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A Tetracoordinated Phosphasalen Nickel(III) Complex

Thi-Phuong-Anh Cao, Grégory Nocton, Louis Ricard, Xavier F. Le Goff, and Audrey Auffrant*

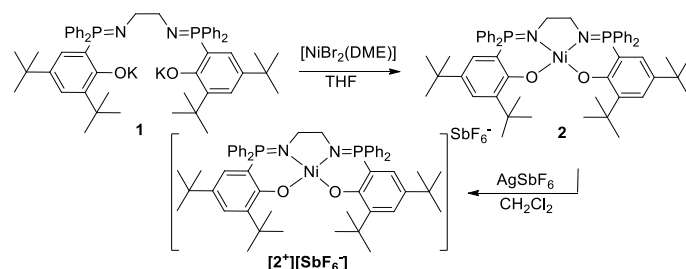
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N,N'-bis(salicylidine)ethylenediamine (salen) derivatives constitute a very successful class of ligand that have found numerous applications in inorganic chemistry and catalysis.^[1] Its extraordinary popularity comes from its easy synthesis, allowing a variety of skeleton variations, and its ability to coordinate a great number of different metal ions. Moreover the presence of two phenoxy and imine functions is reminiscent of the coordination environment generated by two histidines and two tyrosines, encountered in several enzymes. Thus, 15 years ago, the one-electron oxidation of a (salen)copper(II) was described, and the resulting persistent phenoxy radical was established as a biomimetic functional model of galactose oxidase.^[2] Since then, one-electron oxidized salen metal 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 (metal centered oxidation) or metal-ligand radical species (ligand centered oxidation). Therefore, various factors may affect the oxidation locus, as it was nicely illustrated in the case of nickel salen complexes. In non coordinating solvents, one electron oxidized nickel salen complexes are generally highly delocalized ligand radical species with a 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 does the locus of the oxidation, allowing the formation of Ni^{III} complexes.^[4a,b, 5] Temperature dependant behaviour, *viz.* 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 phenoxy rings. They influence not only the oxidation locus (which takes place at the most electron rich phenoxy) as evidenced with complexes featuring unsymmetrical salen,^[3c, 7] but also the extent of the radical delocalization.^[3b, 8] The hybridization of the nitrogen atoms is also of prime importance since it may influence the oxidation locus, the spin state of the metal, and the magnetic interaction within the molecule.^[5b, 9]

Astonishingly, despite numerous structural variations proposed for salen ligands, the introduction of heteroatoms in its backbone was

rarely investigated.^[10] As we are interested in iminophosphorane (P=N) based ligands as alternative to conventional imine ones,^[11] we developed a new class of ligand featuring iminophosphoranes in place of imines, which we termed phosphasalen (or Psalen). We have recently demonstrated that these ligands are more flexible and electron-donating than their carbon analogue^[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 phosphasalen nickel(II) 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 to use a ligand featuring substituents on the ortho and para positions of the phenoxy in order to increase its stability, and preferred tertbutyl groups for solubility reason. The required phosphasalen ligand **1** was prepared following a procedure we recently published.^[13b] Reaction of **1** with [NiBr₂(DME)] in THF led, after removal of the potassium salts, to the formation of the nickel(II) complex **2** as a purple solid in 92% yield (Scheme 1). In the ³¹P{¹H} NMR spectrum the coordination is indicated by a deshielding of the phosphorus nuclei appearing as a singlet at $\delta(\text{CD}_2\text{Cl}_2) = 36.0$ ppm. This complex was characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. As expected for a d⁸ complex, **2** adopts a square planar geometry around the metal with a slight deviation from planarity (8.5°, see SI).



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

The cyclic voltammogram of **2** exhibits three oxidation waves in CH₂Cl₂ at +0.16, +0.96, and +1.22 V versus ferrocene/ferrocenium (Fc/Fc⁺). The first oxidation is much easier than the one reported for the related [Ni(^tBu-salen)] ($\Delta E \sim 420$ mV, table 1),^[5b, 14] in agreement 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 salen nickel complexes, the two first oxidations are known to occur on both phenoxyes. Within the Ni(II) salen complexes series, the rather large separation between the two first half-wave potentials observed for [Ni(^tBu-salen)] was interpreted as a result of the strong electronic communication between the two phenoxyes.^[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 may be metal centered.

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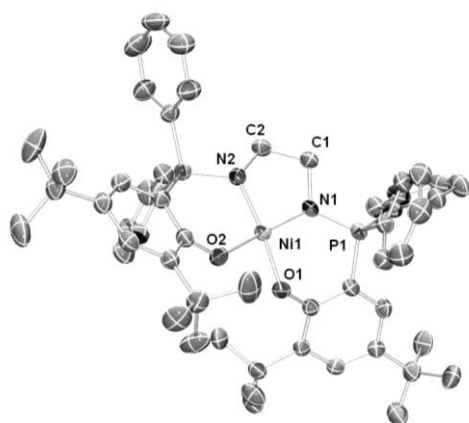
Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

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(^bBu-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(^b Bu-Salen)]	0.58	1.04	

This latter result prompted us to investigate the chemical oxidation of **2**. The cation [2⁺] was synthesized by addition of one equivalent of a silver salt to a CH₂Cl₂ solution of **2**. This induced a rapid color change from blue to red-brown. Monitoring the reaction with ³¹P{¹H} NMR spectroscopy shows the disappearance of the starting material and the formation of a paramagnetic species, whose ¹H NMR signals spread in the chemical shifts values already observed for Ni(III) complexes.^[15] Variable temperature experiments confirmed the temperature dependence of those chemical shifts. Different silver salts were used and led to similar results nevertheless only [2⁺][SbF₆⁻] did crystallize, which encouraged us to focus on this complex. Complex [2⁺] is stable for months in the solid state and days in toluene or dichloromethane solution, at room temperature under an inert atmosphere.

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 (°): Ni(1)-O(1) 1.828 (2), Ni(1)-O(2) 1.844(2), Ni(1)-N(1) 1.875 (3), Ni(1)-N(2) 1.842(3), P(1)-N(1) 1.639 (3), P(2)-N(2) 1.650 (3), O(1)-C(3) 1.327 (4), O(2)-C(30) 1.326(5), N(1)-C(1) 1.486(5), N(2)-C(2) 1.486(5), N(1)-Ni(1)-O(1) 94.9(1), O(2)-Ni(1)-N(2) 95.3(1), N(1)-Ni(1)-N(2) 86.8(1), O(1)-Ni(1)-O(2) 84.2(1), O(1)-N(1)-N(2)-O(2) 11.06.

The ORTEP plot of the cation [2⁺] is presented in Figure 1. The nickel ion adopts a slightly distorted square planar geometry (deviation from planarity O(1)-N(1)-N(2)-O(2): 11.06°). No stacking interaction or hydrogen bond was observed with the SbF₆⁻ anion. The O-C_{Ph} bonds do not vary 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 in the neutral complex). Interestingly, the contraction of the coordination sphere is not symmetrical, and is stronger along the O(1)-Ni-N(2) axis than on the O(2)-Ni-N(1) one. 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 P(1)-N(1) and P(2)-N(2) respectively, again N(2) experiences the

largest variation. This may indicate a lower stabilization of the nitrogen lone pairs by phosphorus.

In order to get insights in 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 SI). 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 SI). Upon oxidation this degeneracy is suppressed, as one electron is removed from the orbital featuring an antibonding interaction of the d_{yz} orbital of the Ni and the p_π orbitals of O(1) and N(2). This explains why the oxidation causes a stronger contraction on this particular axis. Importantly, this coincides with the highest occupied quasi-restricted orbital calculated for [Ni(^bBu-Psalen)]⁺ [2⁺] as well as the Mulliken spin distribution, which is mainly concentrated on the Ni (0.69), O(1) (0.13), and N(2) (0.12) atoms. Therefore, from the DFT calculations, and contrary to its salen analog [Ni(^bBu-salen)]⁺, [2⁺] may be described as a high valent Ni^{III} complex rather than a ligand radical metal complex.

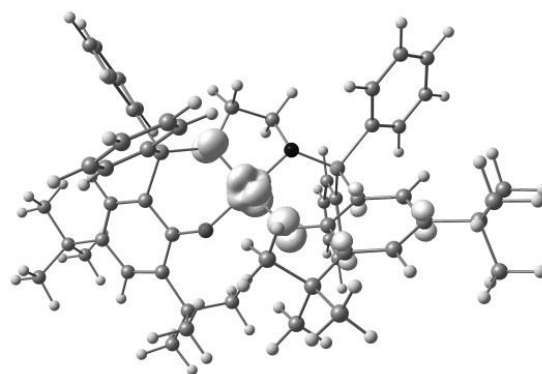


Figure 2. Spin density distribution in complex [2⁺]

X-Band EPR of [2⁺][SbF₆⁻] was recorded in a toluene/benzene mixture at different temperatures. At 5 K, [2⁺][SbF₆⁻] displayed a large g-tensor anisotropy (Figure 3) with g₁= 2.29, g₂= 2.215 and g₃= 2.061 (g_{iso} = 2.19), indicative of a S=1/2 ground state in a rhombic symmetry centered on the nickel ion, *i.e.* a Ni^{III} metal center. When temperature is increased, the EPR signal tends to decrease but no change in the g strengths have been noted up to 100 K. Above this temperature, the signal is very weak which prevents reasonable simulation and disappears so that [2⁺][SbF₆⁻] 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 d⁷ complexes, and may also relate to the loss of intensity of the EPR signal at higher temperature.^[16, 17] In a perfect square planar geometry the g matrix orientation would be as g_x = g_y >> g_z.^[18] In the case of [2⁺][SbF₆⁻], g₁ > g₂ >> g₃ and indeed indicates a predominance of the xy plane (g₁ and g₂) over the z axis (g₃) but with a significant distortion in the xy plane (g₁ differs from g₂). This observation is in good agreement with the X-ray data that feature two different sets of distances in the xy plane for the N(1)-Ni-O(2) and N(2)-Ni-O(1) axes but, unfortunately, no hyperfine coupling with the ¹⁴N and/or the ³¹P atoms in the x and y

axis could be observed to further sharpen this analysis. Powder EPR of $[2^+][SbF_6^-]$ is also in agreement with a Ni^{III} complex (see 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 $g_3 = 2.09$, $g_{iso} = 2.21$; see Supporting Information). As the decrease of EPR intensity signal may have been associated with valence tautomerism,^[5b] temperature dependant magnetic data were recorded in the solid state for $[2^+][SbF_6^-]$. The data show a Curie behaviour over the 4-300 K temperature range ($\chi_M = C/T$) (See SI). The $\chi_M T$ value ($C = 0.46 \text{ cm}^3 \cdot \text{K/mol}$) 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} obtained from EPR ($g_{iso} = 2.19$). No decrease of the $\chi_M T$ value was observed in a 4-300K temperature range which reinforces that the oxidized phosphasalen nickel features a d^7 high valent Ni^{III} which persists upon increasing the temperature.

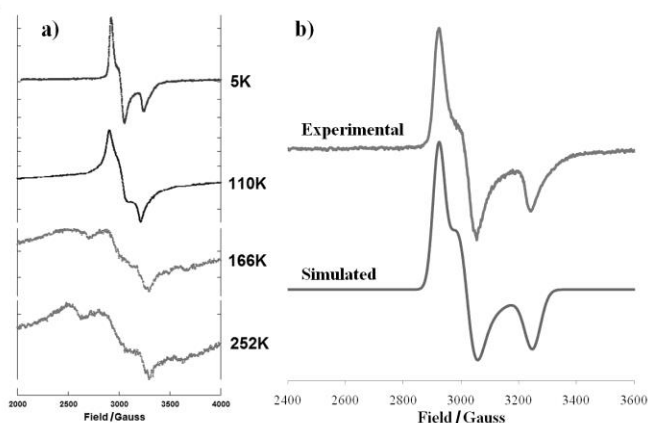


Figure 3. X-band EPR spectra of $[2^+][SbF_6^-]$ at different temperatures. $[2^+][SbF_6^-]$ (4 mM) in toluene:benzene, frequency 9.3690 GHz, P = 0.1mW at 5K, 60 mW at other temperatures. (b) Experimental spectrum (at 5k) and simulated one.

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 $\lambda_{max} = 565 \text{ nm}$ (17700 cm^{-1}) and $\lambda_{max} = 665 \text{ nm}$ (15040 cm^{-1}) (see Figure S4) that account for MLCT charge transfer, typical in nickel(II) square planar complexes.^[4a] When one electron is removed and **2** is oxidized to $[2^+][SbF_6^-]$, the purple colour of **2** changes to black and is indicative of high absorption in the visible range. The visible spectrum indeed possesses high absorption coefficients and two broad bands centered in toluene at $\lambda_{max} = 490 \text{ nm}$ (20400 cm^{-1}) and $\lambda_{max} = 990 \text{ nm}$ (10100 cm^{-1}) with absorption coefficients over $5000 \text{ cm}^{-1} \cdot \text{M}^{-1}$ (Figure 4). In order to better understand this particular spectrum, a Time-Dependant DFT analysis was performed using the optimized geometry of $[2^+]$ described above. This predicts three principal transitions at 11337 cm^{-1} (**I**, $f_{osc} = 0.066$) and 11661 cm^{-1} (**II**, $f_{osc} = 0.064$) and 22409 cm^{-1} (**III**, $f_{osc} = 0.094$), with energies that agree to some extent with the experimental transitions (*viz.* 10100 cm^{-1} and 20400 cm^{-1}) (see Figure S10). All of them have a multiconfigurational character that do not allow sharp conclusions,^[19] but it appears clearly from this analysis that **I** and **II** are essentially composed of LMCT and explain well broad intense transitions and dark coloured complexes. 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 nickel(II) complex incorporating an original tertbutyl substituted phosphasalen ligand was synthesized and characterized. Upon oxidation, this complex led to a high valent nickel(III)^[20] complex as demonstrated by X-ray, EPR, magnetism, 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 at low temperature, in 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 $[2^+][SbF_6^-]$ evidenced a fast oxidative ability that remains yet difficult to control. Our current efforts are devoted to this, considering a fine tuning of the ligand structure. Further studies will also focus on the oxidation of other phosphasalen complexes differing from **2** by the nature of the metal.

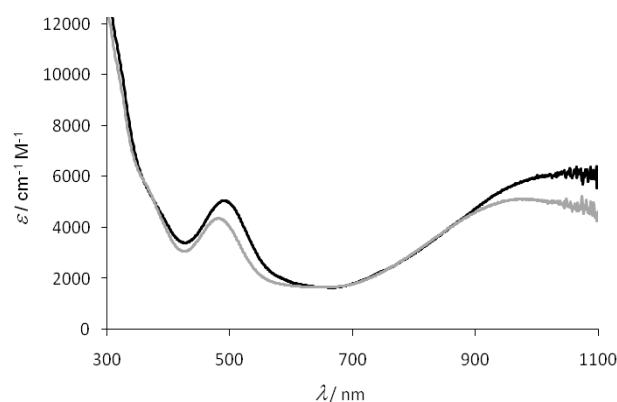


Figure 4. UV spectra of $[2^+][SbF_6^-]$ in dichloromethane (black) and in toluene (grey).

Experimental Section

Synthesis $[2^+][SbF_6^-]$

Addition of $AgSbF_6$ (34.4 mg, 0.1 mmol) into a solution of complex **2** (89.4 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) induced a rapid colour change from blue to deep red and precipitation of silver. After removal of Ag by centrifugation, dichloromethane 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 , which were then isolated by centrifugation and dried under reduced pressure. (104 mg, 95 %). $^1\text{H NMR}$: δ 19.10 (s, 2H, $CH(OAr)$), 15.30 (s, 2H, $CH(Oar)$), 8.31 (s, br, 16H, $CH(PPh_2)$), 7.20 (s, br, 4H, $CH(PPh_2)$), 3.17 (s, 18H, $C(CH_3)_3$), 2.50 (s, 18H, $C(CH_3)_3$), 1.68 (s, 2H, $N-CH_2-CH_2-N$), 1.63 (s, br, 2H, $N-CH_2-CH_2-N$). Anal. Calcd for $[2^+][SbF_6^-]$ $C_{54}H_{64}F_6N_2NiO_2P_2Sb$: C, 57.42; H, 5.71; N, 2.48. Found: C, 57.50; H, 5.80; N, 2.37.

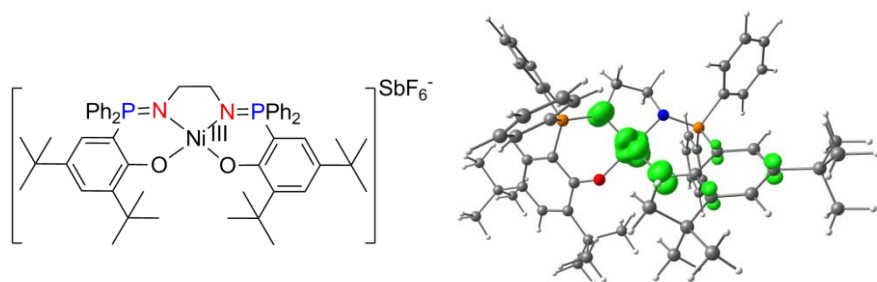
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P=N does not equal C=N!

One electron oxidation of a nickel(II) complex incorporating an original phosphasalen ligand (*t*Bu-Psalen) leads to a rare tetracoordinated Ni^{III} complex. The oxidation locus is demonstrated by the use of various spectroscopic tools such as X-ray, EPR, magnetism, and visible spectroscopy as well as with DFT calculations.

ABSTRACT

The oxidation of a nickel(II) complex bearing a tetradentate phosphasalén ligand, which differs from salen by the presence of iminophosphoranes (P=N) in place of imines, was easily achieved by addition of a silver salt. The locus of this oxidation was investigated with a combination of different techniques (NMR, EPR, UV spectroscopy, X-ray crystallography, magnetism measurement) as well as DFT calculations. All data are in agreement with a high valent nickel(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 presence of additional ligands or anions. Therefore, thanks to the good electron donating properties of the phosphasalén ligand, $[\text{Ni}(\text{Psalen})]^+$ represents a rare example of a tetracoordinated high valent nickel complex in presence of a phenoxide ligand.