

A Tetracoordinated Phosphasalen Nickel(III) Complex**

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Abstract: The oxidation of a Ni^{II} complex bearing a tetradentate phosphasalen ligand, which differs from salen by the presence of an iminophosphorane ($P=N$) in place of an imine unit, was easily achieved by addition of a silver salt. The site of this oxidation was investigated with a combination of techniques (NMR, EPR, UV/Vis spectroscopy, X-ray diffraction, magnetic measurements) as well as DFT calculations. All data are in agreement with a high-valent Ni^{III} center concentrating the spin density. This markedly differs from precedents in the salen series for which oxidation on the metal was only observed at low temperature or in the presence of additional ligands or anions. Therefore, thanks to the good electron-donating properties of the phosphasalen ligand, $[Ni(Psalen)]^+$ represents a rare example of a tetracoordinated high-valent nickel complex in presence of a phenoxide ligand.

N,*N'*-ethylenebis(salicylimine) (salen) derivatives constitute a very successful class of ligands that have found numerous applications in inorganic chemistry and catalysis.^[1] Their extraordinary popularity comes from their easy synthesis, allowing a variety of skeleton variations, and their ability to coordinate to a great number of different metal ions. Moreover the presence of two phenoxide and imine functions is reminiscent of the coordination environment generated by two histidine and two tyrosine residues, encountered in several enzymes. Thus, in 1998, the one-electron oxidation of a (salen)copper(II) complex was described, and the resulting persistent phenoxy radical was established as a biomimetic functional model of galactose oxidase.^[2] Since then, one-electron-oxidized metal salen complexes of first-row transition metals have received considerable attention.^[3] Depending on the nature of the redox-active orbitals, oxidation of salen complexes leads either to high-valent metal centers (metal-centered oxidation) or to species where the ligand is oxidized to a radical (ligand-centered oxidation). Therefore, various factors may affect the oxidation site, as it was nicely illustrated in the case of nickel salen complexes. In noncoordinating solvents, one-electron oxidation occurs on the ligand, and the unpaired electron is highly delocalized

over the salen moiety with a small contribution of the nickel orbitals.^[3b,4] However, in coordinating solvents, or in the presence of exogenous ligands such as pyridine or coordinating anions, the geometry of the complex is modified and so is the site of the oxidation, allowing the formation of Ni^{III} complexes.^[4a,b,5] Temperature-dependent behavior, that is, valence tautomerism, was also described in a few examples.^[5b,6] Moreover, the overall electronic distribution may be finely tuned by the substituents of the phenoxide rings. They influence not only the site of the oxidation (which takes place at the most electron-rich phenoxide ring) as evidenced with complexes featuring unsymmetrical salen,^[3c,7] but also the extent of radical delocalization.^[3b,8] The hybridization of the nitrogen atoms is also of prime importance since it may influence the oxidation site, the spin state of the metal, and the magnetic interactions within the molecule.^[5b,9]

Astonishingly, despite numerous structural variations proposed for salen ligands, the introduction of heteroatoms into their backbone was rarely investigated.^[10] As we are interested in iminophosphorane ($P=N$) based ligands as an alternative to conventional imine-based ligands,^[11] we developed a new class of ligands featuring iminophosphorane units, which we termed phosphasalen (or Psalen). We have recently demonstrated that these ligands are more flexible and electron-donating than their carbon analogues^[12] and that they provide efficient and selective initiators for *rac*-lactide polymerization.^[13] In the present work, we wish to report the synthesis and characterization of a Ni^{II} phosphasalen complex and its one-electron oxidation which leads to a temperature-persistent high-valent tetracoordinated Ni^{III} complex.

With the objective of studying the oxidation of a $[Ni(Psalen)]$ complex, we chose a ligand featuring substituents on the *ortho* and *para* positions of the phenoxide rings to increase its stability, and preferred *tert*-butyl groups for solubility reasons. The required phosphasalen ligand **1** was prepared following a procedure we recently published (Scheme 1):^[13b] Reaction of **1** with $[NiBr_2(dme)]$ in THF led, after removal of the potassium salts, to formation of the Ni^{II} complex **2** as a purple solid in 92 % yield. In the $^{31}P\{^1H\}$ NMR spectrum the coordination is indicated by a deshielding of the phosphorus nuclei appearing as a singlet at $\delta(CD_2Cl_2) = 36.0$ ppm. This complex was characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. As expected for a d^8 complex, **2** adopts a square-planar geometry around the metal center with a slight deviation from planarity (8.5° , see the Supporting Information).

The cyclic voltammogram of **2** exhibits three oxidation waves in CH_2Cl_2 at +0.16, +0.96, and +1.22 V versus ferrocene/ferrocenium (Fc/Fc^+ ; Table 1). The first oxidation is much easier than the one reported for the related complex $[Ni(tBu-salen)]$ ($\Delta E \approx 420$ mV, Table 1),^[5b,14] in agreement

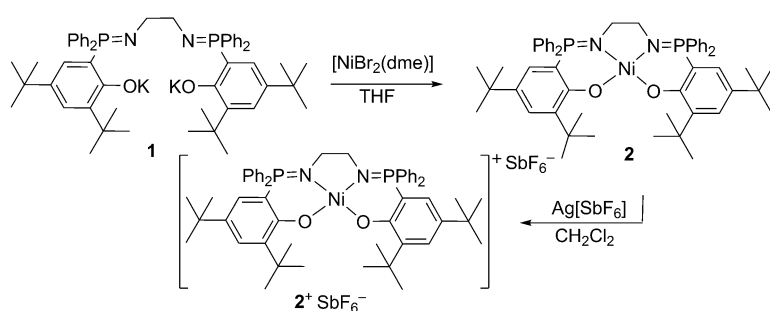
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Scheme 1. Synthesis of nickel complexes **2** and **2**⁺ SbF₆[−].

Table 1: Electrochemical data for **2** (3.0 mmol L^{−1} in CH₂Cl₂; [Bu₄N][BF₄]: 0.12 M^{−1}; 50 mV s^{−1}) and [Ni(*t*Bu-salen)]^[5b,14]. Potential values given relative to E_{1/2}(Fc⁺/Fc).

Complex	E _{1/2,1} [V]	E _{1/2,2} [V]	E _{1/2,3} [V]
2	0.16	0.96	1.22
[Ni(<i>t</i> Bu-salen)]	0.58	1.04	

with the better electron-donating ability of the phosphasalen. Moreover the difference between the first and second oxidation waves of **2** is large ($\Delta E^{1/2} = 0.8$ V) compared to that observed for the salen analogue ($\Delta E^{1/2} = 0.46$ V).^[5b,14] In nickel salen complexes, the two first oxidations are known to occur on both phenoxide rings. Within the series of Ni^{II} salen complexes, the rather large separation between the two first half-wave potentials observed for [Ni(*t*Bu-salen)] was interpreted as a result of the strong electronic communication between the two phenoxide rings.^[5b,14] Therefore the even larger peak separation observed for **2** may indicate that the first oxidation in this complex does not occur on the ligand but might be metal centered.

This latter result prompted us to investigate the chemical oxidation of **2**. Cation **2**⁺ was synthesized by adding one equivalent of a silver salt to a CH₂Cl₂ solution of **2**. This induced a rapid color change from purple to black. Monitoring the reaction with ³¹P{¹H} NMR spectroscopy showed disappearance of the starting material and formation of a paramagnetic species, whose ¹H NMR signals were in the range of chemical shift values already observed for Ni^{III} complexes.^[15] Variable-temperature experiments confirmed the temperature dependence of these chemical shifts. Various silver salts were used and led to similar results nevertheless only **2**⁺ SbF₆[−] did crystallize, which is why we focused on this complex. Complex **2**⁺ is stable for months in the solid state and for days in toluene or CH₂Cl₂ solution, at room temperature under an inert atmosphere.

The ORTEP plot of **2**⁺ is presented in Figure 1. The nickel ion adopts a slightly distorted square-planar geometry (deviation from planarity O1–N1–N2–O2: 11.06°). No stacking interaction or hydrogen bond was observed with the SbF₆[−] anion. The O–C_{Ar} bonds do not change significantly upon oxidation (1.327(4) Å and 1.326(5) Å vs 1.317(3) Å), whereas all Ni–O and Ni–N bonds shorten (1.875(3) Å and 1.842(3) Å for Ni–N and 1.828(2) Å and 1.844(2) Å for Ni–O in **2**⁺ vs

1.887(2) Å and 1.881(2) Å, respectively, in the neutral complex). Interestingly, the contraction of the coordination sphere is not symmetrical, and is stronger along O1–Ni–N2 than along O2–Ni–N1. Noteworthy, the shortening of the Ni–N bond is accompanied by an elongation of the P–N bond from 1.619(2) Å in **2** to 1.639(3) Å and 1.650(3) Å for P1–N1 and P2–N2, respectively, again N2 experiences the largest variation. This may indicate a lower stabilization of the nitrogen lone pairs by phosphorus.

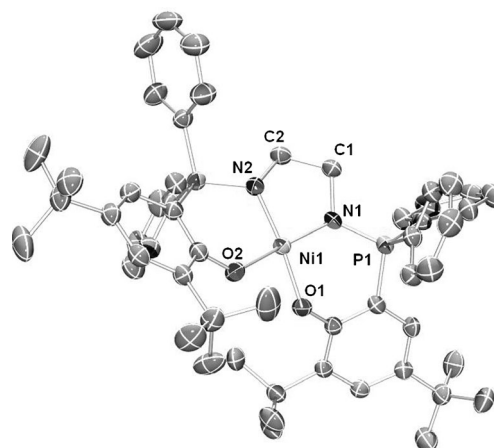


Figure 1. ORTEP view of the cation **2**⁺. The SbF₆[−] anion, solvent molecules, and hydrogen atoms have been omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Selected distances [Å] and angles [°]: Ni1–O1 1.828(2), Ni1–O2 1.844(2), Ni1–N1 1.875(3), Ni1–N2 1.842(3), P1–N1 1.639(3), P2–N2 1.650(3), O1–C3 1.327(4), O2–C30 1.326(5), N1–C1 1.486(5), N2–C2 1.486(5); N1–Ni1–O1 94.9(1), O2–Ni1–N2 95.3(1), N1–Ni1–N2 86.8(1), O1–Ni1–O2 84.2(1), O1–N1–N2–O2 11.06.

To get insight into the structural features of **2** and **2**⁺, DFT calculations were carried out on both complexes. For the oxidized complex, calculations were carried out with and without the anion, giving comparable results (see the Supporting Information). The geometry optimizations well reproduce the experimental structures, including the non-symmetric contraction of the coordination sphere upon oxidation (see Table S6). In the neutral complex **2**, the two highest occupied molecular orbitals, which are of similar energy, result from antibonding interactions between the d_{xz} or d_{yz} orbital of Ni and p_π orbitals of the oxygen atoms (see the Supporting Information). Upon oxidation this degeneracy is removed, as one electron is removed from the orbital featuring an antibonding interaction of the Ni d_{yz} orbital and the p_π orbitals of O1 and N2. This explains why the oxidation causes a stronger contraction on this particular axis. Importantly, this observation is in accordance with the highest occupied quasi-restricted orbital calculated for [Ni(*t*Bu-Psalen)]⁺ (**2**⁺) as well as the Mulliken spin distribution, which is mainly concentrated on Ni (0.69), O1 (0.13), and N2 (0.12) (Figure 2). Therefore, from the DFT calculations, and

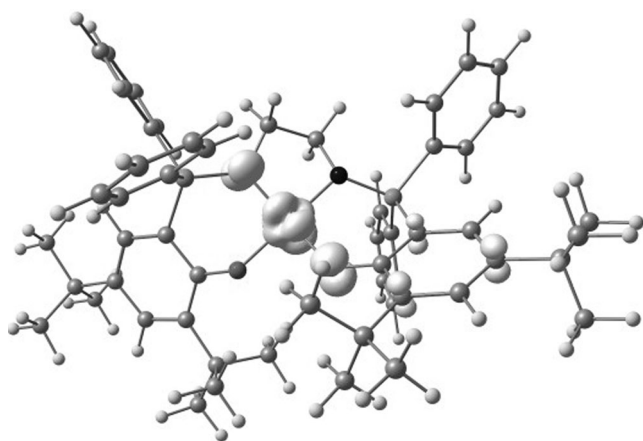


Figure 2. Spin-density distribution in complex 2^+ .

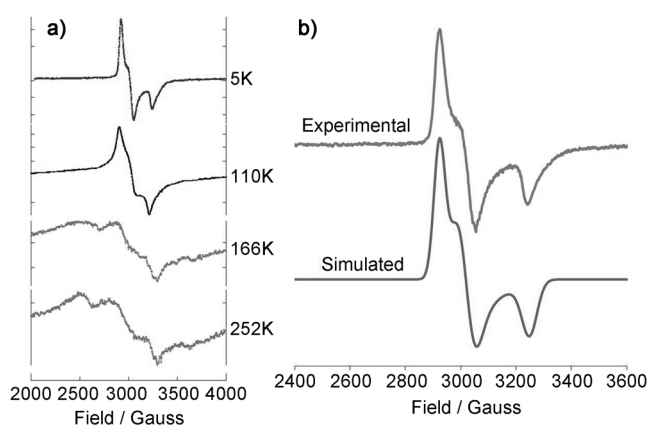


Figure 3. a) X-band EPR spectra of 2^+SbF_6^- at different temperatures. 2^+SbF_6^- (4 mM) in toluene:benzene, frequency 9.3690 GHz, $P=0.1$ mW at 5 K, 60 mW at other temperatures. b) Experimental (at 5 K) and simulated spectrum.

contrary to its salen analogue $[\text{Ni}(\text{tBu-salen})]^+$, 2^+ may be described as a high-valent Ni^{III} complex rather than a metal complex with a phenoxy radical ligand.

The X-band EPR spectrum of 2^+SbF_6^- was recorded in a toluene/benzene mixture at different temperatures. At 5 K, 2^+SbF_6^- displayed a large g -tensor anisotropy (Figure 3) with $g_1 = 2.29$, $g_2 = 2.215$, and $g_3 = 2.061$ ($g_{\text{iso}} = 2.19$), indicative of a $S = 1/2$ ground state in a rhombic symmetry centered on the nickel ion, that is, a Ni^{III} center. When the temperature was increased, the EPR signal decreased but no change in the g strengths was noticed up to 100 K. Above this temperature, the signal was very weak, which prevented reasonable simulation, and finally disappeared so that 2^+SbF_6^- is EPR-silent at room temperature. Large g values account for significant orbital contributions that allow low-lying states to mix through spin-orbit coupling. This is rather usual in d^7 complexes, and may also relate to the loss of intensity of the EPR signal at higher temperatures.^[16,17] In a perfect square-planar geometry the g matrix orientation would be as $g_x = g_y \gg g_z$.^[18] In the case of 2^+SbF_6^- , it is as $g_1 > g_2 \gg g_3$ and indeed indicates a predominance of the xy plane (g_1 and g_2)

over the z axis (g_3) but with a significant distortion in the xy plane (g_1 differs from g_2). This observation is in good agreement with the X-ray data that feature two sets of distances in the xy plane for the axes N1-Ni-O2 and N2-Ni-O1 but, unfortunately, no hyperfine coupling with ^{14}N and/or ^{31}P in the x and y axes could be observed to further sharpen this analysis. The powder EPR spectrum of 2^+SbF_6^- is also in agreement with a Ni^{III} complex (see the Supporting Information), ruling out an eventual axial solvent coordination in solution. EPR g -tensor calculations were also performed on 2^+SbF_6^- and gave a very similar outcome ($g_1 = 2.34$, $g_2 = 2.21$, and $g_3 = 2.09$, $g_{\text{iso}} = 2.21$; see the Supporting Information).

As the decrease of the EPR signal intensity could be associated with valence tautomerism,^[5b] temperature-dependent magnetic data were recorded in the solid state for 2^+SbF_6^- . The data show a Curie behavior over the temperature range 4–300 K ($\chi_M = C/T$; see the Supporting Information). The $\chi_M T$ value ($C = 0.46 \text{ cm}^3 \text{ K mol}^{-1}$) is a little higher than expected for a d^7 low-spin complex but can be fitted with a g_{iso} value of 2.22, which is in very good agreement with the g_{iso} value obtained from EPR ($g_{\text{iso}} = 2.19$). No decrease of the $\chi_M T$ value was observed in the temperature range 4–300 K, which reinforces that the oxidized nickel phosphasalen complex features a d^7 high-valent Ni^{III} center which persists upon increasing the temperature.

Visible spectroscopy was also performed on 2 and 2^+SbF_6^- at room temperature in CH_2Cl_2 and toluene. Complex 2 presents two bands at $\lambda_{\text{max}} = 565 \text{ nm}$ (17700 cm^{-1}) and $\lambda_{\text{max}} = 665 \text{ nm}$ (15040 cm^{-1} ; see Figure S4) that account for metal \rightarrow ligand charge transfer (MLCT), typical in Ni^{II} square-planar complexes.^[4a] When one electron is removed by oxidizing 2 to 2^+SbF_6^- , the purple color of 2 changes to black, which is indicative of high absorption in the visible range. Two broad bands are centered in toluene at $\lambda_{\text{max}} = 490 \text{ nm}$ (20400 cm^{-1}) and $\lambda_{\text{max}} = 990 \text{ nm}$ (10100 cm^{-1}) with absorption coefficients over $5000 \text{ cm}^{-1} \text{ M}^{-1}$ (Figure 4). To better understand this particular spectrum, a time-dependent DFT analysis was performed using the optimized geometry of

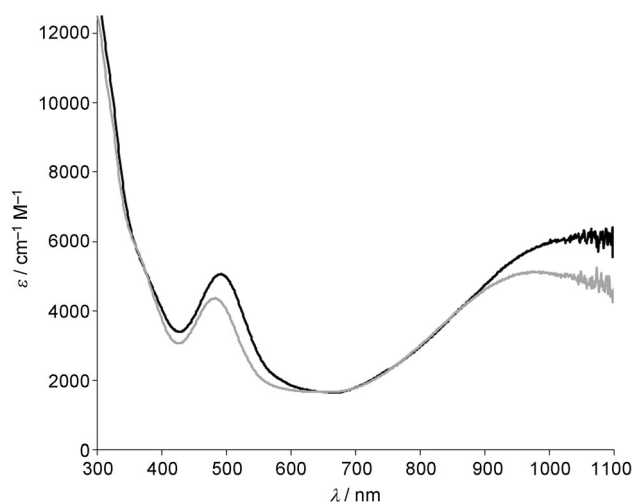


Figure 4. UV/Vis spectra of 2^+SbF_6^- in CH_2Cl_2 (black) and toluene (gray).

2^+ described above. This analysis predicted three principal transitions at $11\,337\text{ cm}^{-1}$ (I, $f_{\text{osc}} = 0.066$), $11\,661\text{ cm}^{-1}$ (II, $f_{\text{osc}} = 0.064$), and $22\,409\text{ cm}^{-1}$ (III, $f_{\text{osc}} = 0.094$), with energies that agree to some extent with the experimental transitions ($10\,100\text{ cm}^{-1}$ and $20\,400\text{ cm}^{-1}$; see Figure S10). All calculated transitions have a multiconfigurational character that does not allow sharp conclusions,^[19] but this analysis indicates that I and II are essentially composed of $L \rightarrow M$ CTs and explains well the broad and intense transitions and the dark color of the complex. No other significant transition is predicted at lower energy which reinforces the picture of a localized Ni^{III} center versus a delocalized system.^[4a]

In summary, a Ni^{II} complex with a novel *tert*-butyl substituted phosphasalen ligand was synthesized and characterized. Upon oxidation, this complex led to a high-valent $\text{Ni}^{\text{III}[20]}$ complex as demonstrated by X-ray analysis, EPR spectroscopy, magnetic measurements, and visible spectroscopy as well as DFT calculations. 2^+SbF_6^- is therefore one of the rare tetracoordinated Ni^{III} complexes,^[15,16,18a,21] and to the best of our knowledge the only one featuring a phenoxide ligand. This observation markedly differs from precedents in the salen chemistry where Ni^{III} complexes were observed only at low temperature, or in the presence of additional ligands or anions. It can be rationalized by the better electron-donating ability of iminophosphoranes compared to imines, and by the decreased electron density at the phenol rings which are substituted by an electron-demanding phosphorus atom.^[12] Preliminary investigations concerning the reactivity of 2^+SbF_6^- showed it to have a high but difficult to control oxidation capacity. Our current efforts are devoted to this, considering a fine tuning of the ligand structure. Further studies will also focus on the oxidation of phosphasalen complexes of metals different from nickel.

Experimental Section

Synthesis of 2^+SbF_6^- : Addition of AgSbF_6 (34.4 mg, 0.1 mmol) to a solution of **2** (89.4 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) induced a rapid color change from purple to black and precipitation of silver. After removal of Ag by centrifugation, CH_2Cl_2 was evaporated and the residue was dissolved in toluene (1.5 mL), giving a deep red-brown solution. Dark crystals were obtained after one week of storage at -40°C , isolated by centrifugation, and dried under reduced pressure (104 mg, 95%). $^1\text{H NMR}$: $\delta = 19.10$ (s, 2H, $\text{CH}(\text{OAr})$), 15.30 (s, 2H, $\text{CH}(\text{OAr})$), 8.31 (s, br, 16H, $\text{CH}(\text{PPh}_2)$), 7.20 (s, br, 4H, $\text{CH}(\text{PPh}_2)$), 3.17 (s, 18H, $\text{C}(\text{CH}_3)_3$), 2.50 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.68 (s, 2H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$), 1.63 ppm (s, br, 2H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$). Analysis calcd for 2^+SbF_6^- ($\text{C}_{54}\text{H}_{64}\text{F}_6\text{N}_2\text{NiO}_2\text{P}_2\text{Sb}$): C 57.42; H 5.71; N 2.48; found: C 57.50; H 5.80; N 2.37.

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