 11.07. Found (%): C, 76.09; H, 6.34; N, 11.09. FAB-mass (m/z) = Calc. 252.33, Found: 252. Anal. Calc. for \(C_{16}H_{16}N_2O\) \((L^4)\) Calc. (%): C, 71.48; H, 5.40; N, 10.38. FAB-mass (m/z) = Calc. 268.33, Found: 268. Anal. Calc. for \(C_{16}H_{16}N_2O\) \((L^5)\) Found: (%): C, 71.55; H, 5.96; N, 10.43. Calc. (%): C, 71.50; H, 5.91; N, 10.40. FAB-mass (m/z) = Calc. 268.33, Found. 268.
2.3. Synthesis of [Ni(L^1)_2](ClO_4)_2(I); [Ni(L^2)_2](ClO_4)_2(2); [Ni(L^3)_2](ClO_4)_2(3); [Ni(L^4)_2](ClO_4)_2(4); and [Ni(L^5)_2](ClO_4)_2(5). All the present complexes were synthesized by following general procedure. The 2:1 equimolar ratio to a MeOH solution of NaClO_4 (2.0 mmol, 0.25 g), a MeOH solution of Schiff bases L^1 (2.0 mmol, 0.27 g), L^2 (2.0 mmol, 0.50 g), L^3 (2.0 mmol, 0.50 g), L^4 (2.0 mmol, 0.53 g), and L^5 (2.0 mmol, 0.53 g), respectively, was added with stirring for 30 min at 25°C. A MeOH solution (10 mL) of NaClO_4 (2.0 mmol, 0.25 g) was added for another 30 min at RT. Complexes that are green (I), light green (2) and (3), and red colors (4) and (5) microcrystalline solid deposited were collected by filtration and washed with MeOH. The obtained solid was dried in air and stored in a CaCl_2 desiccator at RT. Yield varied at the range 80–85%. Anal. Calc. for C_4H_9N_2Cl_2Ni_10O_10 (I): Calc. (%): C, 31.75; H, 3.02; N, 10.5. Found (%): C, 31.70; H, 3.00; N, 10.5. FAB-mass (m/z): Calc. 529.01; Found 530. Anal. Calc. for C_32H_32Ni_2Cl_2NiO_10 (2): Calc. (%): C, 50.43; H, 4.20; N, 7.35. Found (%): C, 50.38; H, 4.18; N, 7.30. FAB-mass (m/z): Calc. 761.37; Found: 761. Anal. Calc. for C_32H_32Ni_2Cl_2NiO_10 (3): Calc. (%): C, 50.40; H, 4.28; N, 7.30. Found (%): C, 50.42; H, 4.16; N, 7.25. FAB-mass (m/z): Calc. 761.37; Found: 761. Anal. Calc. for C_32H_32Ni_2Cl_2NiO_12 (4); Calc. (%): C, 48.40; H, 4.03; N, 7.05. Found (%): C, 48.35; H, 4.01; N, 7.02. FAB-mass (m/z): Calc. 793.37; Found: 793. Anal. Calc. for C_32H_32Ni_2Cl_2NiO_12 (5); Calc. (%): C, 48.38; H, 4.01; N, 7.03. Found (%): C, 48.33; H, 4.00; N, 7.01. FAB-mass (m/z): Calc. 793.37; Found: 793.

3. Results and Discussion

3.1. Synthesis and Characterization. The mononuclear complexes prepared in high yield by reacting nickel (II) salt with bidentate Schiff bases in 2:1 molar ratio to give complexes of general composition [Ni(A)_2]. The reactions proceed in the following manner (Scheme 2):

\[ \text{Ni}^2+ + 2\text{A} \rightarrow [\text{Cu} (\text{A})_2] \]  (3)

where A = L^1, L^2, L^3, L^4, and L^5. The Schiff base ligands were prepared by refluxing equimolar amounts of benzoylhydrazine and 4-methoxyacetophenone; 4-methoxyacetophenone; 2-methoxyacetophenone; 2-methoxyacetophenone, respectively, in ethanol for 4–6 h. Complexes are green (I), light green (2) and (3), red colour (4) and (5) are stable in partially soluble in water but soluble in most of organic solvent. These complexes were prepared in good yields and characterized by microanalysis. All the complexes decompose between 170 and 280°C. The molar conductivity values in DMSO solutions are very low (3.51–12.32 Ω^−1 cm^2 mol^−1) of 10^−3 M solutions, at room temperature indicate that they are nonelectrolytes [22]. The value of µ_elec at room temperature of the Ni (II) complexes is 2.94 B.M. for (I), 2.69 B.M. for (2), 2.73 B.M. for (3), 2.83 B.M. for (4), and 2.92 B.M. for (5), suggesting that this is essentially diamagnetic. For the d^8 electronic configuration, diamagnetism generally implies that the metal has square planar configuration [23].

3.2. Spectroscopic Study. The room temperature ligand field spectra (electronic spectra) of these complexes have been recorded in 100% DMSO solution at 25°C. In present Ni (II) complexes, the highest energy d-d energy transition from the lower lying fully occupied 3d_{x^2−y^2} orbital to the upper empty 3d_{xy} orbital ("B ← A" transition) at 405 ± 5 nm is obscured by the MLCT transition. The other three lower energy d-d transitions from the occupied 3d_{xy}, 3d_{xz}, and 3d_{yz} orbitals to the empty 3d_{xy} orbital ("B ← A", "B ← A", and "A ← A" transition, resp.) are less intense, appear as a broad envelope around at the range 615 ± 5 nm region, and are typical of square planar mononuclear nickel (II) complexes [24]. In addition, MLCT transition is located at the range 420 ± 5 nm. The azomethine (–HC=N–) characteristib band in the IR for the free ligand was observed at ~1650 ± 5 cm^−1. The IR-spectra of the complexes show coordination C=N bonds [25] in the range of 1602–1628 and of 460–490 cm^−1. A strong band, observed at ca. 1205–1329 cm^−1 is assigned to coordination through phenolic oxygen [26]. In addition, these complexes show strong bands at 1053–1083 cm^−1 indicating the presence of ClO_4 groups [27] in agreement with their noncoordinating character. Vibrations at ~460 weak (and expected below 400 cm^−1, out of our measuring limit) can be attributed to M–O and M–N vibrations [28].

3.3. Electrochemical Study. Electroactivity of the complexes was studied in DMSO with 0.1 M NaClO_4 as supporting electrolyte using cyclic voltammetry at a platinum working electrode. “Supplementary material” and redox potential values are given in Table I. The redox processes assigned as Ni (II)/Ni (I) couples are fully irreversible [29]. The voltammograms of these complexes consist of two well-separated peaks, one cathodic potential (E_{pc}) and one anodic potential (E_{pa}). In these complexes reduction waves are observed at more negative potentials. In these cases, the peak potential differences increase as the scan rate increases. Constancy of E_0 shows that in all the cases both peaks are complementary to each other. The peak current ratio I_{pa}/I_{pc} is less than unity showing that the electron transfer reaction is followed by a chemical reaction (EC mechanism) [30].

3.4. Superoxide Dismutase Activity. The SOD activities for the complexes were measured. Superoxide was enzymatically supplied from alkaline DMSO and SOD activity was evaluated by the NBT assay [31] following the reduction of NBT to M^′′ Phoretically at 560 nm. These complexes exhibit significant catalytic activity towards the dismutation of superoxide anions. The concentration causing 50% inhibition of NBT reduction is IC_{50}. The SOD activity of [Ni(L^1)_2](ClO_4)_2 was shown in Figure 1. The observed IC_{50} values of the nickel (II) complexes (50 for I, 40 for 2, 49 for 3, 41 for 4, and 48 for 5 μmol dm^−3) are higher than the value exhibited by the native enzyme (IC_{50} = 0.04 μmol dm^−3) on a molar base (note that the smaller the IC_{50} value, the higher the activity). The observed IC_{50} values of the present complexes are comparable to reported values [32] for nickel (II) (Table 2). The catalytic activity of NiSOD [6], however,
Scheme 2
Table 1: Cyclic voltammetry data for 1 mM solution of the nickel (II) complexes in DMSO containing 0.1 M NaClO₄ as supporting electrolyte.

| Scan rate (mV/s) |  \( E_{pc} \) (mv) |  \( I_{pc} \) (μA) |  \( E_{pa} \) (mv) |  \( I_{pa} \) (μA) |  \( \Delta E_p \) |  \( E'_0 \) |  \( I_{pa}/I_{pc} \) (μA) |
|------------------|---------------------|-------------------|-------------------|-------------------|----------------|--------------|-------------------|
| [Ni(L₁)₂](ClO₄)₂(1) | -637 | 1.148 | -552 | 0.682 | 115 | 609 | 0.594 |
| 200 | -683 | 0.895 | -560 | 0.485 | 123 | 621 | 0.541 |
| [Ni(L₂)₂](ClO₄)₂(2) | -790 | 1.120 | -672 | 0.755 | 118 | 731 | 0.674 |
| 200 | -793 | 1.722 | -668 | 1.549 | 125 | 730 | 0.899 |
| [Ni(L₃)₂](ClO₄)₂(3) | -685 | 1.148 | -552 | 0.916 | 133 | 618 | 0.797 |
| 200 | -688 | 1.118 | -570 | 1.044 | 118 | 629 | 0.933 |
| [Ni(L₄)₂](ClO₄)₂(4) | -685 | 1.140 | -548 | 0.680 | 137 | 616 | 0.596 |
| 200 | -690 | 0.790 | -564 | 0.482 | 126 | 628 | 0.610 |
| [Ni(L₅)₂](ClO₄)₂(5) | -782 | 1.125 | -670 | 0.756 | 112 | 726 | 0.672 |
| 200 | -787 | 1.925 | -664 | 1.550 | 122 | 726 | 0.805 |

\( \Delta E_p = E_{pa} - E_{pc} \); \( E'_0 = (E_{pa} + E_{pc})/2 \).

Table 2: Superoxide dismutase activity of some nickel (II) complexes.

| Serial number | Complexes | IC₅₀ (μmol dm⁻³) | Reference |
|---------------|-----------|-----------------|-----------|
| (1)           | [Ni(tren)(Phen)](ClO₄)₂ | 40 | [17] |
| (2)           | [Ni(tren)(bipy)](ClO₄)₂ | 48 | [17] |
| (3)           | [Ni(SAA)(PMDT)]:H₂O | 43 | [17] |
| (4)           | [Ni(SAA)](TPTZ) | 58 | [17] |
| (5)           | [Ni(BPSE)]:BF₄ | 65 | [24] |
| (6)           | [Ni(5-BST)(CH₃OH)]ClO₄ | 48 | [24] |
| (7)           | [Ni(L₁)₂](ClO₄)₂(1) | 50 | This work |
| (8)           | [Ni(L₂)₂](ClO₄)₂(2) | 40 | This work |
| (9)           | [Ni(L₃)₂](ClO₄)₂(3) | 49 | This work |
| (10)          | [Ni(L₄)₂](ClO₄)₂(4) | 41 | This work |
| (11)          | [Ni(L₅)₂](ClO₄)₂(5) | 48 | This work |

Figure 1: Superoxide dismutase activity of [Ni(L₁)₂](ClO₄)₂(1).
3.5. Antimicrobial Activity. The in vitro antimicrobial (antibacterial) activities of these complexes were tested using paper disc diffusion method; the chosen strains were G (+) *Streptococcus aureus* and *Escherichia coli*. Three concentrations of the present complexes were taken, that is, 5 mM, 10 mM, and 15 mM. Paper disc were prepared and dipped with the help of these different solution. The susceptibility of the certain strains of bacterial towards the nickel (II) was determined by measuring the size of inhibition diameter. The growth inhibitory effects were observed against all the bacterial/fungal strains. Both bacteria are pathogens for humans, which cause dysentery and food poisoning, respectively. Complexes 1 and 2 were tested for their antibacterial and antifungal activity. The antibacterial activity of [Ni(L1)2](ClO4)2 1 is graphically presented in Figure 2. Results of these antimicrobial and antifungal assessments of complexes are presented in Tables 3 and 4. The area of zone of inhibition is less in the concentration of 5 mM in both microorganisms and more in 15 mM concentration. This kind of observation is suggestive of that these complexes are effective against both pathogens. In case of complex 1 diameter of inhibition zone (20 nm) is highest for *E.coli*. It was noted that complex 1 was more effective against *E. coli* than *Streptococcus aureus*. Similar observations were found for complex 2. Among fungal species, two isolates were taken into consideration and were *Aspergillus* and *Penicillium* sp.; similar trends were observed as in the case of bacteria. It was noted that *Penicillium* sp. was highly susceptible against complex 1. Another fungi *Aspergillus* sp. showed least effectiveness against complex 2 but comparatively more susceptible towards complex 1. Similar antimicrobial results were reported by Tarafder et al. [33] and also by Patel School [34] on simple nickel (II) binary and ternary complexes. It is observed from these test that metal chelates have a higher activity than the free ligands such that increased activity of the metal chelated can be explained on the basis of Tweedy’s chelation theory [35]. These complexes also disturb the respiratory processes of the cell and thus block the synthesis of protein, which restricts further growth of the organisms.

### 4. Conclusion

Five new nickel (II) complexes, namely, [Ni(L1)2](ClO4)2 1; [Ni(L2)2](ClO4)2; [Ni(L3)2](ClO4)2 3; [Ni(L4)2](ClO4)2 4; [Ni(L5)2](ClO4)2 5, have been synthesized and characterized by various physicochemical and spectroscopic techniques. The magnetic and spectroscopic data of complexes 1–5 indicate square planar geometry. The SOD activity of reported complexes in the increasing order 2 < 4 < 5 < 3 < 1. Complexes 1 and 2 have shown excellent antibacterial activity against *E. coli* comparable to that of *Streptococcus aureus*.

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**Table 3: Antibacterial activity of nickel (II) complexes 1 and 2.**

| Complexes (mM) | Diameter of inhibition zone (in mm) |
|---------------|----------------------------------|
|               | *Streptococcus aureus* | *E. coli* |
| [Ni(L1)2](ClO4)2(1) |                               |
| 5             | 6                               | 7         |
| 10            | 9                               | 11        |
| 15            | 12                              | 18        |
| [Ni(L1)2](ClO4)2(1) |                               |
| 5             | 4                               | 6         |
| 10            | 7                               | 10        |
| 15            | 13                              | 15        |

**Table 4: Antifungal activity of nickel (II) complexes 1 and 2.**

| Complexes (mM) | % Inhibition of spore germination |
|---------------|---------------------------------|
|               | *Aspergillus* sp. | *Penicillium* sp. |
| [Ni(L1)2](ClO4)2(1) |                       |
| 5             | 10                          | 12          |
| 10            | 13                          | 16          |
| 15            | 18                          | 20          |
| [Ni(L1)2](ClO4)2(1) |                       |
| 5             | 5                           | 8           |
| 10            | 7                           | 11          |
| 15            | 13                          | 18          |
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