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Antioxidant Activity of Stannous Complexes Containing Amide Functionality

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ABSTRACT. Oxidative stress induced by free radicals is closely associated with aging and various degenerative diseases, prompting the search for efficient antioxidant systems. Metal chelation is known to enhance the biological activity of organic ligands by altering their electronic and redox characteristics. In this study, penta- and tetra-coordinated stannyl complexes of N,N′-bis(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L_1) and N-(pyridine-2-yl)picolinamide (HL_2) were synthesized and evaluated for their antioxidant activity using the DPPH free radical scavenging assay. Penta and tetra coordinated stannyl derivatives of *N, N′*-Bis(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L^1) and *N*-(pyridine-2-yl)picolinamide (HL^2) have been synthesized by the reported procedure and selected for the antioxidant studies. The free radical scavenging activity of ligands and the metal complexes have been analyzed by means of their interaction with stable free radical 1, 1-diphenyl-2-picrylhydrazyl (DPPH). The molecular structures and electronic properties of complexes and the mechanism involved in the scavenging activity were well analyzed by GAUSSIAN 03 suit of programs.

Keywords: Amide complexes, computational, DPPH, free radical

INTRODUCTION

Antioxidants have attracted significant attention in the field of medicinal chemistry due to their association with aging and degenerative diseases, stemming from the oxidation of biological components induced by free radicals (Karen et al., 2021). These highly reactive compounds possess an odd or unpaired electron, making them neutral, short-lived, unstable, and prone to pairing with an odd electron to achieve a stable configuration. Once these radicals form, they can initiate a chain reaction, attacking healthy cells and compromising their structure and function, potentially leading to impaired cell function or even cell death (Nisansala et al., 2025).

The fundamental characteristic of antioxidants lies in their capacity to capture and neutralize free radicals. In biological systems, highly reactive free radicals and oxygen species are abundant, originating from various sources. These radicals can potentially oxidize nucleic acids, proteins, lipids, or DNA, thereby triggering degenerative diseases. Serious conditions such as cancer and atherosclerosis have been associated with oxidative stress (Matthew et al., 2022). As a result, a crucial therapeutic strategy involves the supplementation of antioxidants to counteract these detrimental effects. There are many reports on the enhancement of pharmacological activities of compounds by metal chelation (Wardha et al., 2021; İlhami et al., 2022; Sadaf et al., 2021). Organostannous(IV) complexes are put to use in various fields (Rachana et al., 2023; Sharifah et al., 2021) and exhibit potential biological application such as insecticidal, fungicidal, and antitumor activities. N-, O-, and S Donor

ligands have been used to enhance the biological activity of organotin derivatives fields (Mohammad et al., 2004; Jason et al., 2000). Also organotin compounds with N- and O-donor ligands have widely been tested for their possible use in cancer chemotherapy (Zhou et al., 2005)

Antioxidants safeguard cellular components by neutralizing free radicals—unstable molecules with unpaired electrons capable of inflicting oxidative damage on DNA, proteins, and lipids. This neutralization transpires through several primary mechanisms like Hydrogen Atom Transfer (HAT) in which antioxidants donate a hydrogen atom (comprising both an electron and a proton) to free radicals. This donation stabilizes the free radicals, effectively halting the chain reactions that propagate oxidative stress. This mechanism is prevalent among phenolic antioxidants, such as vitamin E and polyphenols. Also the Single Electron Transfer (SET) mechanism involves antioxidants donating a single electron to free radicals, converting them into less reactive species.

Antioxidant properties of amide and stannous complexes reported earlier (Thomas et al., 2012;

Thomas et al., 2013). In the context mentioned above and in continuation to our work on metallic complexes of group 14 (Thomas et al., 2012; Thomas et al., 2013; Pardasani et al., 2004; Sharma et al., 2008, Sharma et al., 2005, Thomas et al., 2019), we analyzed the antioxidant activities of stannous complexes of pyridine amide ligands.

EXPERIMENTAL SECTION

Chemicals

2, 2-Diphenyl-1-picryl-hydrazyl (DPPH) was purchased from Sigma-Aldrich, India. The 1:1 stannous complexes derived from N, N'-bis(2-pyridyl)pyridine-2,6-dicarboxamide (H_2L^1) and N-(pyridine-2-yl) picolinamide (HL^2) have been used for antioxidant activity. Dried methanol is used as solvent. Complexes analyzed for antioxidant activity synthesized by the standard procedure (Thomas et al., 2019) and are listed below in **Figure 1**.

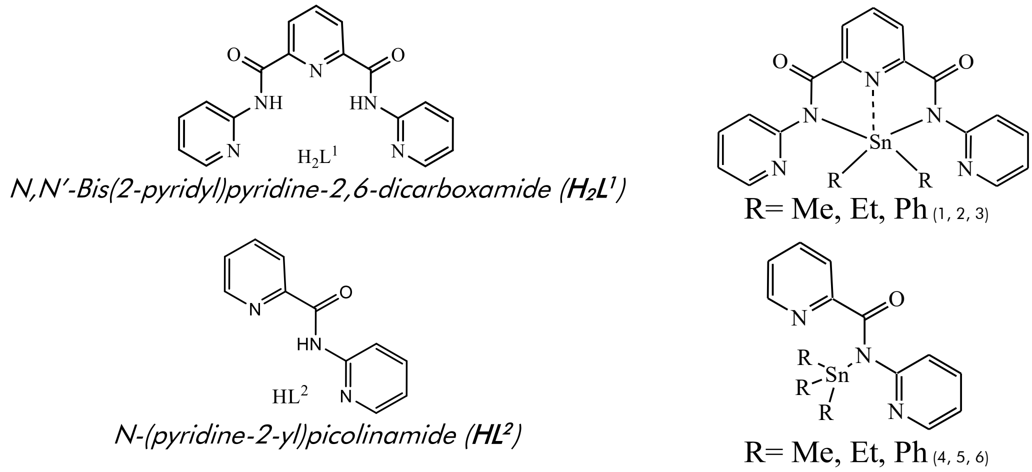
DPPH is identified as a stable free radical due to the effective delocalization of the spare electron across the entire molecule, preventing the molecules from undergoing dimerization, a common occurrence with most other free radicals. This delocalization also contributes to the development of a deep violet color, characterized by an absorption band in methanol solution centered around 515 nm. Upon mixing a solution of DPPH with that of a substance capable of donating a hydrogen atom, it undergoes a transformation into the reduced form, accompanied by the loss of the violet color, though a residual pale yellow color may persist due to the presence of the picryl group. Representing the DPPH radical by Z• and the donor molecule by AH, the primary reaction is where ZH is the reduced form and A• is free radical produced in first step.

$$Z^{\bullet} + AH = ZH + A^{\bullet}$$

The latter radical then undergoes further reactions which control the overall stoichiometry, that is, the number of molecules of DPPH reduced (decolorized) by one molecule of the reductant. The above reaction is therefore intended to provide the link with the reactions taking place in an oxidising system, such as the autoxidation of a lipid or other unsaturated substance.

Computational Details

Nowadays computational analysis is using to understand the mechanism of different reactions and properties of different reactants and products. Molecular geometries of all complexes under study have been carried out using Gaussian 03 suit of programs. Optimizations were done by the density functional theory (DFT) method. The density functional B3LYP can produce accurately and economically the heats of formation for compounds containing transition metal. (Chen et al., 1999; Mayhall et al., 2009). This method is combined with a mixed valence basis set of 631-g(d) for nonmetallic atoms and LanL2DZ for metallic atoms (Sakajiri et al., 2012). For essentially all levels, the minimum character of all optimized structures was verified by evaluation of the harmonic vibrational frequencies.



*N,N′-Bis(2-pyridyl)pyridine-2,6-dicarboxamide (**H_2L^1**)*

R= Me, Et, Ph (1, 2, 3)

*N-(pyridine-2-yl)picolinamide (**HL^2**)*

R= Me, Et, Ph (4, 5, 6)

Figure 1. Selected compound for the antioxidant activity

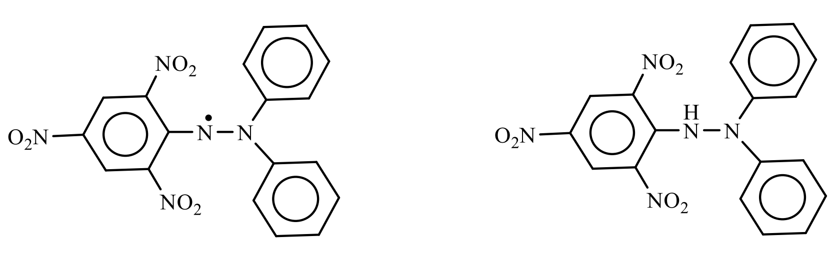


Figure 2. DPPH radical and reduced form

Antioxidant Activity

A stock solution of DPPH was made upto 250 mL standard flask by appropriate weighing of 0.05 g in methanol. Different concentrations of all compounds were prepared by dissolving appropriate amount to obtain 80, 60, 40, 20, 10 µg each. A volume of 2.5 mL of each solution was mixed with 2.5 mL of DPPH solution and kept for incubation in a dark place. The control solution was prepared by mixing methanol and DPPH radical solution (0.3 mL). The experiment was done in triplicate for each concentration for all ligand and their complexes. All the absorbance values at 515 nm were collated by using shimadzu spectrophotometer and tabulated where DPPH inhibition was determined. The radical scavenging activity percentage was expressed as a percentage, and calculated using the following formula:

$$RSC\ (\%) = 100 \times [(A_{blank}-A_{sample})]/\ A_{blank}$$

where A_{blank} is the absorbance of the control reaction (containing all reagents except the test compounds) and A_{sample} is the absorbance of the test compound.

The free radical scavenging capacity is evaluated by the inhibitory concentration 50 (IC_{50}), defined as the concentration of the substrate that causes 50% loss of the DPPH signal (colour) (i.e., that scavenge 50% of free radicals); the higher the antioxidant activity, the lower IC_{50}.

RESULTS AND DISCUSSION

The main area of interest was to see any modulation in antioxidant activity takes place upon chelation of chosen ligands with organotin. The DPPH assay was collected *via* spectral acquisition as opposed to just absorbance determinations at 515 nm. The inhibition studies began first with the use of positive control namely ascorbic acid. This showed a relatively complete inhibition of the DPPH solution around 95 % after 15 min incubation period. The percentage inhibitions of the samples are tabulated in **Table 1**.

Figure 2 mentions DPPH inhibition assay for the tested compounds at 80 µg/mL concentration. From the figure it is observed that methyl derivatives have higher inhibition than ethyl and phenyl derivatives. For the comparison of scavenging efficiency of amide ligands and tin derivatives, percentage inhibitions of the samples were plotted against concentration (**Figure 3 and Figure 4**).

The IC_{50} value is a crucial parameter for assessing antioxidant potency, with lower values signifying higher free radical scavenging ability. From the **Figure 3**, IC_{50} values were calculated and depicted in **Table 2**. Methyl derivative (1) has lowest IC_{50} value, which leads to higher antioxidant activity. The same procedure was followed for monoamide tin derivatives, whose percentage inhibitions x concentration graph are plotted in **Figure 4**.

Based on the figure, IC_{50} values were determined and are listed in **Table 2**. The DPPH scavenging activity rises almost linearly with increasing complex concentration, and at higher concentrations each complex outperforms its parent ligand in both series— an effect attributed to metal chelation, which amplifies antioxidant potency.

Table 1. Percentage inhibition of the tested samples

Compound	Concentration (µg/mL)					
	0	10	20	40	60	80
Ascorbic acid	0	95.65	96.02	96.94	97.17	97.98
H_2L^1	0	20.73	26.74	36.48	44.18	66.55
1	0	15.92	16.07	39.71	59.83	71.62
2	0	23.6	24.52	39.96	57.02	67.82
3	0	16.77	33.75	36.17	49.32	66.54
HL^2	0	2.27	32.95	37.13	46.76	65.29
4	0	8.55	37.65	42.37	62.71	66.54
5	0	17.07	29.53	42.42	56.57	67.82
6	0	21.7	36.01	40.25	55.64	68.15

1: Me, 2: Et, 3: Ph, 4: Me, 5: Et. 6: Ph

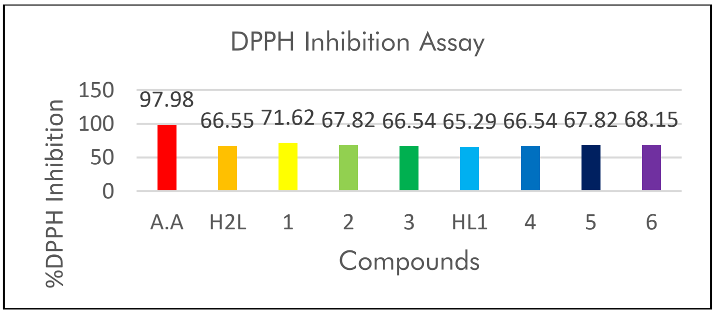


Figure 2. DPPH inhibition assay for the tested compounds at 80 µg/mL concentration;

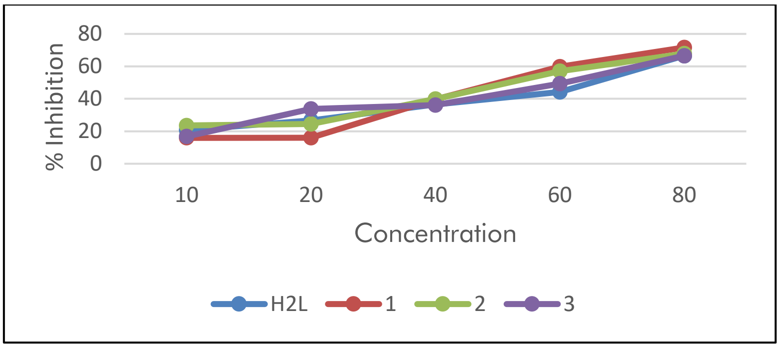


Figure 3. Percentage Inhibition x concentration plot for H_2L^1, 1, 2 and 3.

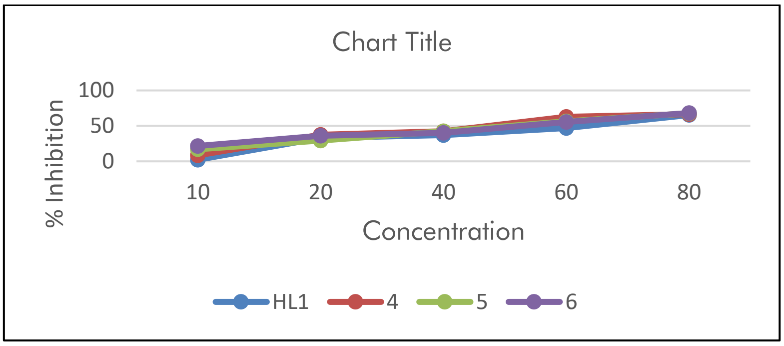


Figure 4. Percentage Inhibition x concentration plot for HL^2, 4, 5 and 6.

Table 2. IC_{50} values for the tested compounds

Compound	H_2L^1	1	2	3	HL^2	4	5	6
IC_{50} (μg/mL)	65.69	49.97	51.89	60.77	63.69	47.37	50.49	52.65

IC_{50} Value

The IC_{50} value, or half-maximal inhibitory concentration, is a key metric in antioxidant studies, particularly in DPPH assays. It represents the concentration of a substance required to reduce the initial concentration of DPPH radicals by 50%. A lower IC_{50} value indicates higher antioxidant efficiency, as less of the compound is needed to achieve significant radical scavenging.

As shown in **Table 2**, methyl-substituted derivatives exhibit the lowest IC_{50} values among the tested compounds, signifying superior free radical scavenging activity. This enhanced activity is likely due to the electron-donating nature of the methyl group, which increases electron density on the molecule, facilitating more effective neutralization of free radicals.

Overall, all synthesized derivatives demonstrated improved antioxidant activity compared to the parent ligand, with methylated complexes showing the most pronounced effect.

Computational Analysis

To establish the starting geometries of the compounds studied and the locations of the structures with minimum energy, a conformational analysis was performed. For all of the optimized structures, harmonic vibrational frequencies were calculated in order to verify the stationary points on the potential energy surfaces (PES).

The antioxidant properties of the molecules studied were described by calculating the numerical parameters (at 298 K) associated with their antioxidant mechanisms (described above), such as their bond dissociation enthalpies (BDE; the HAT mechanism), ionization potentials (IP; SET-PT mechanism) and the spin density (SD): For this we optimized all the possible pathways for the formation of dimethyl diamide derivative (1) so that set an ideal mechanism for the redox process, using mixed valence basis set by Gaussian 03 software could be proposed (Frisch et al; 1998). The bond dissociation energy of the molecule can be calculated by using the following equation (1):

$$BDE = H_r + H_H - H_m \qquad (1)$$

where H_r is the enthalpy of the radical, H_H is the enthalpy of the H atom, and H_m is the enthalpy of the parent molecule. The ionization potential of the molecule, can be calculated by using equation (2)

$$AIP = E_{cr} - E_m \qquad (2)$$

where E_{cr} is the total energy of the cation radical, and E_m is the total energy of the parent molecule.

BDE of the C-H bond in complex (**1**) is 111.40 kcal/mol which is much lower than IP of 167.65 kcal/mol. In addition, N-H bond dissociation energy of DPPHH is 172.22 kcal/mol, much higher than C-H

BDE of the selected compound and IP of DPPH$^-$ is 59.6 kcal/mol. These facts leads to the conclusion that electron transfer reaction is forbidden. Thus HAT mechanism is preferred for the antioxidant activity.

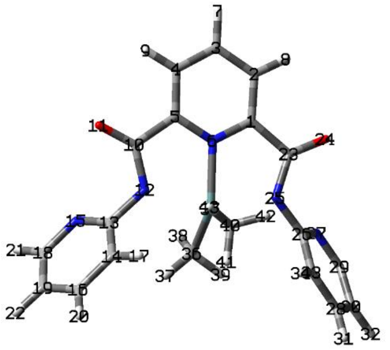
We optimized all other free radicals produced from other five reactions in the same level of theory as used for dimethyl derivative. The optimized energies of the radial derivative and spin densities of the selected atoms of radical (1r) from complex (1) are depicted in **Table 3**.

The spin density is another important parameter to characterize the stability of free radicals, because the energy of a free radical can be efficiently decreased if the unpaired electron is highly delocalized through the conjugated system. The more delocalized the spin density in the radical, the more readily it will be formed and thus lower will be the BDE. In the case of diamide derivatives (**1, 2** and **3**) both the side chain pyridine rings have same possibility for free radical attack due to their structural similarity. Spin density distribution in the free radicals (**1r**) and (**2r**) formed from (**1**) and (**2**) are shown in (**Figure 5**).

The spin density was delocalized slightly to the carbonyl group in case of radical (**1r**) which is absent in (**2r**) leading to more stabilized radical from complex (**1**). The BDE and SD data of (**2r**) and (**3r**) formed from diamide derivatives (**2**) and (**3**) are listed in **Table 5.** From the **Tables 4** and **5**, it is concluded that the free radical formed from the methyl derivative (**1r**) have lower bond dissociation energy and higher delocalization of spin density than the other two (**2r** and **3r**). Thus complex (**1**) is expected to show higher antioxidant activity which has been further supported by the experimental data.

Table 3. BDE and SD of free radical (1r) from Compound (1)

Atom number	BDE = 111.401 (Kcal/mol)
	SD
23	0.001036
24	0.006991
25	-0.003093
26	0.057630
27	0.090010
28	0.033576
29	0.820928
30	-0.011274
33	-0.029037



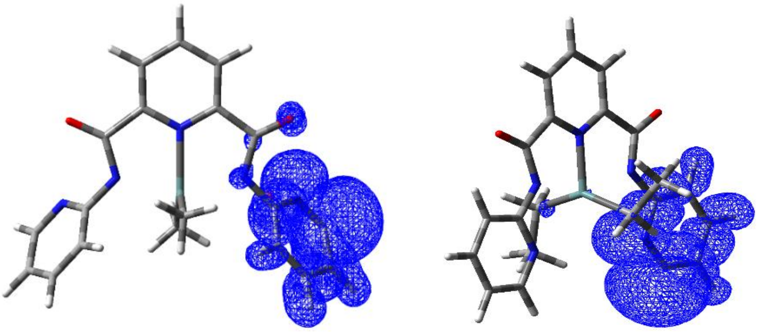
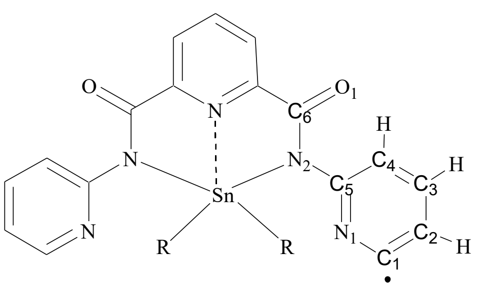


Figure 5. Spin density distribution on 1r and 2r



2: R = Et
3: R = Ph

Figure 6. Atomic numbering pattern in (2r) and (3r)

Table 4. BDE and SD of free radicals (2r) and (3r)

Atom number	Radical (**2**r) BDE = 113.5950 (kcal/mol)	Radical (**3**r) BDE = 117.9726 (kcal/mol)
C_6	0.000471	0.001156
O_1	0.005473	0.001645
N_2	-0.002091	-0.002653
N_1	0.052178	0.054250
C_3	0.038076	0.052142
C_2	0.068920	0.040865
C_1	0.869289	0.880277
C_4	-0.035402	-0.020397
C_5	-0.018337	-0.035693

In vitro assays, such as the DPPH radical scavenging test, have demonstrated that complex (1) exhibits a lower IC_{50} value than the free ligand, indicating a higher free radical scavenging capacity. This enhancement is attributed to the metal chelation effect, which facilitates electron donation and stabilizes radical intermediates. For instance, studies have shown that metal complexation significantly enhances the antioxidant activity of ligands, with complexes displaying improved radical scavenging abilities compared to their parent compounds.

Computational analyses support these findings by revealing that metal coordination alters the electronic structure of the ligand, leading to increased electron density and improved redox properties. This modification enhances the molecule's ability to neutralize free radicals effectively.

In the case of mono amide derivatives, there are two different sites for cleavage of C-H bond near nitrogen atom in the pyridine ring. This is analyzed by computing BDE for both the C-H bonds, the C-H bond that has lowest bond dissociation energy and higher delocalization of spin density of the free radical formed, will be more stable. To explore the reaction mechanism, we followed the same strategy which is used for diamide derivative. Mono amide triethyl derivative (**5**) was used as model reaction. Molecular electrostatic potential map (**Figure 6**) gave an insight into the most preferred center for the nucleophilic attack; its being the pyridine hydrogens adjacent to oxygen.

The BDE of both the free radicals produced from different sites were calculated and are represented in **Table 5.** From **Figure 8** and **Table 5,** it is observed that there is a slight delocalization of spin density towards oxygen (radical at C_1) which is absent in the case of other (radical at C_{16}).

Also BDE and energy values confirm that free radical formed at position C_1 is more stable. Keeping this in mind, other two free radicals formed from compound (**4**) and (**6**) are optimized and BDE calculated. Energy, SD and BDE (**Table 6**) calculations were also performed for other two compounds, ie., (**4**) and (**6**), and the respective data are tabulated in **Table 6.**

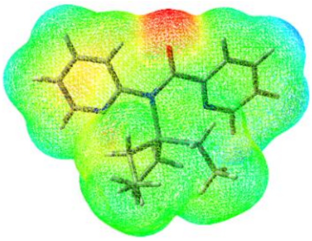


Figure 7. MESP plot for complex (5)

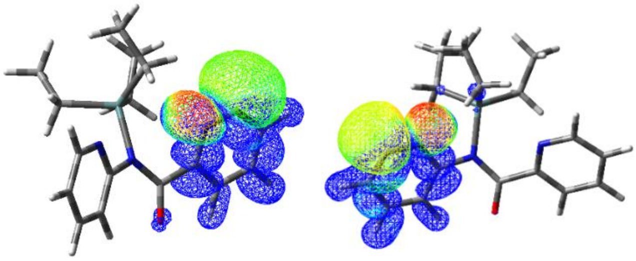


Figure 8. Spin density distribution in radical (5r) by attack on two sites (C_1 and C_{16})

Table 5. BDE and SD of free radical from compound (5) after two attack

Atom number	Radical at position C_1	Atom number	Radical at position C_{16}
	BDE = 111.919 (kcal/mol)		BDE = 112.389 (kcal/mol)
C_{11}	0.002058	C_{11}	0.000431
O_{12}	0.000073	O_{12}	-0.001963
C_1	0.878218	C_{14}	0.054321
C_2	-0.018816	C_{15}	-0.035769
C_3	0.039701	C_{16}	0.877041
C_4	-0.036585	C_{17}	0.040311
C_5	0.054981	N_{13}	0.000215

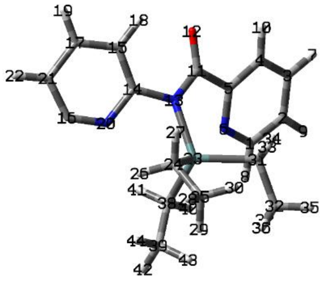
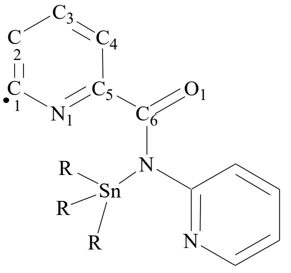


Table 6. Energy and SD of free radicals (4r) and (6r)

Atom number	Radical (**4r**) BDE = 110.461 (kcal/mol)	Radical (**6r**) BDE =114.725 (kcal/mol)
C_1	0.846512	0.885094
C_2	-0.012950	-0.009368
C_3	0.036052	0.032474
C_4	-0.031408	-0.027823
N_1	0.060861	0.057269
C_5	0.079062	0.080341
C_6	-0.002464	-0.001785
O_1	0.003923	0.003329



From BDE and spin density values, it is evident that free radical from methyl derivative have highest spin delocalization and lowest BDE. From the computational analysis, Hydrogen atom transfer mechanism have been proposed for the study. In this mechanism, the antioxidant scavenges free radicals by the transfer of an H-atom from the molecule to the free radical:

$$\mathrm{RSH} + \dot{\mathrm{X}} \longrightarrow \mathrm{R\dot{S}} + \mathrm{XH}$$

The produced radical can be undergoing reaction by further H-atom transfer or by reacting with another radical, thereby interrupting the initiation of a new chain of reaction.

CONCLUSIONS

The antioxidant activities of the stannous complexes of mono and diamide derivatives have successfully been evaluated experimentally and the mechanisms are well explained computationally. From theoretical analysis, Hydrogen Atom Transfer (HAT) mechanism is proposed for the antioxidant activity of complexes. Among all the complexes, methyl derivatives (**1**) and (**4**) have lower IC50 value and this is confirmed from the low BDE from computational calculations, suggesting high antioxidant activity of these compounds. All the stannous complexes have higher scavenging efficiency than the parent ligand indicating metal chelation to have a profound effect on biological performance.

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