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# Regiospecific *ortho*-Aromatic Hydroxylation via Cyclonickelation Using Hydrogen Peroxide and Other Oxygen Donors: Synthesis of Metalloazosalophens

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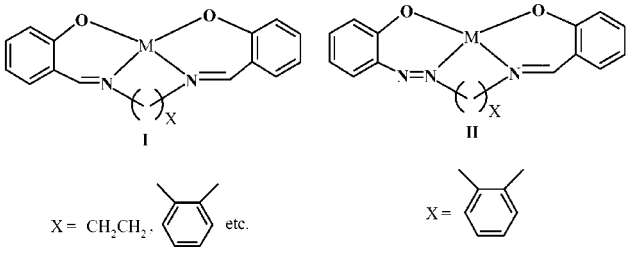
The new ligands *N*-[2-(arylazo)phenyl]salicylideneamine, $H_2L_{sal}$ [where H represents the dissociable protons upon complexation and aryl groups of $H_2L_{sal}$ are phenyl for $H_2L^1{}_{sal}$, *p*-methylphenyl for $H_2L^2{}_{sal}$, and *p*-chlorophenyl for $H_2L^3{}_{sal}$], were prepared by the reaction of 2-(arylazo)aniline, $H_2L$, with salicylaldehyde. $H_2L_{sal}$ ligands afforded stable ortho-metalated complexes, $(L_{sal})Ni$, upon treatment with $Ni(CH_3COO)_2{\cdot}4H_2O$. The dianionic $(L_{sal})^{2-}$ ligands bind $Ni^{II}$ in tetradentate (C,N,N,O) fashion in distorted square-planar geometry. Reaction of $(L_{sal})Ni$ with *meta*-chloroperbenzoic acid, *tert*-butyl hydroperoxide, or hydrogen peroxide furnished the metalloazosalophens, $(OL_{sal})Ni$, as a result of oxygen insertion into the Ni–C bond. The X-ray structures of $(L^1{}_{sal})Ni$ and $(OL^1{}_{sal})Ni$ were determined as representatives for unequivocal characterization. Treatment of $(OL^1{}_{sal})Ni$ with dilute $HClO_4$ liberated 2-(2-aminophenylazo)phenol, $H_2L^1OH$, which is an *ortho*-hydroxylated derivative of $H_2L^1$. The cyclic voltammograms of $(OL_{sal})Ni$ complexes display a reversible reductive response near –1.06 V vs. SCE.



## Introduction

The rich chemistry and usefulness of transition-metal complexes incorporating tetradentate (O,N,N,O) *salen* and its derivatives (also termed *metallosalens*, in general), **I**, have drawn interest in the areas of coordination chemistry,[1] catalysis,[2] and biochemistry research.[3] The challenge of the design and synthesis of new analogues of metallosalens prompted us to investigate the synthesis of azo-aldimine complexes as shown in **II**. These new complexes of type **II** are termed *metalloazosalophens* in this paper, in analogy to *metallosalophens*.

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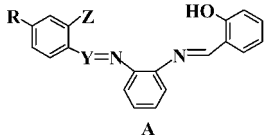
The preparation of metalloazosalophen complexes was contemplated after successful preparation of the new ligand, *N*-[2-(arylazo)phenyl]salicylideneamine, $H_2L_{sal}$, **1**, which comprises of two types of N-donor ligands: azo (–N=N–) and aldimine (–CH=N–). The $H_2L_{sal}$ ligand is similar to 1,2-*N*,*N*-disalicylidene phenylamine, **2** (commonly known as "salophen"), as shown in **A**, where Z = H and Y = N for $H_2L_{sal}$ while Z = OH and Y = CH for "salophen" ligands.




| No | Abbreviations of compounds | Y | Z |
|---|---|---|---|
| 1 | $H_2L_{sal}$ | N | H |
| 2 | salophen | CH | OH |
| 3 | $H_2OL_{sal}$ (azosalophen) | N | OH |

It was further realized that the substitution of Z (i.e., H) in $H_2L_{sal}$ by OH would afford the "azosalophen" analogue, $H_2OL_{sal}$, **3**, of "salophen" and the corresponding phenolato complex of this ligand would be the metalloazosalophens of type **II**.

Metal complexes incorporating azo ligands exhibited interesting electron-transfer properties, photophysical behavior, and biological activities.[4] Therefore, metalloazosalophens may not only possess the properties of enhanced performance compared with that of metallosalophens but also there are possibilities of new and interesting characteristics.

Metal-assisted chemical transformations have received attention in recent years because of their potential application in planned and directed organic synthesis for the preparation of target compounds which have not been prepared thus far by applying conventional synthetic protocols. Oxygenation (addition of an O atom in between a C–H bond) is highly desirable for functionalization of an aromatic ring. The regiospecificity of such an oxygenation has been appreciated for intended synthesis. One of the strategies towards regiospecific oxygenation is to activate a particular C–H bond through metal–carbon bond formation, followed by stoichiometric insertion of an oxygen atom within the metal–carbon bond. Therefore, the search for cheaper and easily available metal substrates and convenient reaction conditions to carry out such stoichiometric reactions, leading to the preparation of desired molecules, is important in terms of wide applicability and cost control. In this aspect it is worthwhile to mention that transition-metal-assisted aromatic hydroxylation has been recognized in essential biological reactions (e.g., oxygenase activity)[5] and in several complicated organic syntheses.[6]

Orthometalation is one of the processes of C–H bond cleavage (a precondition of C–H activation), which is reported amply in the cases of $Pd^{II}$ and $Pt^{II}$,[7] whereas it is scarce for $Ni^{II}$, the 3d congener of group 10 metals.[8] The usage of 3d metal ions in C–H activation has an edge over heavier members of group 10 metals in terms of cost effectiveness and availability.

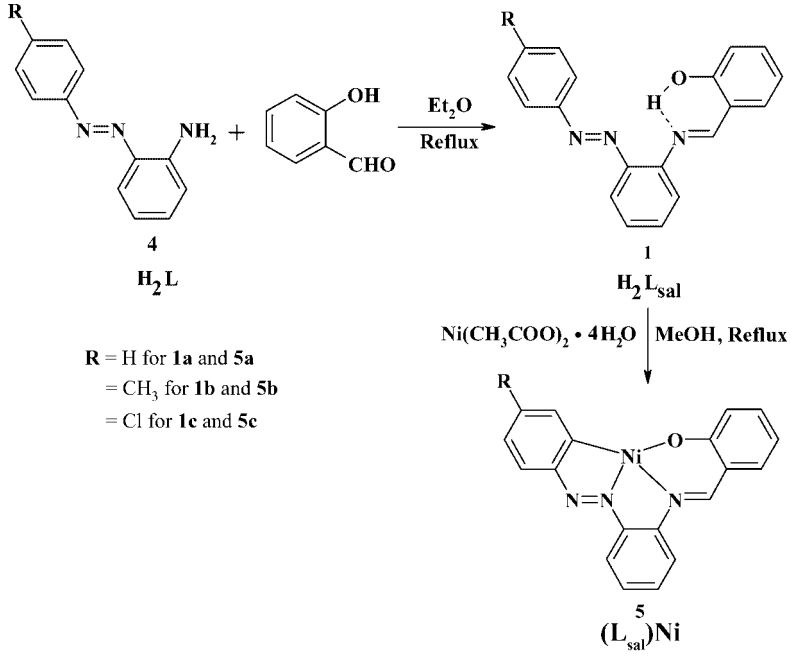
Studies on orthopalladation and orthoplatination in azobenzene-related ligands were initiated after the discovery of the "Cope complex".[9] Later, stoichiometric regiospecific *ortho*-hydroxylation of azobenzene derivatives by cyclopalladation were reported.[7c,7d] In contrast, the preparative method based on oxygen insertion into nickel–aryl bonds to give new aryl oxide compounds was reported to occur either with $N_2O$ or $O_2$.[10,11] This background information on metal-assisted routes to the oxy-functionalization of aryl rings provides a stimulus to contemplate the preparation of new metalloazosalophen complexes of type **II**.

Herein, we report the syntheses of new cyclometalated $Ni^{II}$ complexes incorporating the dianion of deprotonated $H_2L_{sal}$ and its conversion to the corresponding aryloxy form (metalloazosalophen complex of type **II**) by oxidation with *meta*-chloroperbenzoic acid (*m*CPBA), *tert*-butyl hydroperoxide (TBHP), or hydrogen peroxide ($H_2O_2$) by oxygen insertion into the nickel–carbon bond. TBHP and *m*CPBA are non-atom-efficient reagents as oxidants, whereas $H_2O_2$ is an atom-efficient oxidant since water is the sole by-product and it can therefore be classified as a green oxidant.[12] Furthermore, oxidation with aqueous $H_2O_2$ is cheap, safe, and easy to handle.[13] Also, this report may provide valuable information concerning the issue of organonickel-intermediate formation during the oxygenation of hydrocarbons on the nickel surface.[14] The synthesis of the specifically *ortho*-hydroxylated derivative 2-(2-aminophenylazo)phenol is also described.

## Results and Discussion

### Synthesis and Reactions

The strategy of the preparation of the target metalloazosalophen complexes of type **II** is based on three major steps: (i) synthesis of the precursor ligand, $H_2L_{sal}$, **1**, (ii) nickel–carbon bond formation by orthonickelation in $H_2L_{sal}$, and (iii) regiospecific oxygenation by way of oxygen insertion into the nickel–carbon bond of new orthonickelated complexes.




Scheme 1.

### *Syntheses of $H_2L_{sal}$ Ligands and Cyclonickelated ($L_{sal}$)Ni Complexes*

The azo-aldimine hybrid ligand *N*-[2-(arylazo)phenyl]salicylideneamine, $H_2L_{sal}$, **1**, was prepared by refluxing 2-(arylazo)aniline, $H_2L$, **4**, with salicylaldehyde in diethyl ether (Scheme 1). The solid, obtained upon evaporation of $Et_2O$, was used for further reactions without purification since the $^1$H NMR spectra (see later) exhibited good purity. The reaction of $H_2L_{sal}$ with nickel acetate tetrahydrate, $Ni(CH_3COO)_2{\cdot}4H_2O$, in refluxing methanol precipitated the orthonickelated green complex ($L_{sal}$)Ni, which was collected by filtration. The reaction is shown in Scheme 1. A further crop of product was isolated upon concentrating the filtrate. The total yield of ($L^1_{sal}$)Ni was 70%. Such a facile formation of cyclonickelated compounds upon treatment of $Ni(CH_3COO)_2{\cdot}4H_2O$ with tri- and bidentate azo ligands has not been reported so far.

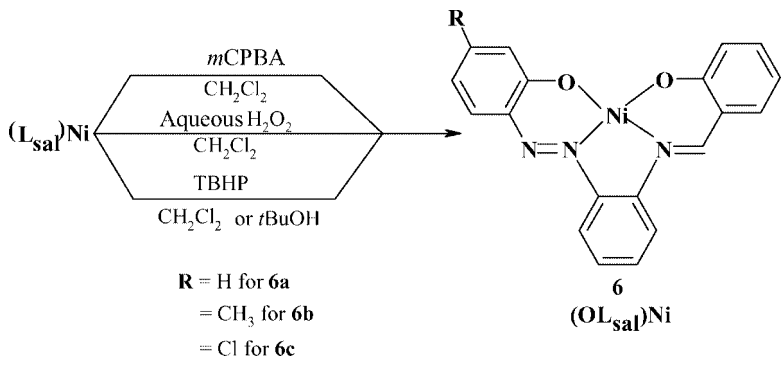
### *Synthesis of ($OL_{sal}$)Ni from ($L_{sal}$)Ni*

The new metalloazosalophen complexes, ($OL_{sal}$)Ni, were prepared by the highly selective metaloxylation[15] of ($L_{sal}$)Ni with the oxidants *m*CPBA, TBHP, or $H_2O_2$. The oxygen insertion into the Ni–C bond of ($L_{sal}$)Ni occurred upon treatment with *m*CPBA or TBHP in either aprotic (dichloromethane) or protic (*tert*-butyl alcohol) solvent at room temperature to afford the diamagnetic and electroneutral $Ni^{II}$ complex, ($OL_{sal}$)Ni (Scheme 2). Furthermore, the reaction of ($L_{sal}$)Ni in $CH_2Cl_2$ with aqueous $H_2O_2$ (a better choice of oxidant) furnished ($OL_{sal}$)Ni after stirring for a period longer than that of the reactions of *m*CPBA or TBHP with ($L_{sal}$)Ni. The formation of ($OL_{sal}$)Ni complexes from ($L_{sal}$)Ni was monitored spectrophotometrically up to the extent of 85% conversion for all the reactions. Considerable delay in metaloxylation with aqueous $H_2O_2$ can be attributed to the heterogeneous solvent mixture ($CH_2Cl_2/H_2O$). The $^1$H NMR spectrum of the crude product, as obtained after oxidation, exhibited good purity of ($OL_{sal}$)Ni indicating the likelihood of quantitative transformation [the spectrum of crude ($OL^1_{sal}$)Ni is available as Supporting Information, Figure S24]. Nevertheless, after every reaction, pure ($OL_{sal}$)Ni complexes were isolated in ca. 65% yield by employing a conventional purification procedure using the silica gel preparative TLC plate. Pure product separated well, leaving an unidentified material at the bottom. Since the $^1$H NMR spectrum of crude ($OL_{sal}$)Ni exhibited good purity,[16] the unidentified material was assumed to be the decomposition product of ($OL_{sal}$)Ni on the silica plate.

Oxygen insertions into Pd–C σ bonds of arylpalladium(II) complexes, induced by *m*CPBA, have been reported.[7c–7e] These reactions followed a straightforward second-order rate law (first order in both organopalladium substrate and in *m*CPBA).[7c–7e] The probable mechanism was proposed to follow a concerted one-step process leading to O insertion into the Pd–C bond on the basis of kinetic results.[7c–7e] Reaction of *m*CPBA with ($L_{sal}$)Ni was so fast that it could not be monitored spectrophotometrically for kinetic studies. The reaction completed to the extent of 86% within one minute. However, by analogy with the proposed mechanism of O insertion into the Pd–C bond,[7c–7e] the oxygen insertion into the Ni–C bond of ($L_{sal}$)Ni with *m*CPBA has been assumed to follow a similar concerted one-step process via formation of intermediate **I-A** as shown in Scheme 3.

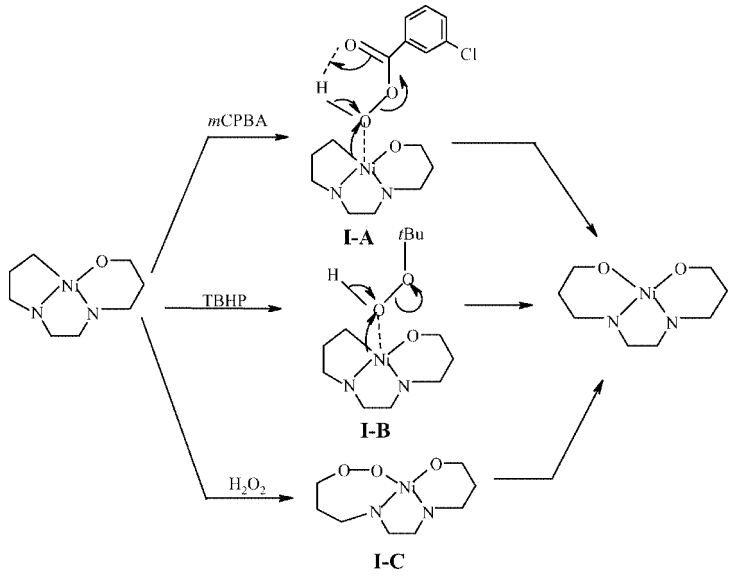
Realizing the fact that the Ni–C bond of ($L_{sal}$)Ni complexes is much more susceptible to metaloxylation compared with the Pd–C bond of orthopalladated complexes incorporating tridentate azo ligands,[7c–7e] oxidation was attempted with milder oxidizing agents such as TBHP or $H_2O_2$.

($L_{sal}$)Ni underwent oxygenation in the solvents *t*BuOH and $CH_2Cl_2$ with TBHP. The beneficial effect of protic solvents (*t*BuOH) in the metaloxylation of organopalladium complexes with TBHP has been reported.[17] Formation of alcohol oxide species (RHO–O) in protic solvents was believed to be the actual oxygen-donating agent in oxygen-transfer reactions by TBHP because the RHO–O species can provide an oxenoid oxygen atom and a neutral leaving group.[17] It is tempting to believe that TBHP reacts directly with ($L_{sal}$)Ni to afford ($OL_{sal}$)Ni, following a concerted one-step mechanism via formation of intermediate **I-B** as shown in Scheme 3. Nevertheless, formation of a ($L_{sal}$)$Ni^{IV}$=O intermediate[18] can not be excluded unequivocally though it is expected to be unstable for $Ni^{IV}$ ($d^n$ oxo system, $n > 4$),[19,7d] and a doubly bonded $Ni^{IV}$=O species is unlikely to be involved since it is better represented as either $Ni^{III}$–O· or $Ni^{IV}$–$O^-$.[18a]




Scheme 2.




Scheme 3.

Interestingly, ($L_{sal}$)Ni could be oxidized to ($OL_{sal}$)Ni upon treatment with aqueous $H_2O_2$. Although there are studies on the formation of peroxo-bridged dinuclear nickel complexes upon treatment of square-planar $Ni^{II}$ with $H_2O_2$, to the best of our knowledge, there is no report on oxygen insertion into a Ni–aryl bond with $H_2O_2$.[20] It was demonstrated previously that the oxygen insertion into a Ni–aryl bond had taken place upon reaction with air (i.e., $O_2$), where formation of a peroxo–nickel(II) intermediate was postulated in the reaction trajectory.[10d] By analogy, a mechanism of O insertion into the Ni–aryl bond of ($L_{sal}$)-Ni with $H_2O_2$ has been proposed to proceed via formation of the peroxo–$Ni^{II}$ intermediate **I-C** as shown in Scheme 3. It is worthwhile to mention that the ($L_{sal}$)Ni did not undergo metaloxylation upon prolonged bubbling of air into an acetonitrile solution of the complex.

### *Synthesis of 2-(2-Aminophenylazo)phenol, $H_2L^1OH$*

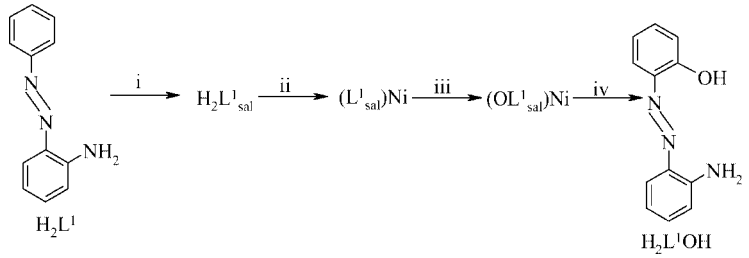
The new organic substrate $H_2L^1OH$ [a specifically *ortho*-hydroxylated phenyl derivative of 2-(phenylazo)aniline, $H_2L^1$] was obtained upon treatment of ($OL^1_{sal}$)Ni with dilute $HClO_4$ in acetonitrile solution. Demetalation and hydrolysis of the aldimine bond[21] occurred in acid medium, liberating the free 2-(2-aminophenylazo)phenol, $H_2L^1OH$, in good yield. Therefore in general, the new hydroxylated derivative, $H_2L^1OH$, was obtained in four steps as a result of regiospecific hydroxylation of 2-(phenylazo)aniline (Scheme 4). It is important to mention that the synthesis of authentic $H_2L^1OH$ has not been reported so far, so we cannot compare the merits of different procedures. It seems that the conventional synthetic protocol for the preparation of $H_2L^1OH$ would require carrying out several nonspecific reactions followed by careful work-up and separation of products after each step. The present reaction sequence is not associated with the formation of side products, and the chemicals used are cheap and easy to use.

## Spectral Characterization

The new ligands and complexes were characterized by UV/Vis, IR, $^1H$ NMR, and mass spectral studies.

### *UV/Vis and IR Spectra*

Dichloromethane solutions of $H_2L_{sal}$ ligands display an intense broad absorption near 316 nm in the UV/Vis spectra, characteristic of the overlapping n → π* transitions of azo (N=N) and aldimine (N=CH) functionalities.[22] The UV/Vis spectra of the green solutions of ($L_{sal}$)Ni in $CH_2Cl_2$ feature a relatively weak absorption band near 630 nm for




Scheme 4. (i) Salicylaldehyde in diethyl ether; (ii) $Ni(CH_3COO)_2{\cdot}4H_2O$ in refluxing methanol; (iii) *m*CPBA, TBHP, or $H_2O_2$ in $CH_2Cl_2$; (iv) dilute $HClO_4$ in $CH_3CN$.

the d–d transition,[23] while four absorption bands in the range 315 to 460 nm are assigned to MLCT transitions (N=N and C=N).[22] The absorption for the d–d transition in ($OL_{sal}$)Ni occurs at lower energy (640 nm) than that of the parent complex ($L_{sal}$)Ni. In addition, there are five MLCT absorptions in the range 340 to 520 nm in the UV/Vis spectra. Representative spectra of $H_2L^1_{sal}$, ($L^1_{sal}$)Ni, and ($OL^1_{sal}$)Ni are shown in Figure 1. The UV/Vis spectrum of $H_2L^1OH$ is different from that of either $H_2L^1_{sal}$ or $H_2L^1$ with an intense absorption at 450 nm in addition to the absorption at 318 nm due to the n → π* transition for the N=N functionality.

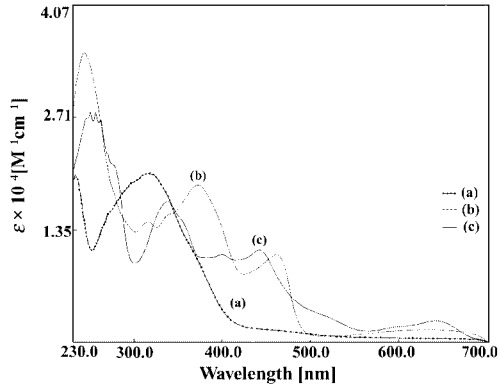



Figure 1. UV/Vis spectra of (a) $H_2L^1_{sal}$ ($C = 3.98 \times 10^{-5}$ M), (b) ($L^1_{sal}$)Ni ($C = 3.62 \times 10^{-5}$ M), and (c) ($OL^1_{sal}$)Ni ($C = 2.67 \times 10^{-5}$ M).

A sharp single band near 1614 $cm^{-1}$ in the IR spectra (KBr disc) of $H_2L_{sal}$ is characteristic of $\nu_{C=N}$.[22] The IR band near 1450 $cm^{-1}$ is assigned to $\nu_{N=N}$ by comparing the same band for other azo ligands and considering the extent of redshift upon coordination (see later).[23] The $\nu_{O-H}$ for the phenol OH of the salicylidene fragment is absent in conformity with the intramolecular hydrogen-bonded form of $H_2L_{sal}$. The $\nu_{C=N}$ and $\nu_{N=N}$ of ($L_{sal}$)Ni appear at slightly lower frequency (1605 and 1380 $cm^{-1}$, respectively) than those of the ligands, indicating coordination of aldimine (N=CH) and azo (N=N) nitrogen atoms. The $\nu_{C=N}$ and $\nu_{N=N}$ stretches of ($OL_{sal}$)Ni complexes appear near 1610 and 1375 $cm^{-1}$, respectively, consistent with azo (N=N) and aldimine (N=CH) coordination. The $\nu_{O-H}$ and $\nu_{NH_2}$ of $H_2L^1OH$ are observed at 3284 and 3407 $cm^{-1}$, respectively, in the IR spectrum while the $\nu_{N=N}$ appears at 1468 $cm^{-1}$.

### *$^1$H NMR Spectra*

The $H_2L_{sal}$ ligands display well-resolved $^1$H NMR spectra in $CDCl_3$, indicating good purity of products. The phenol OH of $H_2L_{sal}$ appears as a singlet near $\delta$ = 13.60 ppm which is absent in ($L_{sal}$)Ni and ($OL_{sal}$)Ni complexes, consistent with the phenolato coordination. The singlet resonance for the aldimine (N=CH) proton of the $H_2L_{sal}$ ligand near $\delta$ = 8.62 ppm is shifted marginally in the spectra of ($L_{sal}$)-Ni, observed in the range $\delta$ = 8.43 to 8.57 ppm. The resonance for the same aldimine proton of ($OL_{sal}$)Ni undergoes considerable upfield shift and appears within the range $\delta$ = 8.38 to 8.40 ppm. The $^1$H NMR spectral features for the aromatic protons of all the ligands and complexes are consistent with their structures. Data are collected in the Experimental Section.

The phenol OH proton and the $NH_2$ protons of $H_2L^1OH$ appear as singlets at $\delta$ = 12.84 and 6.19 ppm, respectively. Aromatic protons appear within the region $\delta$ = 6.75 to 7.76 ppm, in the sets of doublets at $\delta$ = 6.75, 7.67, and 7.76 ppm, triplets at $\delta$ = 6.83, 7.20, and 7.29 ppm, and a multiplet within the range $\delta$ = 6.99 to 7.04 ppm, with a total of eight equivalent protons. These spectral features are consistent with the structural formula. All the original $^1$H NMR spectra are given in the Supporting Information (Figures S18–S28).

### *Mass Spectra*

The electrospray mass spectrometry in $CH_2Cl_2$ solution (positive mode) was investigated for ($L^1_{sal}$)Ni and ($OL^1_{sal}$)-Ni as representatives. The mass spectra are consistent with the compositions and molecular masses. The major envelope, in each case, is satisfactorily simulated on the basis of formulae $C_{19}H_{13}N_3NiO$ and $C_{19}H_{13}N_3NiO_2$ for ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni, respectively.

### X-ray Structures of ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni

Unequivocal characterization of the cyclonickelated complex, ($L^1_{sal}$)Ni, and the corresponding oxygenated metalloazosalophen complex, ($OL^1_{sal}$)Ni, was performed by X-ray structure analysis. Figures 2 and 3 show the perspective views of ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni molecules, respectively. Selected bond lengths and angles are collected in Tables 1 and 2. The dianions $(L^1_{sal})^{2-}$ and $(OL^1_{sal})^{2-}$ bind $Ni^{II}$ in distorted square-planar geometry in both complexes. The structure of the ($L^1_{sal}$)Ni crystal did not refine well ($R_w$ = 17%) because of bad quality but it could be characterized unequivocally (in combination with $^1$H NMR and mass spectral results, vide infra). The accuracy of bond lengths, angles, and anisotropic parameters were satisfactory after several full-matrix least-square refinements. The Ni($N_2OC$) and Ni($N_2O_2$) coordination spheres of ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni are planar with mean deviations 0.006 and 0.003 Å, respectively. In the case of ($L^1_{sal}$)Ni, the Ni–C [1.984(10) Å] and Ni–O [1.820(6) Å] distances are comparable to reported values.[8d,22a]

The oxygen insertion into the nickel–carbon bond was confirmed as a result of the appearance of O2 in the molecular structure of ($OL^1_{sal}$)Ni. The Ni–N(azo) distance [Ni1–N2 1.8365(17) Å] of ($OL^1_{sal}$)Ni is shorter than the Ni–N-(aldimine) distance [Ni1–N3 1.8570(16) Å], indicating a stronger π-acidity of the azo (N=N) group relative to that of the aldimine (HC=N) group. Accordingly, the Ni1–O1 bond *trans* to N2 is longer [1.8420(15) Å] than the Ni1–O2 bond [1.8311(14) Å] *trans* to N1. However, the Ni–N and Ni–O distances are within the normal range.[22a] All the atoms in both the molecules ($L^1_{sal}$)Ni and ($OL^1_{sal}$)-Ni are coplanar with maximum deviations 0.08 and 0.75 Å, respectively, from the mean plane. Molecular stacking in

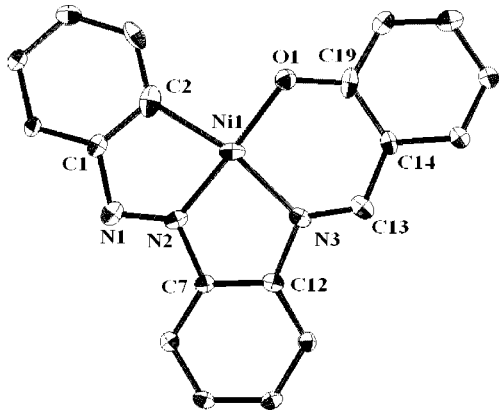



Figure 2. Perspective view (30% probability ellipsoids) of the molecular structure of $(L^1_{sal})Ni$ with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

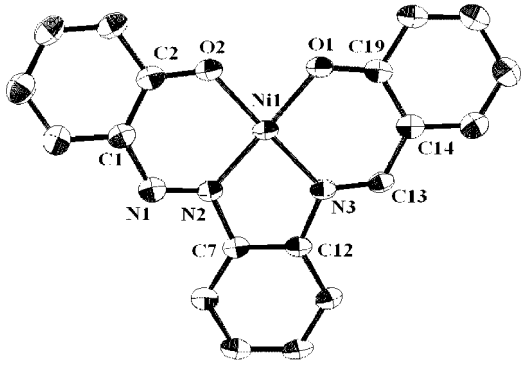



Figure 3. Perspective view (50% probability ellipsoids) of the molecular structure of $(OL^1_{sal})Ni$ with atom numbering scheme. The hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for compound $(L^1_{sal})Ni$.

| | | | |
|---|---|---|---|
| Ni1–O1 | 1.820(6) | N3–C12 | 1.426(11) |
| Ni1–N3 | 1.924(7) | N3–C13 | 1.291(12) |
| Ni1–N2 | 1.791(7) | C1–C2 | 1.374(13) |
| Ni1–C2 | 1.984(10) | C14–C19 | 1.449(13) |
| O1–C19 | 1.313(12) | C13–C14 | 1.411(13) |
| N1–N2 | 1.308(10) | C7–C12 | 1.405(12) |
| N1–C1 | 1.418(11) | | |
| N2–N1–C1 | 107.8(7) | Ni1–N3–C12 | 112.0(5) |
| O1–Ni1–N3 | 98.0(3) | N2–Ni1–C2 | 81.4(4) |
| O1–Ni1–C2 | 95.5(3) | N1–N2–C7 | 118.9(7) |
| N3–Ni1–C2 | 166.5(4) | N2–Ni1–N3 | 85.1(3) |

the crystal lattices exhibited that the planar molecules are held as *trans* pairs with Ni···Ni distances 3.199 and 3.136 Å in $(L^1_{sal})Ni$ and $(OL^1_{sal})Ni$, respectively. However, the crystal lattices feature slanted stacked arrangement of the *trans* pairs as shown in Figure 4 for $(L^1_{sal})Ni$. In contrast, the superposed molecules of Ni(salophen) are stacked infinitely in its crystal lattice,[24] unlike the Ni(azosalophen) analogue $(OL^1_{sal})Ni$.

Table 2. Selected bond lengths [Å] and angles [°] for compound $(OL^1_{sal})Ni$.

| | | | |
|---|---|---|---|
| Ni1–O1 | 1.8420(15) | N3–C12 | 1.421(3) |
| Ni1–N3 | 1.8570(16) | N3–C13 | 1.299(2) |
| Ni1–N2 | 1.8365(17) | C1–C2 | 1.432(3) |
| O1–C19 | 1.304(2) | C14–C19 | 1.424(3) |
| N1–N2 | 1.285(2) | C13–C14 | 1.410(3) |
| N1–C1 | 1.378(3) | C7–C12 | 1.393(3) |
| O2–C2 | 1.296(2) | Ni1–O2 | 1.8311(14) |
| N2–N1–C1 | 120.68(17) | Ni1–N3–C12 | 113.10(12) |
| O1–Ni1–N3 | 95.34(7) | N2–Ni1–O2 | 94.48(7) |
| O1–Ni1–O2 | 84.02(6) | N1–N2–C7 | 116.06(16) |
| N3–Ni1–O2 | 179.35(7) | N2–Ni1–N3 | 86.16(7) |
| Ni1–O2–C2 | 125.64(13) | | |

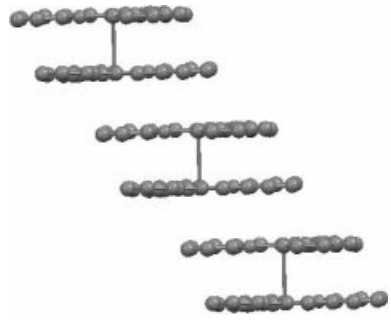


Figure 4. Partial packing of $(L^1_{sal})Ni$ showing the stairlike arrangement of planar molecules. The line between a pair indicates the weak Ni···Ni interaction at a distance of 3.199 Å.

## Electrochemistry

The cyclic voltammograms (Figure 5) of $(OL_{sal})Ni$ complexes display a reversible reductive response near –1.06 V vs. SCE in acetonitrile solution. This reductive response has been assigned to the $Ni^{II}/Ni^{I}$ couple according to Equation (1).

$$[(OL_{sal})Ni^{II}] + e^- \rightleftharpoons [(OL_{sal})Ni^{I}]^-$$

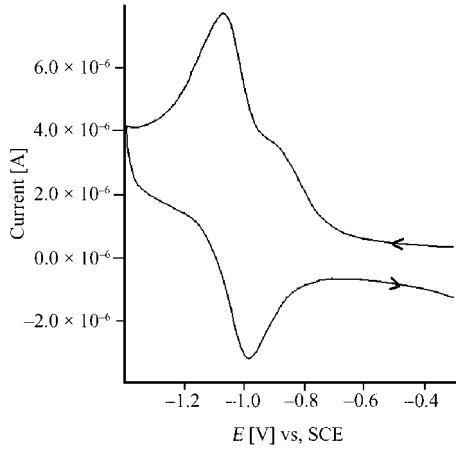



Figure 5. Cyclic voltammogram of $(OL^1_{sal})Ni$ in $CH_3CN$ and 0.1 M TEAP.

Similar reversible reduction for the [$Ni^{II}$(salen)] complex was reported to occur at –1.77 V vs. Ag/AgCl, and electrogenerated [Ni(salen)]$^-$ was demonstrated to be useful for the purpose of carrying out organic reactions.[25] Therefore, new electrogenerated [($OL_{sal}$)Ni]$^-$ may be active in a similar fashion as in the case of [Ni(salen)]$^-$.

## Conclusions

Unprecedented metalloazosalophen analogues of metallosalophens were prepared by way of oxygen insertion into the Ni–C bond of the precursor complex ($L_{sal}$)Ni. This facile Ni–C bond formation followed by oxygen insertion induced by peroxo reagents is a valuable report in terms of stoichiometric and catalytic oxo-functionalization of organic substrates. In addition to the synthesis of target metalloazosalophens, a synthetic procedure for the preparation of the regiospecifically hydroxylated derivative 2-(2-aminophenylazo)phenol, $H_2L^1OH$, has emerged to enhance the scope of further studies in this area. Although the O insertion into a Ni–C bond with $N_2O$[10a,10b] or $O_2$ (dioxygen)[10d] was documented previously, the use of peroxo reagents (especially $H_2O_2$) for O insertion into a Ni–C bond are described for the first time in this report. This information may provide important clues towards the design of appropriate organic substrates that are prone to form Ni–C σ bonds for oxygen insertion. The re-combination of $H_2L^1OH$ ($H_2LOH$, in general) with several other *ortho*-hydroxy aryl aldehydes are expected to afford a wide range of free azosalophen ligands. The metalloazosalophens derived from there may be useful for obtaining models of potential catalysts.

## Experimental Section

**Materials:** The solvents used in the reactions were of reagent grade obtained from E. Merck, Kolkata, India and were purified and dried by reported procedures.[26] Nickel acetate, salicylaldehyde, $HClO_4$, and $H_2O_2$ (6% in aqueous solution) were purchased from E. Merck, Kolkata, India. *m*CPBA (≈70%) and TBHP (≈70% in aqueous solution) were obtained from Aldrich, USA and were used as received (the activity of *m*CPBA was determined iodometrically before use). Silica gel G with binder was used for thin layer chromatography. 2-(Arylazo)aniline ligands were prepared according to the procedure described earlier.[23]

**Physical Measurements:** UV/Vis spectra were recorded with a Shimadzu UV-2401 PC spectrophotometer. IR spectra were obtained with a Perkin–Elmer L120–00A FTIR spectrophotometer (4000–225 $cm^{-1}$) using KBr pellets. Elemental analyses (C, H, N) were performed with a Perkin–Elmer 240C elemental analyzer. NMR spectra were recorded with Bruker Avance RPX 500 MHz and Bruker Avance DPX 300 spectrometers in $CDCl_3$ using TMS as the internal standard. Electrochemical measurements were made under dinitrogen using a PAR model VERSASTAT-II potentiostat. A glassy-carbon working electrode, platinum-wire auxiliary electrode, and standard saturated calomel electrode (SCE) were used in a three-electrode configuration. Tetraethyl perchlorate (0.1 M) was used as supporting electrolyte. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. ESI mass spectra were recorded with a micromass Q-TOF mass spectrometer (serial no. YA 263).

**Syntheses of Ligands, $H_2L_{sal}$ (1)**

The three ligands $H_2L^1_{sal}$, $H_2L^2_{sal}$, and $H_2L^3_{sal}$ were prepared by a similar procedure. The detailed procedure for the preparation of $H_2L^1_{sal}$ is given.

***N*-[2-(Phenylazo)phenyl]salicylideneamine, $H_2L^1_{sal}$ (1a):** To a solution of 2-(phenylazo)aniline, $H_2L^1$, (100 mg, 0.50 mmol) in diethyl ether (40 mL) was added a little excess of salicylaldehyde (67 mg, 0.55 mmol). The resulting mixture was then heated to reflux for 8 h. The solvent was then evaporated in vacuo for 2 h to obtain the partially solid mass after removal of excess salicylaldehyde. It was further kept in a vacuum desiccator for 24 h to obtain the solid product of $H_2L_{sal}$. Isolated yield: 145 mg (95%). M.p.: 96 °C. $C_{19}H_{15}N_3O$ (301): calcd. C 75.74, H 4.98, N 13.95; found C 75.90, H 4.75, N 13.85. IR (KBr): $\tilde{\nu}$ = 1614 (C=N), 1450 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.91 (t, 1 H), 7.06 (d, 1 H), 7.33 (t, 1 H), 7.37 (d, 3 H), 7.46 (d, 1 H), 7.48–7.52 (m, 3 H), 7.78 (dd, 1 H), 7.92–7.95 (m, 2 H), 8.61 (s, 1 H), 13.59 (s, 1 H, OH) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 316 (18890), 232 (18750) nm.

***N*-[2-(*p*-Tolylazo)phenyl]salicylideneamine, $H_2L^2_{sal}$ (1b):** Isolated yield: 141 mg (95%). M.p.: 80 °C. $C_{20}H_{17}N_3O$ (315.37): calcd. C 76.19, H 5.39, N 13.33; found C 76.00, H 5.50, N 13.25. IR (KBr): $\tilde{\nu}$ = 1615 (C=N), 1452 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 2.42 (s, 3 H, *p*-$CH_3$), 6.93 (t, 1 H), 7.06 (d, 1 H), 7.31 (d, 2 H), 7.36 (t, 1 H), 7.46 (d, 1 H), 7.38–7.40 (m, 3 H), 7.51 (t, 1 H), 7.78 (d, 1 H), 7.85 (d, 2 H), 8.63 (s, 1 H), 13.59 (s, 1 H, OH) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 325 (26570), 233 (27114) nm.

***N*-[2-(*p*-Chlorophenylazo)phenyl]salicylideneamine, $H_2L^3_{sal}$ (1c):** Isolated yield: 137 mg (95%). M.p.: 92 °C. $C_{19}H_{14}ClN_3O$ (335.79): calcd. C 67.95, H 4.17, N 12.51; found C 67.80, H 4.15, N 13.90. IR (KBr): $\tilde{\nu}$ = 1617 (C=N), 1452 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.94 (t, 1 H), 7.07 (d, 1 H), 7.35 (t, 1 H), 7.40–7.42 (m, 3 H), 7.49 (d, 2 H), 7.57 (t, 1 H), 7.79 (d, 1 H), 7.90 (d, 2 H), 8.65 (s, 1 H), 13.58 (s, 1 H, OH) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 322 (24980), 233 (22250) nm.

**Syntheses of Complexes, ($L_{sal}$)Ni (5)**

All three complexes ($L^1_{sal}$)Ni, ($L^2_{sal}$)Ni, and ($L^3_{sal}$)Ni were prepared by a similar procedure. The detailed procedure for the preparation of ($L^1_{sal}$)Ni is given.

**($L^1_{sal}$)Ni (5a):** To $H_2L^1_{sal}$ (120 mg, 0.40 mmol) dissolved in methanol (40 mL) was added $Ni(OAc)_2{\cdot}4H_2O$ (100 mg, 0.40 mmol). The mixture was then heated to reflux for 12 h to obtain a green precipitate of ($L^1_{sal}$)Ni. The solid product was then filtered and washed with water and a little ethanol. The volume of the filtrate was reduced to ca. 20 mL and kept in a beaker covered with a watch glass. After 12 h a further crop of product was collected by filtration. All the product was taken together and recrystallized from dichloromethane/petroleum ether to obtain pure ($L^1_{sal}$)Ni. Yield: 99.82 mg (70%). $C_{19}H_{13}NiN_3O$ (358.04): calcd. C 63.74, H 3.63, N 11.74; found C 63.70, H 3.65, N 11.80. IR (KBr): $\tilde{\nu}$ = 1605 (C=N), 1389 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.57 (t, 1 H), 6.98 (d, 1 H), 7.12–7.14 (m, 1 H), 7.23–7.27 (m, 2 H), 7.39–7.43 (m, 3 H), 7.56 (d, 1 H), 7.67 (d, 1 H), 8.57 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 630 (1740), 460 (10867), 371 (19378), 341(15800), 315 (14820), 242 (35480) nm. ESI-MS: *m*/*z* = 358.

**($L^2_{sal}$)Ni (5b):** This complex was prepared by following a similar procedure as that described for ($L^1_{sal}$)Ni, using ligand $H_2L^2_{sal}$ in place of $H_2L^1_{sal}$. Yield: 89.91 mg (60%). $C_{20}H_{15}NiN_3O$ (372.07): calcd. C 64.59, H 4.03, N 11.29; found C 64.67, H 4.00, N 11.35.

IR (KBr): $\tilde{\nu}$ = 1605 (C=N), 1374 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 2.31 (s, 3 H, *p*-$CH_3$), 6.57 (t, 1 H), 6.90 (d, 1 H), 7.02 (d, 1 H), 7.14–7.19 (m, 3 H), 7.24–7.27 (m, 1 H), 7.38 (t, 1 H), 7.56 (d, 2 H), 7.65 (d, 1 H), 8.57 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 631 (2829), 460 (19244), 378 (30420), 340 (24340), 319 (20690), 243 (58351) nm.

**($L^3_{sal}$)Ni (5c):** This complex was prepared by following a similar procedure as that described for ($L^1_{sal}$)Ni, using ligand $H_2L^3_{sal}$ in place of $H_2L^1_{sal}$. Yield: 97.84 mg (62%). $C_{19}H_{12}ClNiN_3O$ (392.49): calcd. C 58.13, H 3.05, N 10.70; found C 58.18, H 3.00, N 10.75. IR (KBr): $\tilde{\nu}$ = 1606 (C=N), 1372 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.55 (t, 1 H), 6.93 (d, 1 H), 7.05 (d, 1 H), 7.12 (d, 1 H), 7.15 (t, 1 H), 7.22–7.29 (m, 2 H), 7.43 (t, 1 H), 7.51 (d, 2 H), 7.62 (d, 1 H), 8.43 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 634 (1990), 455 (13413), 372 (24432), 338 (18393), 314 (17445), 243 (44052) nm.

**Syntheses of Complexes, ($OL_{sal}$)Ni (6)**

All complexes were prepared by a similar procedure. The details for the preparation of ($OL^1_{sal}$)Ni are given.

**($OL^1_{sal}$)Ni (6a):** A solution of *m*CPBA (143 mg, 0.824 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of ($L^1_{sal}$)Ni (100 mg, 0.279 mmol) in dichloromethane (25 mL). Immediately the color of the solution began to change from deep green to olive green. The stirring was continued for 10 min. Evaporation of the solvent in vacuo afforded a greenish solid mass. The solid mass was washed with diethyl ether (3 × 5 mL). The product was then purified by preparative TLC using a benzene/acetonitrile (19:1) mixture as eluent. Upon evaporation of the solvent, the pure target complex ($OL^1_{sal}$)Ni was obtained. Isolated yield: 67.90 mg (65%). $C_{19}H_{13}NiN_3O_2$ (374.04): calcd. C 61.01, H 3.47, N 11.23; found C 60.95, H 3.43, N 11.20. IR (KBr): $\tilde{\nu}$ = 1614 (C=N), 1376 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.68 (t, 1 H), 6.84 (t, 1 H), 7.15 (d, 1 H), 7.24–7.27 (m, 3 H), 7.33–7.40 (m, 4 H), 7.76–7.72 (m, 2 H), 8.17 (d, 1 H), 8.40 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 640 (3846), 442 (15468), 399 (14715), 356 (19842), 340 (23520), 255 (38277) nm. ESI-MS: *m*/*z* = 374.

**($OL^2_{sal}$)Ni (6b):** Complex ($OL^2_{sal}$)Ni was prepared using ($L^2_{sal}$)Ni in place of ($L^1_{sal}$)Ni. Isolated yield: 68 mg (65%). $C_{20}H_{15}NiN_3O_2$ (388.07): calcd. C 61.90, H 3.86, N 11.00; found C 61.46, H 3.92, N 10.91. IR (KBr): $\tilde{\nu}$ = 1611 (C=N), 1376 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 2.28 (s, 3 H), 6.67 (t, 2 H), 7.07 (s, 1 H), 7.14 (d, 1 H), 7.37 (t, 4 H), 7.62 (d, 1 H), 7.72 (d, 1 H), 8.17 (d, 1 H), 8.40 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 631 (3101), 441 (12902), 402 (12603), 356 (15848), 340 (17860), 261 (29455) nm.

**($OL^3_{sal}$)Ni (6c):** Complex ($OL^3_{sal}$)Ni was prepared using ($L^3_{sal}$)Ni in place of ($L^1_{sal}$)Ni. Isolated yield: 63 mg (60%). $C_{19}H_{12}ClNiN_3O_2$ (408.49): calcd. C 58.13, H 2.93, N 10.28; found C 57.91, H 2.82, N 10.32. IR (KBr): $\tilde{\nu}$ = 1611 (C=N), 1374 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.70 (t, 1 H), 6.83 (d, 2 H), 7.12 (d, 2 H), 7.33–7.42 (m, 4 H), 7.73 (t, 2 H), 8.15 (d, 1 H), 8.38 (s, 1 H) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 638 (4209), 441 (7795), 350 (9110), 339 (10340), 2276 (11872), 248 (14061) nm.

**Reaction of ($L_{sal}$)Ni with TBHP:** The reaction of ($L^1_{sal}$)Ni is given in detail. To a stirred solution of ($L^1_{sal}$)Ni (50 mg, 0.140 mmol) in dichloromethane or *tert*-butanol (25 mL) was added dropwise TBHP (0.30 mL, 2.76 mmol). Immediately the color of the solution began to turn from deep green to olive green. The stirring was continued for 30 min. Evaporation of the solvent in vacuo afforded a greenish solid mass. The solid mass was washed with water and diethyl ether. The product was then purified by preparative TLC using a benzene/acetonitrile (19:1) mixture as eluent. Upon evaporation of the solvent, the pure target complex ($OL^1_{sal}$)Ni was obtained. Isolated yield: 34.14 mg (65%).

**Reaction of ($L_{sal}$)Ni with $H_2O_2$:** The reaction of ($L^1_{sal}$)Ni is given in detail. To a stirred solution of ($L^1_{sal}$)Ni (30 mg, 0.083 mmol) in dichloromethane (15 mL) was added dropwise 6% $H_2O_2$ (10 mL). The color of the organic layer began to turn from deep green to olive green after 20 min. The stirring was continued for 1.5 h. Evaporation of the organic solvent, after separation from the aqueous layer, in vacuo afforded a greenish solid mass. The solid mass was washed with water. The product was then purified by preparative TLC using a benzene/acetonitrile (19:1) mixture as eluent. Upon evaporation of the solvent, the pure target complex ($OL^1_{sal}$)Ni was obtained. Isolated yield: 20.5 mg (65%).

**Preparation of 2-(2-Aminophenylazo)phenol, $H_2L^1OH$, from ($OL^1_{sal}$)Ni:** To an acetonitrile solution (20 mL) of ($OL^1_{sal}$)Ni (200 mg, 0.534 mmol) was added dropwise 0.1 M $HClO_4$ (5 mL) with continuous stirring. The color of the solution changed from olive green to yellow. Evaporation of the solvent in vacuo afforded a yellow solid mass. The solid mass was washed (3×) with water and extracted with dichloromethane and purified by preparative TLC using petroleum benzene as eluent. Upon evaporation of the solvent, the pure target compound $H_2L^1OH$ was obtained. Yield: 56.5 mg (50%). $C_{12}H_{11}N_3O$ (213.24): calcd. C 67.60, H 5.16, N 19.71; found C 67.65, H 5.06, N 19.65. IR (KBr): $\tilde{\nu}$ = 3407 ($NH_2$), 3284 (OH), 1468 (N=N) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 6.19 (s, $NH_2$), 6.75 (d, 1 H), 6.83 (t, 1 H), 7.04–6.99 (m, 2 H), 7.20 (t, 1 H), 7.29 (t, 1 H), 7.67 (d, 1 H), 7.76 (d, 1 H), 12.84 (s, OH) ppm. UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, $M^{-1}cm^{-1}$) = 450 (10566), 318 (13124), 230 (10646) nm.

**X-ray Crystallography:** Suitable X-ray-quality crystals of **5a** (0.08 × 0.23 × 0.25) and **6a** (0.13 × 0.13 × 0.20) for X-ray studies were grown by slow evaporation of a dichloromethane solution of **5a** and a dichloromethane/acetonitrile solution of **6a**. Data were collected with a Bruker SMART CCD diffractometer using a Mo-$K_\alpha$ monochromator ($\lambda$ = 0.71043). Structure solutions were performed using the SHELX-97 (PC version) program. The full-matrix least-square and anisotropic refinements were performed on all the atoms. Hydrogen atoms were included at calculated positions.

Table 3. Crystal data for complexes ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni.

| Parameter | ($L^1_{sal}$)Ni | ($OL^1_{sal}$)Ni |
|---|---|---|
| Formula | $C_{19}H_{13}N_3ONi$ | $C_{19}H_{13}N_3NiO_2$ |
| *M* | 358.01 | 374.01 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| *a* [Å] | 10.2834(4) | 10.8790(2) |
| *b* [Å] | 8.1049(4) | 7.8960(2) |
| *c* [Å] | 17.5313(7) | 18.0520(5) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 98.465(2) | 103.4430(10) |
| $\gamma$ [°] | 90 | 90 |
| Wavelength [Å] | 0.71073 | 0.71073 |
| *V* [Å$^3$] | 1445.24(11) | 1508.19(6) |
| Cryst. dimens. [mm] | 0.08 × 0.23 × 0.25 | 0.13 × 0.13 × 0.20 |
| *Z* | 4 | 4 |
| *T* [K] | 250 | 150 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.645 | 1.647 |
| $\mu$ [mm$^{-1}$] | 1.353 | 1.305 |
| *R* (all data) | 0.0873 | 0.0303 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.1901 | 0.0767 |
| $R_1$[a]/Gof | 1.05 | 1.015 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

The data collection parameters and relevant crystal data are collected in Table 3. CCDC-602075 and -617793 for ($L^1_{sal}$)Ni and ($OL^1_{sal}$)Ni complexes, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Figures S1–S7 (UV/Vis spectra), Figures S8–S17 (IR spectra), Figures S18–S28 ($^1$H NMR spectra), Figures S29 and S30 (cyclic voltammograms), and Figures S31 and S32 (ESI-MS spectra).

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[15] The reaction M–C → M–OC has been termed metaloxylation.[7c,7d]

[16] The $^1$H NMR spectrum of crude ($OL^1_{sa\ l}$)Ni is available as Supporting Information (Figure S24).

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