The curious cases of tetrahydrosalen-type ligands interacting with Ni(II): structures and ligand-based oxidation reactions

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ARTICLE

The curious cases of tetrahydrosalen-type ligands interacting with Ni(II): structures and ligand-based oxidation reactions

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This work centers around the nickel complexes derived from two tetrahydrosalen-type proligands: *N*,*N*'-bis(2-hydroxybenzyl)-*o*-phenylenediamine (H_2salophan) and *N*,*N*'-bis(2-hydroxy-3-methylbenzyl)-*o*-phenylenediamine (H_2salophan_Me). The reaction of H_2salophan with $Ni(OAc)_2•4H_2O$ generates a dinuclear complex $Ni_2(Hsalophan)_2(OAc)_2$ or $Na[Ni_2(salophan)_2(OAc)]$ when NaOH is added to assist ligand deprotonation. The reaction of H_2salophan_Me with $Ni(OAc)_2•4H_2O$, however, yields a mononuclear complex $Ni(Hsalophan\_Me)_2$. Unlike the corresponding salen-type nickel complexes, these tetrahydrosalen-type complexes are paramagentic and air sensitive (in solution). Oxidation by O_2 or peroxides results in dehydrogenation of the ligand backbone to form the salen-type complexes.

Introduction

Schiff-base condensation of a diamine with 2 equiv of salicylaldehyde or its derivatives forms a special class of bis-imines that can bind a wide variety of metals through the $[N_2O_2]$ donor set. The resulting metal complexes, which are often referred to as salen-type complexes,[1] find numerous applications as catalysts,[2] therapeutics,[3] nerve agent deactivators,[4] and novel materials.[5] The tetrahydro version of these proligands (i.e., both imine C=N bonds are saturated) is lesser known but has been developed.[6] Its coordination chemistry is, however, far more complicated due to the increased ligand flexibility and the loss of π-accepting ability.

The reactivity differences between salen-type proligands and their tetrahydro analogues are best illustrated in nickel systems. For example, *N*,*N*'-bis(salicylidene)ethylenediamine (H_2salen), which is arguably one of the most frequently studied bis-imines, reacts readily with $Ni(OAc)_2•4H_2O$ to yield the brick-red, diamagnetic Ni(salen) featuring a square-planar coordination geometry.[7] In this reaction, two acetate ligands are expelled from nickel to generate acetic acid as the by-product, implying that the geometry is not disrupted by a mild acid. In stark contrast, the tetrahydro variant of H_2salen,[8] namely *N*,*N*'-bis(2-hydroxybenzyl)ethylenediamine (H_2salan, see Chart 1 for the ligand form), fails to form a diamagnetic nickel complex when reacting with $Ni(OAc)_2•4H_2O$. In the presence of NaOH, the reaction gives a paramagnetic product, which, based on its poor solubility and CHN elemental analysis, was speculated to have a polymeric structure with the formula $[Ni(salan)]_x$.[9] Its pale blue color and effective magnetic moment (μ_{eff}) of 2.94 μ_B also led to the conclusion that the product might have an octahedral nickel center, although the nature of the ligands surrounding the coordination sphere has not been firmly established. Introducing *tert*-butyl groups *ortho* to the hydroxyl groups in H_2salan allows the proligands to react with $Ni(OAc)_2•4H_2O$ and NaOH very differently. The isolated products were described as cherry-red, diamagnetic compounds with a square-planar geometry analogous to Ni(salen).[10]

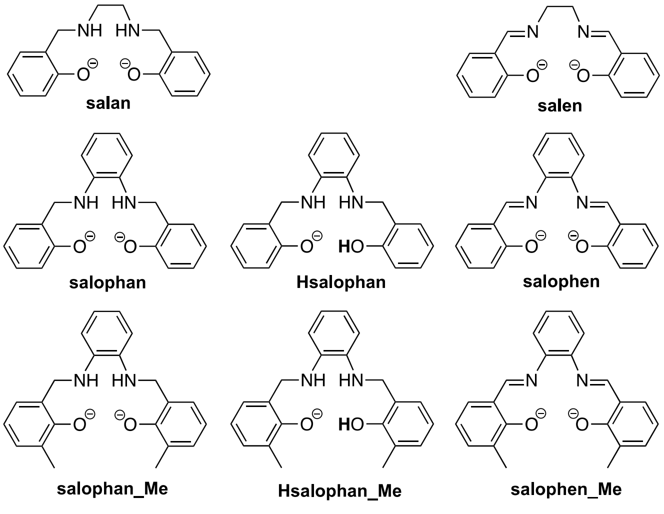

Chart 1 Abbreviations of the ligands discussed in this paper (Schiff base ligands carry the "en" designation; the tetrahydro ligands carry the "an" designation).

Replacing the ethylene linkage with a phenylene linkage can have a profound impact on the coordination chemistry. Compared to H_2salan, *N*,*N*'-bis(2-hydroxybenzyl)-*o*-phenylenediamine (H_2salophan) has a more rigid backbone and decreased basicity at the nitrogen sites. In the absence of an exogenous base, the reaction of H_2salophan with $Ni(OAc)_2•4H_2O$ affords a light sky blue compound, which, in a

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2001 paper,[11] was erroneously characterized as Ni(salophan)(H_2O)$_2$. Our crystallographic study revealed that the product was actually a dimer of Ni(Hsalophan)(OAc).[12] Each nickel center is octahedral with the coordination sphere completed by a monodentate acetate ligand, a tetradentate Hsalophan ligand (see Chart 1 for structure), and a bridging oxygen from the neighbouring Ni(Hsalophan)(OAc) unit. It is worth noting that this dinuclear species is also poorly dissolved in most organic solvents.

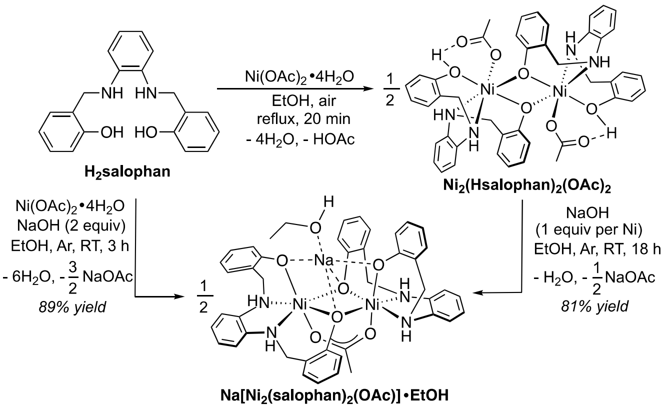
With this background information, it is evident that the tetrahydro proligands behave drastically differently from their parent Schiff bases. Their reactions with Ni(OAc)$_2$•4H_2O are not as straightforward as one might have thought, and the outcomes are incredibly sensitive to the structural modifications to the proligands. In this study, we focus specifically on Ni(II) complexes derived from H_2salophan and its methylated derivative, H_2salophan_Me. Our work here highlights the critical roles that an exogenous base and the methyl groups adjacent to the oxygen donors can play in determining the structures of the formed nickel complexes. These tetrahydrosalen-type Ni(II) complexes, whether dinuclear or mononuclear, are susceptible to ligand-based oxidation under air or by peroxides, in part driven by the formation of the more stable salen-type complexes. This type of reactivity is uncommon but can be potentially leveraged to mimic oxygenases or develop selective catalysts for O_2 oxidation reactions.

Results and discussion

Synthesis of Ni(II) complexes from H_2salophan

As introduced earlier, the reaction of H_2salophan with Ni(OAc)$_2$•4H_2O in EtOH produced a light sky blue powder analyzed as Ni$_2$(Hsalophan)$_2$(OAc)$_2$ (Scheme 1).[12] The reaction proceeded well under reflux conditions or at room temperature, typically in an open flask without any issues. The isolated compound was shown to have high-spin Ni(II) centers (S = 1) with a μ_{eff} of 3.09 μ_B per metal. Consistent with the structure probed by X-ray crystallography (Fig. 1),[13] the IR spectrum showed two medium-intensity bands at 1555 and 1424 cm^{-1}, which are attributable to the acetate ligand. Under the same conditions, the Schiff base, H_2salophen, reacted with Ni(OAc)$_2$•4H_2O to give a diamagnetic product Ni(salophen) as a maroon powder. These results reinforce the notion that the tetrahydro proligand lacks the rigidity and donor properties to induce the low-spin state.

Scheme 1 Ni(II) complexes synthesized from H_2salophan and Ni(OAc)$_2$•4H_2O



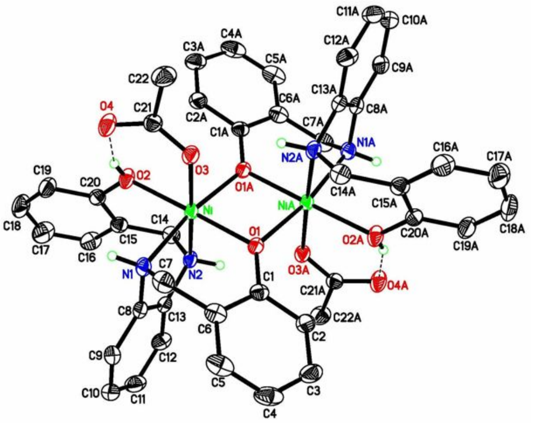


Fig. 1 ORTEP of Ni$_2$(Hsalophan)$_2$(OAc)$_2$•2CH_3COCH_3 at the 50% probability level. Two co-crystallized acetone molecules and all hydrogen atoms except the ones bound to nitrogen and oxygen are omitted for clarity (intramolecular hydrogen-bonding interactions shown by dashed lines).

In an attempt to promote the formation of Ni(salophan) by neutralizing the by-product (i.e., acetic acid), 2 equiv of NaOH was added to the reaction of H_2salophan with Ni(OAc)$_2$•4H_2O, which at first was conducted at room temperature under an argon atmosphere. The isolated compound displayed an aquamarine color. The same product was obtained when Ni$_2$(Hsalophan)$_2$(OAc)$_2$ was treated with 2 equiv of NaOH in EtOH under argon (Scheme 1). The chemical composition, Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH, was supported by CHN elemental analysis, IR spectroscopy, and mass spectrometry. The IR spectrum of the solid sample featured two ν_{N-H} bands at 3295 and 3243 cm^{-1}.[14] The [NaNi$_2$(salophan)$_2$]$^+$ ion (m/z = 775.13) was detected by ESI-MS, although under the mass spectral conditions, the most intense peak was identified to be [HNi$_3$(salophan)$_3$]$^+$. Unlike Ni$_2$(Hsalophan)$_2$(OAc)$_2$, which has limited solubility in acetone, the new compound dissolved readily in acetone-d_6. Its ^{1}H NMR spectrum exhibited paramagnetically shifted resonances (15 were located between 170 and –170 ppm) as well as the 3 diamagnetic resonances for a fully dissociated EtOH molecule. The μ_{eff} was determined to be 2.83 μ_B per metal, indicating that the nickel remains in an octahedral coordination environment with two unpaired electrons (S = 1).

It should be mentioned that the synthesis of Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH is best carried out under an inert atmosphere. The reaction of H_2salophan with Ni(OAc)$_2$•4H_2O and NaOH in EtOH, if performed in an open flask, would yield a mixture of Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH and Ni(salophen) that is difficult to separate. The formation of Ni(salophen) is a result of aerobic oxidation of Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH or the transient intermediate Ni(salophan) (vide infra).

Interestingly, when an acetone-d_6 solution of $Na[Ni_2(salophan)_2(OAc)]$ was left undisturbed in a closed J. Young NMR tube, light turquoise crystals slowly formed over time, usually within hours. X-ray crystallographic study of these crystals revealed a dinuclear structure as shown in Fig. 2. In essence, the addition of NaOH did successfully deprotonate both hydroxyl groups of H_2salophan, which should favor the formation of Ni(salophan). However, the octahedral coordination geometry is still preferred by Ni(II) with the salophan ligand adopting the *fac-mer* coordination mode.[15] The remaining coordination sites are occupied by one of the salophan oxygen donors and an acetate ligand that bridge two Ni(II) centers. The counterion Na^+ is encapsulated in an "oxygen cage" built by the two salophan ligands and an acetone molecule. This type of coordination environment for sodium (i.e., 5-coordinate) is rare but has been previously observed with sodium salts of certain carbohydrates.[16]

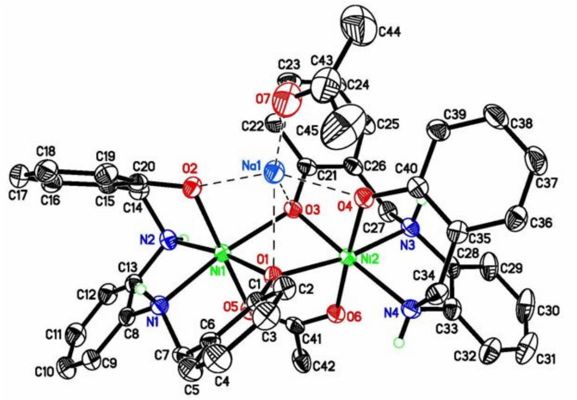
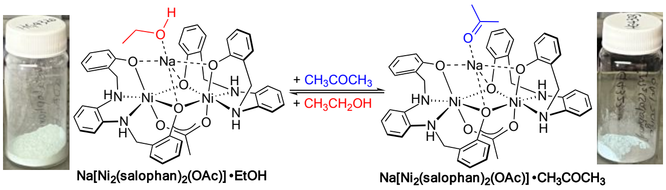


Fig. 2 ORTEP of $Na[Ni_2(salophan)_2(OAc)]•4CD_3COCD_3$ at the 50% probability level. Three co-crystallized CD_3COCD_3 molecules and all carbon-bound hydrogen atoms are omitted for clarity (sodium-oxygen interactions shown as dashed lines).

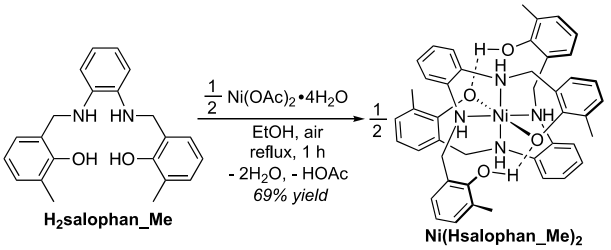
The solvent molecule that interacts with Na^+ is likely labile or exchangeable. The aquamarine-colored product isolated from the reactions carried out in EtOH (Scheme 1) bears one EtOH molecule, presumably bound to Na^+ through the oxygen atom. When the initial product was dissolved in acetone, the coordinated EtOH was rapidly displaced by acetone to give $Na[Ni_2(salophan)_2(OAc)]•CH_3COCH_3$. Subsequent slow co-crystallization with acetone yielded the light turquoise crystals, which, upon isolation, showed a characteristic IR band at 1707 cm^{-1} for the carbonyl group. Treating the isolated compound with EtOH resulted in color being reverted to aquamarine, suggesting that the process outlined in Scheme 2 is reversible.



Scheme 2 Solvate exchange on $Na[Ni_2(salophan)_2(OAc)]$

Synthesis of Ni(II) complexes from H_2salophan_Me

Introducing methyl groups *ortho* to the oxygen donors of H_2salophan would increase the steric congestion around nickel. As a result, it might facilitate the dissociation of the acetate ligand and discourage two Ni(salophan_Me) units from approaching each other to form a dinuclear structure. Consistent with this hypothesis, the reaction of H_2salophan_Me with $Ni(OAc)_2•4H_2O$ in EtOH (performed in an open flask) produced a mononuclear species (Scheme 3). However, the isolated product, a pale lavender powder, proved to be a homoleptic Ni(II) complex supported by two Hsalophan_Me ligands. According to the crystal-structure determinations (Fig. 3),[17] each Hsalophan_Me ligand adopts a facial coordination mode using the $[N_2O]$ donor set while leaving the unbound hydroxyl group to participate in hydrogen-bonding interactions with the nickel-bound oxygen. Once again, the Ni(II) center prefers an octahedral coordination geometry. The coordination sphere is completed by a second Hsalophan_Me ligand instead of acetate or water, even when only 1 equiv of H_2salophan_Me is employed to react with $Ni(OAc)_2•4H_2O$.



Scheme 3 $Ni(Hsalophan\_Me)_2$ synthesized from H_2salophan_Me and $Ni(OAc)_2•4H_2O$

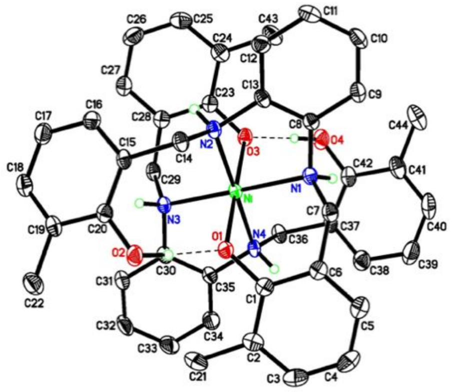
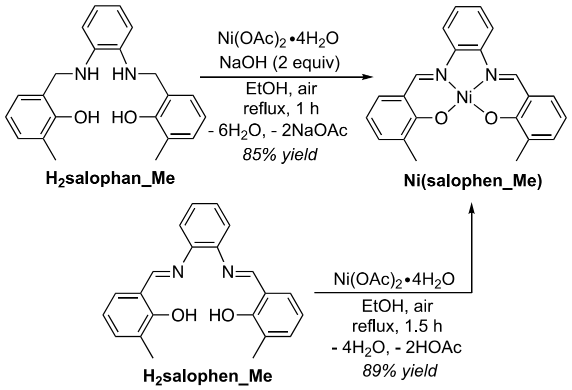


Fig. 3 ORTEP of $Ni(Hsalophan\_Me)_2•2CH_3COCH_3$ at the 50% probability level. Two co-crystallized acetone molecules and all carbon-bound hydrogen atoms are omitted for clarity (hydrogen-bond interactions shown as dashed lines).

The CHN elemental analysis of the pale lavender powder agreed with the formula $Ni(Hsalophan\_Me)_2$. Its μ_{eff} was measured to be 2.98 μ_B, consistent with an octahedral molecule bearing a high-spin Ni(II) center (S = 1). From the IR spectrum, two $\nu_{N\text{-}H}$ bands were located at 3265 and 3236 cm^{-1} whereas ν_{OCO} bands were absent. The structure was further supported by ESI-MS, which showed the protonated ion $[HNi(Hsalophan\_Me)_2]^+$ (m/z = 753.25) as well as the fragment ion $[Ni(Hsalophan\_Me)]^+$ (m/z = 405.25). Interestingly, despite having limited solubility in acetone, $Ni(Hsalophan\_Me)_2$ slowly formed single crystals over time, typically within days, from an acetone suspension. This process is likely enabled by co-crystallization with the solvent molecules. The solubility of Ni(Hsalophan_Me)$_2$ in $CDCl_3$ is significantly higher, providing an invaluable opportunity for NMR analysis. A total of 10 resonances were located between 21.5 and –5.1 ppm, suggesting a C_s symmetric molecule with a Hsalophan_Me ligand that can be bisected by a mirror plane. It is possible that, in solution, the two oxygen atoms in each Hsalophan_Me ligand (i.e., O1/O2 and O3/O4 pairs) rapidly exchange on nickel while shuttling the proton within the hydrogen-bonding network (e.g., converting O2–H…O1 to O2…H–O1).

The effect of NaOH on the reaction of H_2salophan_Me with Ni(OAc)$_2$•4H_2O (1 or 0.5 equiv) was investigated next. When the experiments were conducted in an open flask, the addition of NaOH resulted in an immediate darkening of the reaction mixture followed by the formation of a red precipitate. Under the conditions outlined in Scheme 4, the isolated product was characterized as Ni(salophen_Me), suggesting that the salophan_Me ligand backbone had undergone oxidation or dehydrogenation to form two imine groups. This salen-type nickel complex was independently synthesized from H_2salophen_Me and Ni(OAc)$_2$•4H_2O without the need of adding a base. As expected, Ni(salophen_Me) is a diamagnetic compound with sharp NMR resonances and a relatively planar structure as confirmed by X-ray crystallography (Fig. 4).



Scheme 4 Ni(salophen_Me) synthesized from H_2salophan_Me or H_2salophen_Me

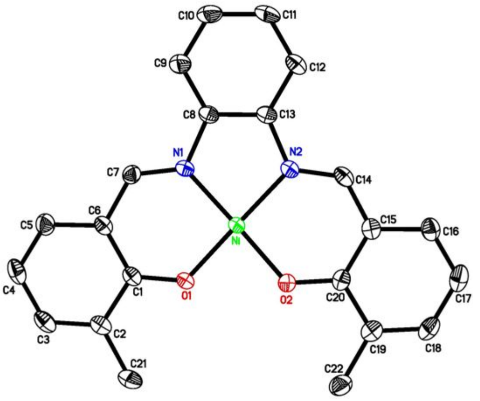


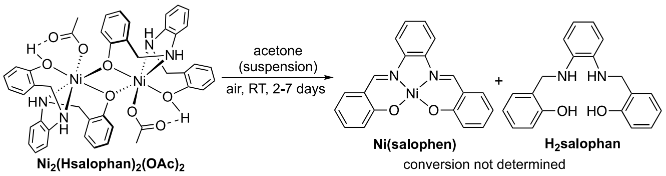
Fig. 4 ORTEP of Ni(salophen_Me) at the 50% probability level. All carbon-bound hydrogen atoms are omitted for clarity.

Under an argon atmosphere, the reaction of H_2salophan_Me with Ni(OAc)$_2$•4H_2O (1 or 0.5 equiv) in the presence of NaOH (2 equiv) afforded a very complicated mixture. The composition varied greatly with reaction temperature, time, and O_2 level, although Ni(Hsalophan_Me)$_2$ was consistently observed. Nevertheless, the 2 : 1 : 4 mixture of H_2salophan_Me, Ni(OAc)$_2$•4H_2O, and NaOH in EtOH stirred at room temperature for 18 h led to the isolation of pure Ni(Hsalophan_Me)$_2$ (73% yield), which was confirmed by CHN elemental analysis, IR spectroscopy, ESI-MS, and X-ray diffraction.

Air stability of the Ni(II) complexes

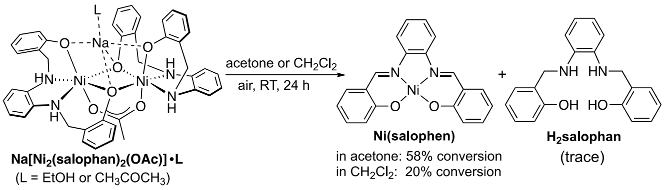
To gauge the air stability of the nickel complexes derived from H_2salophan and H_2salophan_Me, solid samples of Ni_2(Hsalophan)$_2$(OAc)$_2$, Na[Ni_2(salophan)$_2$(OAc)] (the ethanol solvate and the acetone solvate), and Ni(Hsalophan_Me)$_2$ were exposed to air for a week. None of the samples changed color except Na[Ni_2(salophan)$_2$(OAc)] solvated by acetone, which started with a light turquoise color but turned olive green after 24 h and brown after 48 h. The IR spectra of the degraded sample showed the waning $\nu_{C=O}$ band and the appearance of new $\nu_{N\text{-}H}$ bands, suggesting that the decomposition was at least in part due to the loss of acetone.

Though the synthesis of Ni_2(Hsalophan)$_2$(OAc)$_2$ was successfully carried out under air, several observations hinted to us that, in solution, this compound could be reactive towards O_2. Its ESI-MS data were analyzed using a dilute ethanol solution, which showed a number of minor ion peaks consistent with [Ni(Hsalophan)-2H]$^+$, [Ni_2(salophan)(Hsalophan)-2H]$^+$, and [Ni_2(salophan)(Hsalophan)-4H]$^+$. Furthermore, exposing an acetone suspension to air for a week led to the growth of pale crystals attributed to Ni_2(Hsalophan)$_2$(OAc)$_2$ along with some red crystals analyzed as Ni(salophen).[18] In contrast, a sample kept under argon yielded only the crystals of Ni_2(Hsalophan)$_2$(OAc)$_2$. To examine the degradation process more closely, Ni_2(Hsalophan)$_2$(OAc)$_2$ (10 μmol) was suspended in acetone (2 mL) and stirred under air for a week. The soluble component was identified as a mixture of Ni(salophen) and H_2salophan (Scheme 5), whereas the insoluble component was shown to be mainly Ni_2(Hsalophan)$_2$(OAc)$_2$. In halogenated solvents, this dinuclear complex appeared to be sufficiently stable to air. Its CH_2Cl_2 suspension exposed to air for a week showed no sign of oxidation. In $CDCl_3$, Ni_2(Hsalophan)$_2$(OAc)$_2$ also failed to react with the dissolved O_2, even at 80 °C, although the lack of reactivity could be due to the poor solubility.



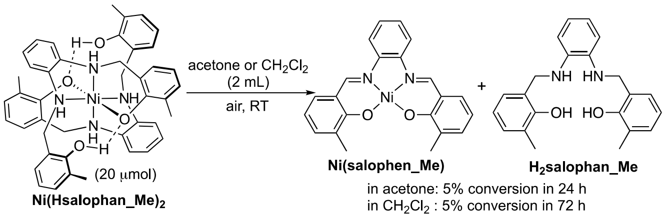
Scheme 5 Aerobic oxidation of Ni_2(Hsalophan)$_2$(OAc)$_2$

A more rapid oxidation process was observed with Na[Ni_2(salophan)$_2$(OAc)]•EtOH and the acetone solvate, which could be fully dissolved in acetone or CH_2Cl_2. The solutions (5 mM) exposed to air changed color within minutes (in acetone) or 1 h (in CH_2Cl_2) and became dark red after 24 h (in both solvents). NMR analysis confirmed that both complexes had undergone ligand-based oxidation to yield Ni(salophen) as the major product (Scheme 6). The oxidation reaction performed in CH_2Cl_2 was substantially slower, consistent with the longer time needed to observe a color change. The ESI-MS data of Na[Ni_2(salophan)$_2$(OAc)]•EtOH (in EtOH) also showed traces of oxidized ions including [Ni(Hsalophan)-2H]$^+$, [NaNi(salophan)-2H]$^+$, [Ni_2(salophan)(Hsalophan)-2H]$^+$, and [NaNi_2(salophan)$_2$-2H]$^+$. These results serve to explain why the synthesis of Na[Ni_2(salophan)$_2$(OAc)]•EtOH and the acetone solvate needs to be conducted under air-free conditions.



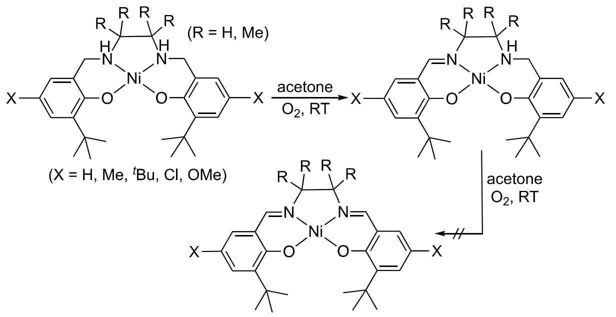
Scheme 6 Aerobic oxidation of Na[Ni_2(salophan)$_2$(OAc)]

The mononuclear complex Ni(Hsalophan_Me)$_2$ also displayed some air sensitivity when mixed with a solvent. Aerobic oxidation of Ni(Hsalophan_Me)$_2$ to Ni(salophen_Me) was observed in both acetone and CH_2Cl_2, which was also accompanied by dissociation of the free proligand H_2salophan_Me (Scheme 7). Oxidation in CH_2Cl_2 was noticeably slower than in acetone, despite the fact that Ni(Hsalophan_Me)$_2$ formed a solution in CH_2Cl_2 but a suspension in acetone. Interestingly, oxidized ions were not observed in the ESI-MS spectrum of Ni(Hsalophan_Me)$_2$ (in EtOH), further supporting that, in solution, Ni(Hsalophan_Me)$_2$ undergoes oxidation more slowly than the dinuclear complexes supported by the [Hsalophan]$^-$ or [salophan]$^{2-}$ ligand. It is possible that the hydrogen-bonding network present in Ni(Hsalophan_Me)$_2$ allows the complex to maintain its structural integrity reasonably well, especially in a weakly-coordinating solvent.



Scheme 7 Aerobic oxidation of Ni(Hsalophan_Me)$_2$

At this stage we are unsure if O_2 would directly attack Ni(Hsalophan_Me)$_2$ or the dinuclear complexes derived from H_2salophan. Based on the relative rates of aerobic oxidation (in acetone > in CH_2Cl_2; Na[Ni_2(salophan)$_2$(OAc)] > Ni_2(Hsalophan)$_2$(OAc)$_2$ > Ni(Hsalophan_Me)$_2$), we favor a mechanistic pathway involving an initial ligand dissociation step to form Ni(salophan_Me) or Ni(salophan), followed by net ligand-based oxidation with O_2.[19,20] This mechanism is also in agreement with the studies of the *tert*-butyl-substituted tetrahydrosalen nickel complexes,[10] where the 4-coordinate species are synthetically accessible and can be used directly to react with O_2. However, the ethylene- or tetramethylethylene-based ligand system stops the oxidation process at the dihydrosalen stage (Scheme 8). The phenylene derivatives presented herein likely make the second ligand-based oxidation event more favorable through the extension of the π-systems. In any case, detecting the dihydrosalen intermediates is conceivable under low O_2-level conditions (e.g., during ESI-MS analysis).



Scheme 8 Aerobic oxidation of *tert*-butyl-substituted tetrahydrosalen nickel complexes

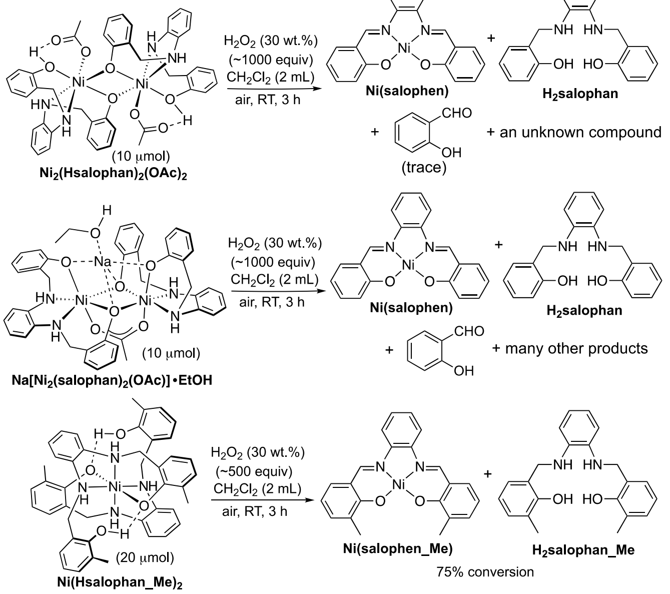
An alternative pathway leading to the dehydrogenation of the ligand backbone may involve β-hydrogen elimination by nickel to yield a nickel hydride intermediate, which can be decomposed by O_2 or other species present in the reaction mixture. Such a mechanism is unlikely to operate here. The NMR samples of Na[Ni_2(salophan)$_2$(OAc)]•EtOH (in $CDCl_3$ or acetone-d_6) and Ni(Hsalophan_Me)$_2$ (in $CDCl_3$) were found stable at 80 °C, as long as O_2 was excluded. Exposing these samples to air led to the formation of Ni(salophen) and Ni(salophen_Me); however, no halogen exchange with $CDCl_3$ or reduction of acetone-d_6 was observed.

Phenoxide complexes can react with CO_2 (present in air) via insertion into the metal-oxygen bonds.[21] The nucleophilicity of the oxygen donors in our tetrahydrosalen-type complexes is, however, attenuated by the hydrogen-bonding interactions as well as the bridging coordination mode. Control experiments showed that none of the tetrahydrosalen-type complexes described in this paper reacted with CO_2 (3 bar, in CH_2Cl_2, RT, 24 h), further confirming that the reactivity mentioned above was due to O_2 oxidation.

Oxidation by peroxides

Tetrahydrofuran (THF), which is a peroxide-forming solvent, caused all the tetrahydrosalen-type Ni(II) complexes to degrade rapidly, and the rates depended on the peroxide level (see Fig. S24 for the visualization of Ni(Hsalophan_Me)$_2$ degrading in THF). The oxidation products were complex, comprising a salen-type complex (Ni(salophen) or Ni(salophen_Me)), an aldehyde fragment (salicylaldehyde or 3-methylsalicylaldehyde), and many unidentified species.

Aerobic oxidation of the tetrahydrosalen-type Ni(II) complexes could potentially generate H_2O_2 as the byproduct, which might accelerate the reactions.[10b] The oxidation of these Ni(II) complexes with H_2O_2 (30 wt.% in water) was thus investigated separately. With an acid catalyst, acetone can react with H_2O_2 to produce explosive acetone peroxide;[22] for safety concerns, the acetone solvate of Na[Ni_2(salophan)$_2$(OAc)] was not used in this study. Mixing the CH_2Cl_2 suspension of Ni_2(Hsalophan)$_2$(OAc)$_2$ with H_2O_2 resulted in a gradual dissolution of the solid and the formation of a reddish solution within 30 min. The oxidation process was complete in 3 h, affording a ~1 : 1 mixture of Ni(salophen) and H_2salophan, a small amount of salicylaldehyde, and an unidentified compound (Scheme 9). The reaction of Na[Ni_2(salophan)$_2$(OAc)]•EtOH under the same conditions was faster and more complicated, giving Ni(salophen), H_2salophan, salicylaldehyde, and many other decomposition products. Oxidation of Ni(Hsalophan_Me)$_2$ with H_2O_2 was considerably slower but more selective, converting 75% of the starting material cleanly to Ni(salophen_Me) and H_2salophan_Me. However, extending the reaction time to 24 h led to further degradation of the nickel complex to many products including 3-methylsalicylaldehyde. Control experiments showed that the two proligands, H_2salophan and H_2salophan_Me, were completely unreactive towards H_2O_2 (monitored for 24 h). Under the same conditions, neither Ni(salophen) nor Ni(salophen_Me) participated in hydrolysis reactions. The aldehyde fragment and other oxidation products must arise from destruction of the ligands that remain bound to nickel.



Scheme 9 Oxidation of the tetrahydrosalen-type Ni(II) complexes with H_2O_2

Conclusions

Through this work, we have demonstrated some unique coordination chemistry associated with tetrahydrosalen-type proligands. They can bind to Ni(II) using the [N_2O_2] or [N_2O] donor set. Their reactions with Ni(OAc)$_2$•4H_2O can lead to a mononuclear or dinuclear structure, partial or full dissociation of the acetate ligand from nickel, and the removal of one or two protons from the proligands. The structures of the resulting nickel complexes depend greatly on the steric properties of the ligands and on whether or not an exogenous base is used in the synthesis. These findings stand in contrast to the behaviors of their parent salen-type proligands, whose reactions with Ni(OAc)$_2$•4H_2O consistently give mononuclear, N_2O_2-complexes devoid of acetate ligands. The reactivity disparities reflect the ligand flexibility as well as the ligand field strength. With the tetrahydrosalen-type ligands, the Ni(II) centers prefer high spin with an octahedral geometry, which requires additional ligands to complete the coordination sphere. The salen-type complexes, on the other hand, benefit from the rigid and planar ligand structure and the π-accepting abilities of the ligands. Their high air stability likely provides the driving force for the tetrahydrosalen-type complexes to undergo ligand-based oxidation reactions with O_2 or peroxides.

Experimental

General methods

Literature procedures were followed for the preparation of H_2salophan,[12] Ni(salophen),[12] Ni_2(Hsalophan)$_2$(OAc)$_2$,[12] and H_2salophan_Me.[6e] Acetone and ethanol used for the synthesis of air-sensitive compounds were deoxygenated by bubbling argon through them for 30 min. NMR spectra were recorded on a Bruker AV400 or Bruker NEO400 NMR spectrometer. The chemical shift values for ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to tetramethylsilane (TMS) or the residual solvent resonances. IR spectra were recorded on a PerkinElmer Spectrum Two spectrometer equipped with an attenuated-total-reflectance (ATR) accessory. ESI mass spectra were recorded on a Thermo Scientific Orbitrap Fusion Lumos mass spectrometer. Elemental analysis service was provided by Atlantic Microlab. Magnetic susceptibilities were measured for solid samples by a Johnson Matthey magnetic susceptibility balance (MSB Mark I model), and diamagnetic corrections[23] were applied when the effective magnetic moments were calculated. For dinuclear complexes, calculations were made on a per-metal basis, assuming that there are no interactions between the two metal centers.

Synthesis of Na[Ni_2(salophan)$_2$(OAc)]•EtOH. Method 1: Under an argon atmosphere, H_2salophan (641 mg, 2 mmol), Ni(OAc)$_2$•4H_2O (498 mg, 2 mmol), and NaOH (160 mg, 4 mmol) were mixed in 50 mL of EtOH and stirred for 3 h. The resulting suspension was filtered under argon using a cannula. The filtrate was discarded; the solid was washed with deoxygenated EtOH (10 mL × 2) and dried under vacuum. The desired product was isolated as an aquamarine powder (783 mg, 89% yield). X-ray quality crystals were grown from an acetone-d_6 solution and solved as Na[Ni_2(salophan)$_2$(OAc)]•4CD_3COCD_3. ^1H NMR (400 MHz, acetone-d_6, δ): 66.46, 46.39, 22.32, 20.92, 20.00, 18.15, 14.17, 13.72, 10.13, 8.75, 3.97, 3.75, 3.57 (q, J = 6.8 Hz, CH_3CH_2OH), 3.37 (s, CH_3CH_2OH), 1.12 (t, J = 6.8 Hz, CH_3CH_2OH), –3.99, –5.77, –6.60. ^1H NMR (400 MHz, $CDCl_3$, δ): 21.60, 17.67, 15.71, 14.59, 14.05, 9.76, 8.95, 3.70 (br, CH_3CH_2OH overlapped with a broad resonance), 1.51, 1.23 (CH_3CH_2OH), –3.89, –6.54. ESI-MS: m/z = 1131.25 ([3M+H]$^+$, M = Ni(salophan), 100%), 871.00 ([2M+NiOAc]$^+$, 1%), 775.13 ([2M+Na]$^+$, 1%), 753.25 ([2M+H]$^+$, 3%), 399.06 ([M+Na]$^+$, 2%), 377.17 ([M+H]$^+$, 4%). ATR-IR (solid, cm^{-1}): 3295, 3243, 1593, 1571, 1478, 1447, 1409, 1312, 1288, 1220, 1110, 1041, 976, 874, 849, 764, 749. Effective magnetic moment (μ_{eff}): 2.83 μ_B per Ni. Anal. calcd for $C_{44}H_{45}N_4O_7NaNi_2$: C, 59.90; H, 5.14; N, 6.35. Found: C, 59.75; H, 5.29; N, 6.22.

Method 2: Under an argon atmosphere, to a suspension of Ni_2(Hsalophan)$_2$(OAc)$_2$ (437 mg, 0.5 mmol) in 25 mL of EtOH was added NaOH (40 mg, 1 mmol) in one portion. The resulting mixture was stirred at room temperature for 18 h. The precipitate was collected by cannula filtration, washed with deoxygenated EtOH (5 mL × 3), and dried under vacuum. The desired product was isolated as an aquamarine powder (356 mg, 81% yield). The ^{1}H NMR and IR data are identical to those described above for the sample prepared using Method 1. Anal. calcd for $C_{44}H_{45}N_4O_7NaNi_2$: C, 59.90; H, 5.14; N, 6.35. Found: C, 59.64; H, 5.23; N, 6.31.

Solvate exchange on Na[Ni$_2$(salophan)$_2$(OAc)]. Under an argon atmosphere, Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH (200 mg, 0.23 mmol) was dissolved in 10 mL of deoxygenated acetone. The resulting solution was stirred for 5 min and then left undisturbed. Light turquoise crystals slowly developed over time. After 16 h, the crystals were collected by filtration and dried under vacuum, which led to the isolation of a pale turquoise powder (103 mg, 48% yield). ATR-IR (solid, cm^{-1}): 3306, 3247, 3005, 1707, 1579, 1477, 1455, 1413, 1364, 1305, 1285, 1227, 1109, 978, 873, 747. Effective magnetic moment (μ_{eff}): 3.00 μ_B per Ni. The elemental analysis data are consistent with the formula Na[Ni$_2$(salophan)$_2$(OAc)]•2CH_3COCH_3.[24] Anal. calcd for $C_{48}H_{51}N_4O_8NaNi_2$: C, 60.54; H, 5.40; N, 5.88. Found: C, 60.40; H, 5.41; N, 5.92. When mixed with EtOH, the pale turquoise solid changed its color back to aquamarine.

Synthesis of Ni(Hsalophan_Me)$_2$. In an open flask, a mixture of H_2salophan_Me (697 mg, 2 mmol), Ni(OAc)$_2$•4H_2O (249 mg, 1 mmol), and EtOH (20 mL) was refluxed (or stirred at room temperature) for 1 h. The resulting suspension was cooled to room temperature and filtered through a Büchner funnel with a Fisherbrand™ P8 grade filter paper. The collected solid was rinsed with a small amount of EtOH and air-dried. The desired product was isolated as a pale lavender powder (520 mg, 69% yield). X-ray quality crystals were grown from a sample suspended in acetone or a solution in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 21.42, 15.14, 13.59, 11.66, 10.12, 8.61, 8.17, 7.63, 2.86 (C*H*$_3$), –5.09. ESI-MS: *m/z* = 809.25 ([M+Ni-H]$^+$, M = Ni(Hsalophan_Me)$_2$, 26%), 753.25 ([M+H]$^+$, 41%), 405.25 ([M-Hsalophan_Me]$^+$, 100%). ATR-IR (solid, cm^{-1}): 3265, 3236, 2860, 1583, 1499, 1458, 1421, 1389, 1258, 1237, 1221, 1088, 1056, 763, 744. Effective magnetic moment (μ_{eff}): 2.98 μ_B. Anal. calcd for $C_{44}H_{46}N_4O_4Ni$: C, 70.13; H, 6.15; N, 7.44. Found: C, 69.99; H, 6.15; N, 7.40.

In a separate synthesis, the amount of H_2salophan_Me was reduced to 1 mmol, which also led to the isolation of Ni(Hsalophan_Me)$_2$ (181 mg, 48% yield) with the same IR and ESI-MS data as described above. Anal. calcd for $C_{44}H_{46}N_4O_4Ni$: C, 70.13; H, 6.15; N, 7.44. Found: C, 70.05; H, 6.12; N, 7.38.

Characterization of H$_2$salophen_Me. This compound was prepared following a reported procedure.[25] ^{1}H NMR (400 MHz, $CDCl_3$, δ): 13.19 (s, O*H*, 2H), 8.60 (s, C*H*=N, 2H), 7.35-7.27 (m, Ar*H*, 2H), 7.25-7.15 (m, Ar*H*, 6H), 6.82 (t, *J* = 7.6 Hz, Ar*H*, 2H), 2.29 (s, C*H*$_3$, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 164.2, 159.7, 142.6, 134.3, 130.1, 127.5, 126.4, 120.2, 118.5, 118.4, 15.6. ATR-IR (solid, cm^{-1}): 2904, 1610, 1568, 1475, 1457, 1430, 1375, 1363, 1322, 1270, 1249, 1204, 1188, 1105, 1082, 1036, 738.

Synthesis of Ni(salophen_Me). Synthesis of this compound has been reported in the literature.[26] The procedure described herein is slightly modified from the reported ones. In an open flask, a mixture of H_2salophen_Me (344 mg, 1 mmol), Ni(OAc)$_2$•4H_2O (249 mg, 1 mmol), and EtOH (20 mL) was refluxed for 1.5 h. The resulting suspension was cooled to room temperature and filtered through a Büchner funnel with a Fisherbrand™ P8 grade filter paper. The collected solid was rinsed with a small amount of EtOH and air-dried. The desired product was isolated as a maroon powder (356 mg, 89% yield). X-ray quality crystals were grown from slow evaporation of an acetone solution. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.27 (s, C*H*=N, 2H), 7.77-7.68 (m, Ar*H*, 2H), 7.26-7.16 (m, Ar*H*, 6H), 6.59 (t, *J* = 7.6 Hz, Ar*H*, 2H), 2.34 (s, C*H*$_3$, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, δ): 165.5, 154.1, 142.9, 135.2, 131.0, 130.1, 127.2, 119.0, 115.6, 114.7, 16.5. ATR-IR (solid, cm^{-1}): 3013, 2903, 1606, 1590, 1579, 1533, 1492, 1454, 1421, 1375, 1342, 1265, 1245, 1201, 1175, 1161, 1113, 1042, 737, 543.

Aerobic oxidation of the Ni(II) complexes. In a scintillation vial, a nickel complex (10 μmol for the dinuclear complex or 20 μmol for Ni(Hsalophan_Me)$_2$) was dissolved or suspended in 2 mL of a solvent of interest (acetone, CH_2Cl_2, or THF). The mixture was vigorously stirred under air. Occasionally additional solvent was added to compensate for solvent loss due to evaporation. The progress of the reaction was monitored by NMR and IR analysis of the residue following evaporation.

Oxidation of the Ni(II) complexes with H$_2$O$_2$. In a scintillation vial, a nickel complex (10 μmol for Ni_2(Hsalophan)$_2$(OAc)$_2$ and Na[Ni$_2$(salophan)$_2$(OAc)]•EtOH, or 20 μmol for Ni(Hsalophan_Me)$_2$) was dissolved or suspended in 2 mL of CH_2Cl_2. A 30 wt.% H_2O_2 solution in water (1 mL, ~10 mmol) was added to the vial. The biphasic mixture was vigorously stirred under air for 3h or 24 h. The progress of the reaction was monitored by NMR analysis of the residue following evaporation.

X-ray crystallographic determinations

For the nickel complexes, the conditions under which single crystals were obtained are already described in the corresponding synthesis and characterization subsections. Single crystals of H_2salophan_Me were obtained from an EtOH solution layered with water. Intensity data were collected at 150 K using Mo Kα radiation, λ = 0.71073 Å, on a Bruker APEX-II CCD diffractometer (for $Na[Ni_2(salophan)_2(OAc)]$•$4CD_3COCD_3$, $Ni(Hsalophan\_Me)_2$•$2CH_3COCH_3$, and Ni(salophen_Me)) or a Bruker D8 Venture Photon-II diffractometer (for $Ni_2(Hsalophan)_2(OAc)_2$•$2CH_3COCH_3$, $Ni(Hsalophan\_Me)_2$•$CHCl_3$, and H_2salophan_Me•H_2O). The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections. The structures were solved by a combination of direct methods and the difference Fourier technique as implemented in the SHELX suite of programs and refined by full-matrix least squares on F^2 for reflections out to 0.75 or 0.80Å resolution. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to nitrogen or oxygen were located directly from the difference map and their coordinates were refined. All remaining hydrogen atoms were calculated and treated with a riding model. The isotropic displacement parameters were defined as a^*U_{eq} of the adjacent atom (a = 1.5 for methyl and hydroxyl, 1.2 for all others). $Ni_2(Hsalophan)_2(OAc)_2$ co-crystallizes with one molecule of acetonitrile (reported in ref. 12) or two molecules of acetone (reported here). $Na[Ni_2(salophan)_2(OAc)]$ co-crystallizes with four molecules of CD_3COCD_3; one of them coordinates to Na^+ via the oxygen atom. $Ni(Hsalophan\_Me)_2$ co-crystallizes with two molecules of acetone or one molecule of chloroform in the lattice. The chloroform molecule in the latter is partially disordered; distance similarity and anisotropic displacement parameter restraints were applied (refined major occupancy is 86%). H_2salophan_Me co-crystallizes with one molecule of water.

Conflicts of interest

There are no conflicts to declare.

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