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Synthesis, spectroscopic, electrochemical, magnetic properties and super oxide dismutase activity of nickel (II) complexes with unsymmetrical Schiff base ligands

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Abstracts: *Five new mixed-ligand nickel (II) complexes; viz; [Ni (BHM)(PMDT)]**1**; [Ni(BHM)(dien)] **2**; [Ni(BHM)(L^1)]**3**; [Ni(BHM)(L^2)] **4**, [Ni(BHM)(L^3)] **5**; where H_2BHM= N′-(1E)-(5-bromo-2-hydroxyphenyl) methylidene] benzoylhydrazide, PMDT= N,N,N’,N,″N″-Pentamethyldiethylenetriamine; dien= diethylenetriamine; L^1 = N,N- dimethyl-N’ (Pyrid-2-yl-methyl) ethylenediamine; L^2= N-methyl-N’-(pyrid-2-ylmethyl)ethylenediamine; L^3 = N,N-dimethyl-N’-(6-methyl)pyrid-2-ylmethyl) ethylenediamine, have been synthesized and characterized by using elemental analyses, FAB (fast atomic bombardment), magnetic measurements, electronic absorption , conductivity measurements, cyclic voltammetry (CV) and IR-spectroscopy . All the complexes yielded an irreversible couple that can be assigned to a $Ni^{II} \rightarrow Ni^{I}$ redox process.* Infrared spectra, ligand field spectra and magnetic susceptibility measurements agree with the observed octahedral environment. H_2BHM is a diprotic tridentate Schiff base ligand (ONO donor atom) whereas L^1-L^3 possessing N_3 coordination sites. *The SOD activities have been measured using alkaline DMSO as a source of superoxide radical (O_2^-) and nitro blue tetrazolium (NBT) as O_2^- scavenger.*

Keywords: *Nickel (II) complexes; Schiff bases; CV; UV-Visible; SOD activity.*

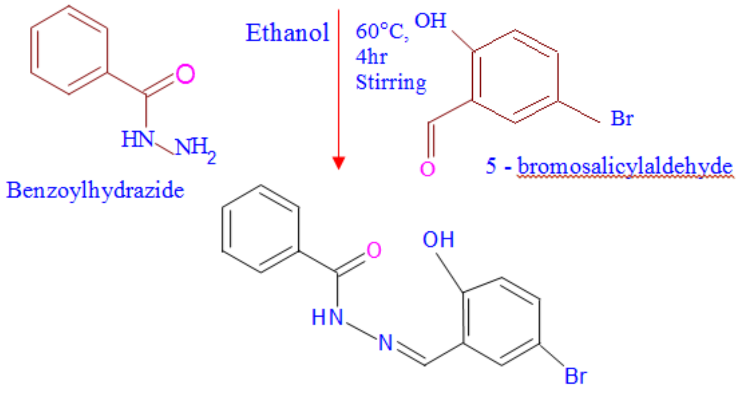
I. Introduction

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]. Nikel-contaning superoxide dismutase (NiSOD) has been isolated from several streptomyces species [4,5].The enzymatic activity of NiSOD [6], is as high has that of Cu-Zn SOD at about 10^9 $M^{-1}S^{-1}$ per metal center. 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 dismutase’s (SODs). These SODs disproportionate the toxic O_2^- radical to molecular oxygen and hydrogen peroxide [8].Oberley and Buettner [9] 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 SOD shows bio catalytic activity towards the dismutation of superoxide according to the following mechanism.

$$O_2^- + \text{Ni (II)} \longrightarrow O_2 + [Ni^I] \qquad (1)$$

$$O_2^- + [Ni^I] + 2H^+ \longrightarrow H_2O_2 + [Ni^{II}] \qquad (2)$$

Transition metal complexes have shown anti-inflammatory, antitumor, anticonvulsant, anti-diabetic, anticancer, anti-carcinogenic, anti-mutagenic and radio protectant activities in animal models of diseased states [10]. Asymmetric tridentate ligands have been extensively used in coordination chemistry [11] of nickel (II). The physical and chemical properties of transition metal complexes are greatly influenced by their structures and the coordination geometries by the ligand design. Transition metal complexes and Schiff bases derived from the reaction of aromatic aldehyde and aliphatic or aromatic amines represents an important series of widely studied organic ligands. Recently Han *et al.* [12] studied transition metal (Cu, Zn) complexes with a Schiff base (salicylideneglycine) and 1, 10- phenanthroline. Schiff bases L^1-L^3 are an important class of N donor ligands, particularly for the transition metals [13]. The presence of nickel in the search for stable, non-toxic, low molecular weight complexes of this metal that have SOD activity (functional models) and could be substituted for SOD in clinical applications with desirable qualities being cell permeability, low cost and non-immunogenicity. Depending on the metal at the active center, there are three general types of SOD enzymes, namely Cu, Zn-SOD and Mn-SOD in mammalian systems Ni-SOD and Fe-SOD in bacterial systems. These SODs disproportionate that toxic O_2^- radical to molecular oxygen and hydrogen peroxide [14]. In a previous paper [15-18], we have reported mixed-ligand Metal (II) complexes with tris (2-aminoethylamine), triethylenetetramine, 1, 10-phenanthroline, 2, 2’-bipyridine, ethylenediamine. This paper describes the synthesis, spectroscopic, electrochemical, magnetic properties and SOD activity of nickel (II) complexes namely [Ni (BHM)(PMDT)] **1**; [Ni(BHM)(dien)]**2**; [Ni(BHM)(L^1)]**3**; [Ni(BHM)(L^2)] **4**, [Ni(BHM)(L^3)] **5**. The superoxide dismutase activity reveals that these complexes catalyze the fast disproportionation of superoxide in DMSO solution. H_2BHM is a diprotic tridentate (Scheme 1) Schiff base ligand having ONO donor atom whereas L^1-L^3 possessing N_3 coordination sites.



Scheme 1-Synthesis of N’-(1E)-(5-bromo-2-hydroxyphenyl) methylidene]benzoylhydrazide

II. Experimental

2.1. Materials used for synthesis

Reagent grade chemicals were used for synthetic work. $CuCl_2.2H_2O$, 5-bromosalicylaldehyde, benzoyl hydrazine were purchased from Across Organics.N, N, N’, N,”N”-Pentamethyldiethylenetriamine; diethylenetriamine; Pyridine-2-carboxaldehyde, N-methylethylenediamine and its derivatives were purchased from S. D. Fine chemicals, India.

2.2. Instrumentation

Elemental analyses were performed on an ElementarVario EL III Carlo Erba 1108 analyser. FAB Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer data system using xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. UV-Visible recording spectrophotometer UV-160 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. 0.1 M $NaClO_4$ was used as supporting electrolyte and DMSO as nitrogen atmosphere. Molar conductivities of freshly prepared 2×10^{-3} M of acetonitrile solutions were measured on a Systronics conductivity TDS meter 308.

2.3 Superoxide dismutase activity

Superoxide dismutase (SOD) activities were evaluated using the following methods. The in *vitro* SOD activity was measured using alkaline DMSO as a source of superoxide radical (O_2^-) and nitrobluetetrazolium chloride (NBT) as O_2^- scavenger [19]. In general, 400µl sample to be assayed was added to a solution containing 2.1 ml of 0.2 M potassium phosphate buffer (pH 8.6) and 1ml of 56 µM of alkaline DMSO solution was added while string. The absorbance was then monitored at 540 nm against a sample prepared under similar condition except NaOH was absent in DMSO. A unit of superoxide dismutase (SOD) activity is concentration of complex, which causes 50% inhibition of alkaline DMSO mediated reduction of nitrobluetetrazolium chloride (NBT).

2.5Preparations

2.5.1 Synthesis of H_2BHM

The Schiff base H_2BHMwas synthesized by condensation of 5-bromo- salicylaldehyde and 2-benzoylhydrazide in 1:1 ratio. The reaction mixture in ethanol was stirred for 4 hour and then placed in freezer for 24 h. Yellow crystals were collected by filtration and washed with diethyl ether. Yield~85% Anal Calc. of $C_{14}H_{10}N_2O_2Br$ (H_2BHM): C, 52.63; H, 3.13; N, 8.77%. Found: C, 52.60; H 3.101%; N, 8.75%. FAB-mass (m/z), Calc, 319. Found: 318.

2.5.2 Synthesis of L^1-L^3

To N-methylethylenediamine (0.74 g, 10mmol) in methanol (20 ml) was added drop wise pyridine-2-carboxaldehyde (1.10 g, 10 mmol) in methanol (20 ml). The mixture was stirred overnight to get a bright yellow solution. To this was added $NaBH_4$ (0.57 g, 15 mmol), the solution stirred for another day and then rota evaporated to dryness. The resulting solid was dissolved in water and the organic layer was extracted with dichloromethane and dried with anhydrous sodium sulphate. The dichloromethane layer was rot evaporated to get N-methyl-N'-(pyrid-2-ylmethyl) ethylenediamine as a yellow oil. Yield: 1.15 g (70%). Anal. Calc for $C_9H_{14}N_3$ (L^1); C, 65.85; H, 8.53; N, 25.60% Found: C, 65.80; H, 8.50; N, 25.55%. FAB-mass (m/z) Calc. 164. Found: 165.The ligand L^2 was prepared by the methods adopted for the preparation of L^1 except that N, N-dimethylethylenediamine (0.88 g, 10 mmol) was used instead of N-methylethylenediamine. Yield: 1.45 g (80%). Anal. Calc. for $C_{10}H_{17}N_3$ (L^2); C, 67.03; H, 9.49; N, 23.46% Found: C, 67.00; H, 9.40; N, 23.40%. FAB-mass (m/z) Calc. 179. Found: 180.The ligand L^3 was prepared by the same method used for the preparation of L^1, except that N, N'-dimethylethylenediamine (0.88 g, 10 mmol) and 6-methylpyridine-2-corboxaldehyde (1.21 g, 10 mmol) were used instead of N-methylethylenediamine and pyridine-2-carboxaldehyde, respectively. Anal. Calc. for $C_{11}H_{19}N_3$ (L^3); C, 68.39; H, 9.84; N, 21.76% Found: C, 68.37; H, 9.82; N, 21.76%. FAB-mass (m/z) Calc. 193. Found: 194.

2.5.3Synthesis of [Ni (BHM)(PMDT)]1

To a solution of $NiCl_2$. $6H_2O$ (1.0 mmol, 0.24 g) in MeOH (20 ml), a MeOH solution of the dibasic tridentate Schiff base H_2BHM (1.0 mmol, 0.32 g) PMDT (1.0 mmol, 0.17 g) was added with stiring for 30 minute at 25°C. One minute later the red colour turned to pink red. The solution was filtered and the placed in freezer for 24 hour. The pink red crystals appeared after 3-2 days and were collected by filtration and washed with diethylethers. Single crystal suitable for X-ray analysis was dried in air at room temperature and stored in $CaCl_2$dseicator. Yield ~ 85%. Anal. Calc for $C_{23}H_{32}BrN_5NiO_2$ **1**: C, 43. 58; H, 4.58; N, 11.05%. Found: 43.53; H, 4.53; N, 11.00%. FAB-mass (m/z) Found: 635.97, Calc; 635.

2.5.4 Synthesis of [Ni(BHM)(dien)]2 and [Ni(BHM)(L^1)]3, [Ni(BHM) (L^2)]4,[Ni(BHM)(L^3)]5.

Complexes **2**, **3, 4, 5** were synthesized by similar method as complex **1** except dien and L^1, L^2, L^3 respectively in place of PMDT. Yield varied at the range 75-80%. Anal Calc. For $C_{18}H_{23}BrN_5NiO_2$**2**: C, 37.23; H, 3.96; N, 12.06. Found: 37.20; H, 3.94; N, 12.04%. FAB-mass (m/z) Found: 580.05; Calc. For $C_{14}H_{27}BrN_5NiO_2$**3:** C, 25.61; H, 4.11; N, 10.67%. FAB-mass (m/z) Calc. 655.88. Found 655. Anal. Calc. for $C_{20}H_{24}BrN_5NiO_2$**4**; C, 44.29; H, 4.42; N, 12.91%. Found: 44.25; H, 4.40; N, 12.90%. FAB-mass (m/z) Calc. 541.88. Found: 541. Anal. Calc. for $C_{25}H_{29}BrN_5NiO_2$**5**: C, 55.55; H, 5.02; N, 12.22%. Found C, 55.53; H, 5.00; N, 12.20% FAB-mass (m/z) Calc. 570.88. Found 570.

III. Results and discussion

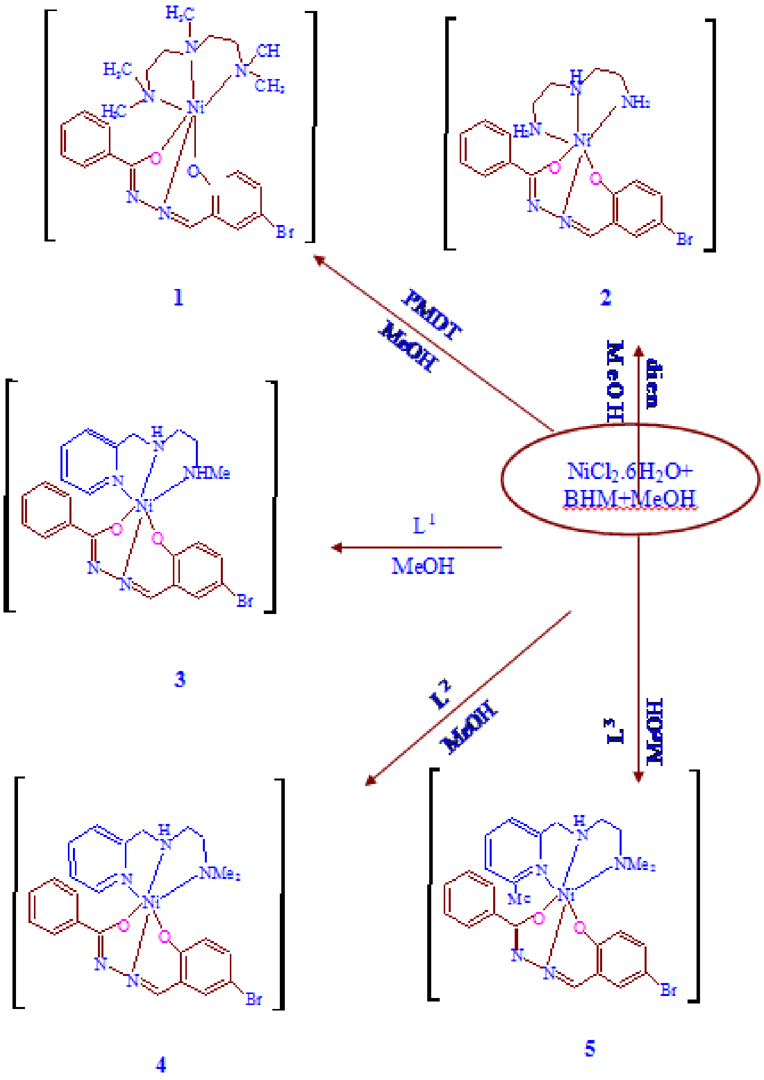
3.1 Synthesis and characterization

The synthetic procedures used to prepare octahedral nickel (II) complexes are straightforward .The present complexes prepared in high yield by reacting nickel (II) salt with N' (1E)-[(5-bromo-2-hydroxyphenyl)methylidene] benzohydrazide and nitrogenous bases in 1:1 molar ratio to give complexes of general composition [Cu(A)(B)]. The reactions proceed in the following manner (Scheme 2).

$$Ni^{2+} + A \rightarrow [Ni\ (A)\ (H_2O)] \qquad (3)$$

$$[N\ (A)\ (H_2O)] + B \rightarrow [Ni\ (A)\ (B)] + H_2O \qquad (4)$$

Where, A = BHM,B =PMDT/ dien/ L^1 -L^3.The obtained crystalline nickel (II) complexes are green (**1**), light green (**2** and **3**) red (**4** and **5**) stable in air, soluble in coordinating solvents such as DMF and DMSO, slightly soluble in ethanol and insoluble in water and most of organic solvents. H_2BHM is diprotic ligand typically act as tridentate, planar chelate ligand coordinating through phenolic atom, amide oxygen and imine nitrogen atom. There were characterized by microanalysis, FAB^+ spectrometry. All the complexes decompose between 175 and 292°C. The molar conductivities of DMF solutions of the complexes (~75 Ohm^{-1} cm^{-1}) indicate 1:1 electrolytes [20]. The μ_{eff} value 2.98 B.M. for **1**; 2.96 B.M. for **2**; 2.75 B.M. for **3**; 2.65 B.M. for **4**; 2.92 B.M. for **5** shows the presence of an octahedral environment around the nickel(II) and agrees with those previously reported[21-23] for other nickel(II) octahedral complexes.



Scheme 2- Synthesis of nickel (II) complexes 1-5.

3.3 *Spectroscopic studies*

The room temperature ligand field spectra (electronic spectra) of these complexes have been recorded in 100% DMSO solution. One representative ligand field spectra is shown in Fig.1. These complexes, very similar to one another, show three strong absorptions ($^3A_{2g}$ → $^3T_{2g}$, $^3A_{2g}$ → $^3T_{1g}$ (F), $^3A_{2g}$ → $^3T_{1g}$ (P)) and one weak absorption, characteristic of regular octahedral nickel (II) complexes [24]. Experimental absorption maxima corresponding to these three transitions are given in Table 1.The presence of distortions ($^3A_{2g}$ → $^3T_{2g}$, $^3A_{2g}$ → $3T_{1g}$ (F), $^3A_{2g}$ → $^3T_{1g}$ (P)) from the ideal octahedral geometry around the Ni (II). However, band shapes and positions (assigned on the basis of O*h* symmetry) and the ligand field parameter Dq ($^3A_{2g}$ → $^3T_{2g}$, lowest energy transition) and B (Racah parameter) values, calculated according to the averaged environment rules, are in the range found for octahedral coordinated nickel (II) ions [25]. The IR-spectra of these complexes show coordinated C=N bands in the range of 1,605-1,630 and of 470-495 $cm^{-1.}$ A strong band, observed at ca. 1,210-1,315 cm^{-1} is assigned to coordination through phenolic oxygen. Vibrations at ~460 weak (and expected below 400 cm^{-1}, out of our measuring limit) can be attributed to Ni-O and Ni-N vibrations [26].

3.4 *Electrochemistry*

Cyclic voltammograms of complexes **1-5** were recorded in DMSO, with sodium perchlorate as supporting electrolyte. The results are presented in Table 2. The electrochemical properties of metal complexes particularly, have been studied in order to minor spectral and structural changes accompanying electron transfer. These complexes **1-5**, a negative scan initiated at 1000mV in the potential range 1200 to –1000mV yielded an irreversible couple that can be assigned to a Ni^{II}→ Ni^{I}redox process [27]. The cathodic peak potential difference increases as the scan rate is increased. Constancy of $E^{o'}$ shows that in all the cases both peaks are complementary to each other. The peak current I_{pa}/I_{pc} is less than unity showing that the electron transfer reaction [28-30], is followed by a chemical reaction (EC mechanism).

3.5 Superoxide dismutase activity

SOD mimetic activities of **1-5** were measured with an indirect method in which alkaline DMSO served as the source for superoxide radicals. The SOD activity of **1** is graphically presented in Fig.2. The chromophore concentration value required to yield 50% inhibition of the reduction of NBT (IC_{50}) of the present complexes are found at the range55±3 μM are higher than the value exhibited by the native enzyme (IC_{50}=0.04 μmol dm^{-3}) (note that the smaller the IC_{50} value, the higher the SOD activity). These values are comparable with other reported [17, 18, 31, 32] values of nickel (II) (Table 3) , but are less active than the native SOD.. These higher values may be due to the strong ligand field created by the tridentate Schiff base ligand which opposes the interaction of the complexed nickel with the superoxide radical .The observed SOD values (IC_{50}) of nickel(II) complexes are in the order **1** > **3** > **5** > **4** > **2**. From this trend, it appears that inclusion of nitrogen donors reduces the SOD activity. The good activities of complexes may be attributed to the flexible H_2BHM and L^1-L^3 ligands which is able to accommodate the geometrical change from Ni^{II} to Ni^{I}, which are proposed to be easily substituted by the substrate O_2^- in the catalytic process, just like the O_2^-, in place of H_2O bound to copper site in the mechanism of dismutation of O_2^- by native SOD. Complex **1-5** show lower IC_{50}, and exhibits higher SOD activity than other mixed-ligand nickel complexes except for two systems including native SOD so for reported [32].

IV. Conclusion

[Ni(BHM)(PMDT)]**1**; [Ni(BHM)(dien)]**2**; [Ni(BHM)(L^1)]**3**; [Ni(BHM)(L^2)]**4**, [Ni(BHM)(L^3)]**5** were synthesized and characterized by using elemental analyses, FAB (fast atomic bombardment), magnetic measurements, electronic absorption , conductivity measurements, cyclic voltammetry (CV) and IR-spectroscopy. The IC_{50} values of nickel complexes (58 μmol dm^{-3} for **1**, 52 μmol dm^{-3} for **2**, 57 μmol dm^{-3} for **3,** 51 μmol dm^{-3} for **4**, 56 μmol dm^{-3} for **5**)) are higher than the value exhibited by the native enzyme (IC_{50}=0.04 μmol dm^{-3}) on a molar base .The elemental analysis and spectroscopic data shows that octahedral environment for the present complexes.

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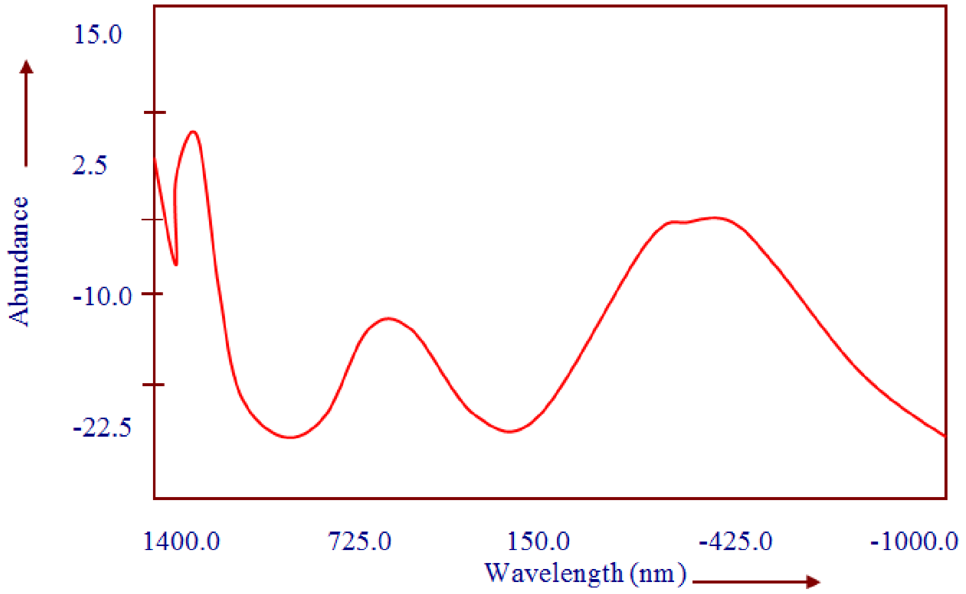

Fig. 1 UV-Vis spectrum (3 × 10^{-3}M) of Complex [Ni(BHM)(PMDT)]BF_4 **1** in DMSO

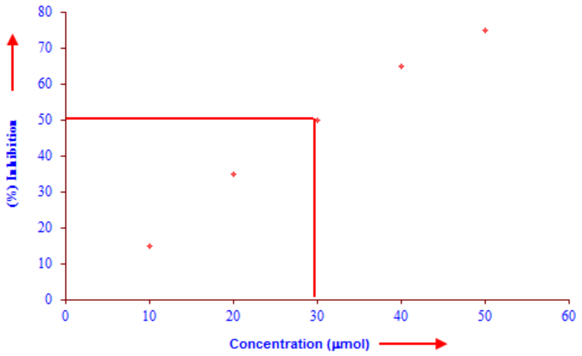

Fig. 2 Superoxide dismutase activity of $[Ni(BHM)(PMDT)]BF_4$**1**

Table 1 Absorption maxima, Dq, β, B and β° of the octahedral Ni(II) complexes (ν_{max} in cm^{-1})

Complex	$^3A_{2g}\rightarrow{}^3T_{1g}(\nu_1)$	$^3A_{2g}\rightarrow{}^3T_{1g}(F)(\nu_2)$	$^3A_{2g}\rightarrow{}^3T_{1g}(P)(\nu_3)$	ν_2/ν_1	Dq	β	B	β°
[Ni(BHM)(PMDT)]**1**	11630	18690	29400	1.60	1163	0.85	880	15
[Ni(BHM)(dien)] **2**	12500	19120	26180	1.53	1250	0.50	520	50
$[Ni(BHM)(L^1)]$ **3**	12270	18145	28145	1.47	1227	0.65	672	35
$[Ni(BHM)(L^2)]$ **4**	11460	17580	28450	1.53	1146	0.75	776	24
$[Ni(BHM)(L^3)]$ **5**	12790	18300	27960	1.43	1279	0.51	526	48

$15B = (\nu_2-\nu_1)-3\nu_1$; $\beta = B/B_0$ $[B_0$ (free ion) $= 1030]$; $\beta° = (1-\beta) \times 100$

Table 2 Cyclic voltammetry data for 1mM solution of the Ni (II) complexes in DMSO containing 0.1 $NaClO_4$ as supporting electrolytes.

Scan rate (m V/s)	E_{pc}(mV)	I_{pc}(μA	E_{pa}(mV	I_{pa}(μA	ΔE_p(mV	E'_0(mV	I_{pa}/I_{pc}(μA
[Ni(BHM)(PMDT)] 1							
100	-390	1.52	-228	0.62	162	-309	0.407
200	-419	2.18	-195	0.91	224	-307	0.417
[Ni(BHM)(dien)] **2**							
100	-389	1.90	-150	1.06	239	-269	0.557
200	-428	2.70	-114	1.51	314	-271	0.559
$[Ni(BHM)(L^1)]$ **3**							
100	-458	1.84	-162	1.18	296	-310	0.641
200	-474	2.63	-142	1.68	332	-308	0.638

$\Delta E_p = E_{pa} - E_{pc}$; $E_{\circ}' = (E_{pa} + E_{pc})/2$

Table 3 SOD activity of nickel (II) complexes by NBT method.

S.No.	Complexes	SOD activity (μ m)	Reference
1.	$[Ni(tren)(phen)](ClO_4)_2$	40	15
2.	$[Ni(tren)(bipy)](ClO_4)_2$	48	15
3.	$[Ni(SAA)(PMDT)].2H_2O$	43	26
4.	[Ni(SAA)](TPTZ)	58	32
5.	$[Ni(BPSE)](BF_4)$	65	17
6.	$[Ni(5\text{-}BST)(CH_3OH)]ClO_4$	48	17
7.	[Ni(BHM)(PMDT)] **1**	58	This work
8.	[Ni(BHM)(dien)]**2**	52	This work
9.	$[Ni(BHM)(L^1)]$**3**	57	This work
10.	$[Ni(BHM)(L^2)]$**4**	51	This work
11.	$[Ni(BHM)(L^3)]$**5**	56	This work

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