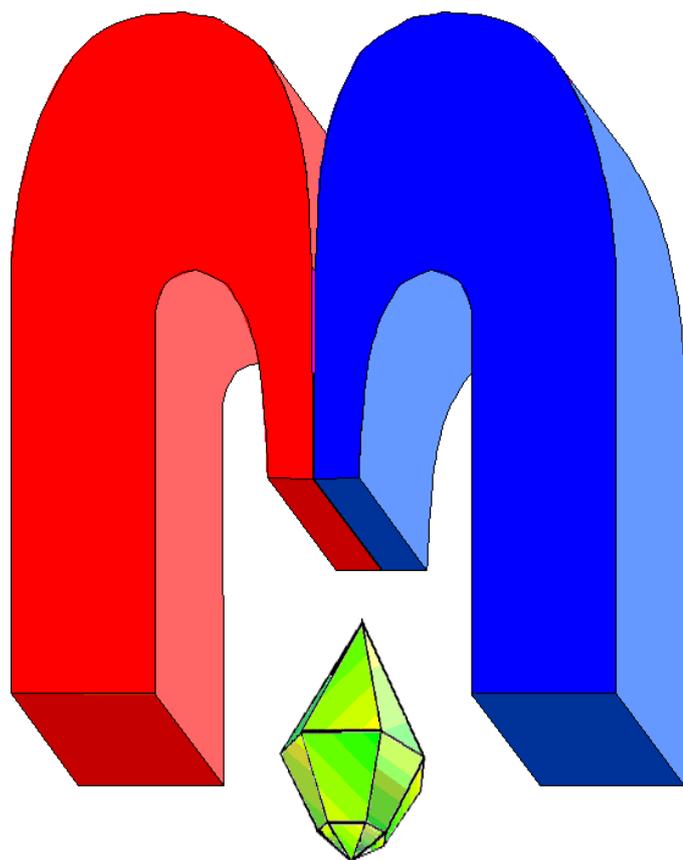


ISSN 2072-5981



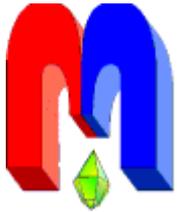
***Magnetic  
Resonance  
in Solids***

Electronic Journal

*Volume 14, 2012*

*No. 2, 12205 – 5 pages*

<http://mrsej.ksu.ru>



Established and published by Kazan University  
Sponsored by International Society of Magnetic  
Resonance (ISMAR)  
Registered by Russian Federation Committee on Press,  
August 2, 1996  
First Issue was appeared at July 25, 1997

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In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# Versatile coordination sphere dynamics in *o*-semiquinonato pincer nickel complexes: an EPR study and mechanistic aspects<sup>†</sup>

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(Received November 26, 2012; accepted December 20, 2012)

*o*-Semiquinonato pincer nickel complexes demonstrate different kinds of coordination sphere dynamics depending from the nature of the phosphorus substituents, the rigidity of the linker in the pincer fragment and the nature of the *o*-semiquinone.

PACS: 33.35.+r, 82.20.-w, 82.37.-j.

Keywords: EPR, spin labels, pincer complexes, *o*-semiquinones, coordination sphere dynamics

## 1. Introduction

Pincer complexes of transition metals are of a great interest last decades. Being fine catalysts for wide scale of reactions they have an excellent chemical stability [1]. On the other hand, the *o*-semiquinonato ligands can be successfully used for studying of the composition of the transition complexes, their geometry and dynamic processes in their coordination sphere as well [2].

In present study we describe some pincer nickel complexes containing different substituents at phosphorus atoms and *o*-semiquinonato ligands with different symmetry and steric properties in *ortho*- and *para*-positions to oxygen atoms (Figure 1).

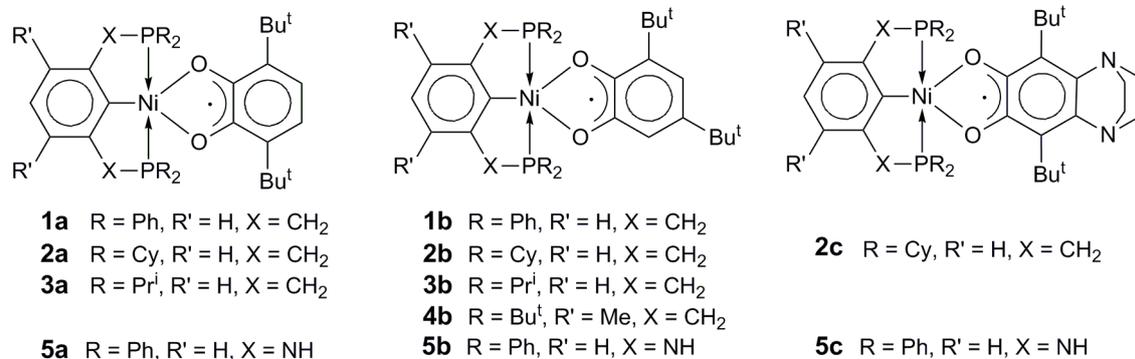


Figure 1. Notation of *o*-semiquinonato pincer nickel complexes.

## 2. Experimental section

The synthesis of complexes **1** - **4** by reaction of corresponding nickel organohalogenide with thallium *o*-semiquinolinate in THF solution was described earlier [3]. Similar procedure (using pentane instead of THF) was used for synthesis of **5a-c**.

Electron paramagnetic resonance (EPR) spectra were recorded on Bruker EMX spectrometer, operating in X-band (work frequency ~ 9.6 GHz) and equipped by NMR-gaussmeter and variable temperature unit. HFC constants, *g*-factor values and linewidths have been obtained by simulation in WINEPR SimFonia (v. 1.25) and EasySpin 4.0.0 [4]. The parameters of the spectra are listed in Table 1.

<sup>†</sup> This paper material was selected at XV International Youth Scientific School "Actual problems of magnetic resonance and its application", Kazan, 22 – 26 October 2012. The paper was recommended to publication in our journal and it is published after additional MRSej reviewing.

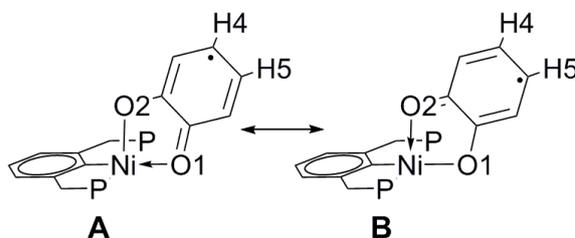
**Table 1.** Parameters of EPR spectra of investigated complexes

Complex	<i>T</i> , K	<i>g<sub>i</sub></i>	<sup>31</sup> P HFC constants, G	SQ HFC constants, G
<b>1a<sup>a</sup></b>	290	2.0060	$a_{P1} = a_{P2} = 24.2$	$a_{H1} = a_{H2} = 2.8$
	180	2.0056	$a_{P1} = a_{P2} = 25.6$	$a_{H1} = 3.4, a_{H2} = 2.2$
<b>1b<sup>a</sup></b>	330	2.0052	$a_{P1} = a_{P2} = 20.3$	$a_H = 2.6$
	200, isomer 1	2.0064	$a_{P1} = a_{P2} = 18.4$	$a_H = 2.4$
	200, isomer 2	2.0041	$a_{P1} = a_{P2} = 24.4$	$a_H = 3.4$
<b>2a<sup>a</sup></b>	340	2.0071	$a_{P1} = a_{P2} = 21.7$	— <sup>b</sup>
	260	2.0071	$a_{P1} = 26.7, a_{P2} = 15.5$	$a_{H1} = 3.6, a_{H2} = 2.2$
	220	2.0071	$a_{P1} = 27.8, a_{P2} = 14.7$	$a_{H1} = 3.6, a_{H2} = 2.2$
<b>2b<sup>a</sup></b>	320	2.0054	$a_{P1} = a_{P2} = 17.9$	— <sup>b</sup>
	220	2.0054	$a_{P1} = 22.7, a_{P2} = 13.4$	$a_H = 2.5$
<b>2c</b>	320	2.0055	$a_{P1} = a_{P2} = 21.2$	— <sup>b</sup>
	220	2.0055	$a_{P1} = 28.0, a_{P2} = 14.5$	— <sup>b</sup>
<b>3a<sup>a</sup></b>	300	2.0055	$a_{P1} = a_{P2} = 19.8$	$a_{H1} = a_{H2} = 2.8$
	190	2.0054	$a_{P1} = 25.3, a_{P2} = 15.7$	$a_{H1} = 3.8, a_{H2} = 2.2$
<b>3b<sup>a</sup></b>	290	2.0054	$a_{P1} = a_{P2} = 16.6$	$a_H = 2.7$
	200, isomer 1	2.0043	$a_{P1} = a_{P2} = 14.4$	$a_H = 2.2$
	200, isomer 2	2.0054	$a_{P1} = 22.2, a_{P2} = 14.2$	$a_H = 2.5$
<b>4b<sup>a</sup></b>	290	2.0062	$a_{P1} = a_{P2} = 14.1$	$a_H = 2.5$
	170	2.0062	$a_{P1} = a_{P2} = 17.0$	$a_H = 2.5$
<b>5a</b>	290	2.0036	$a_{P1} = a_{P2} = 19.4$	$a_{H1} = a_{H2} = 3.0$
	170	2.0036	$a_{P1} = a_{P2} = 19.9$	$a_{H1} = 4.1, a_{H2} = 1.9$
<b>5b</b>	290, signal 1	2.0044	$a_{P1} = a_{P2} = 16.7$	$a_H = 2.55$
	290, signal 2	2.0105	$a_P = 3.1$	$a_H = 2.9$
<b>5c</b>	300	2.0036	$a_P = 3.1$	— <sup>b</sup>
	160	2.0036	$a_{P1} = a_{P2} = 16.7$	— <sup>b</sup>

<sup>a</sup> Cited from [3].<sup>b</sup> Unobserved due to broad lines.

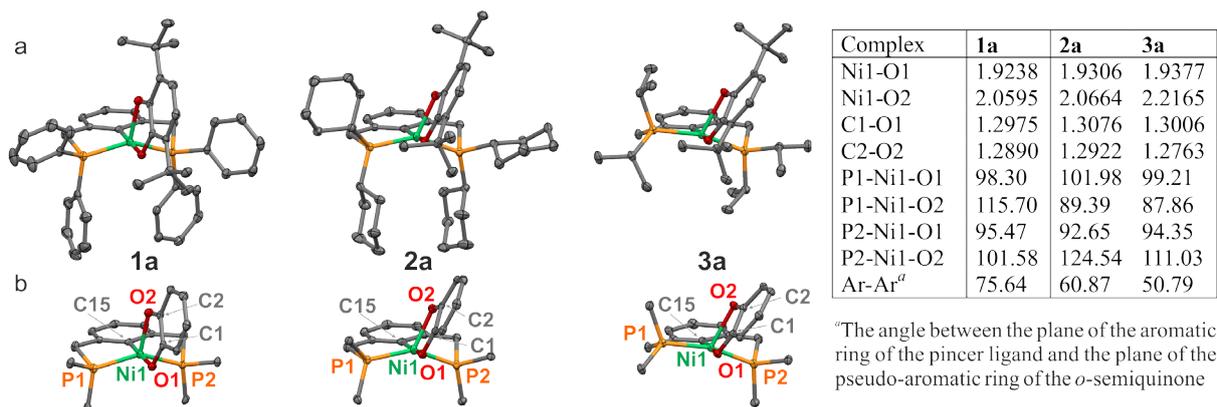
### 3. Results and discussion

EPR spectrum of **1a** at 200 K (Table 1) is triplet 1:2:1 of doublets of doublets resulting from the hyperfine splitting on two equivalent phosphorus nuclei and two non-equivalent protons of *o*-semiquinonato ring. The asymmetry of the spin density distribution inside the *o*-semiquinonic fragment reflects the difference of the bonds lengths (Figures 2, 3) in the chains Ni1-O1-C1 and Ni1-O2-C2. The coordination mode of the *o*-semiquinone can be presented as a sum of the resonance structures **A** and **B** which are responsible for appearing of spin density on the protons H4 and H5. The excess of spin density on the O2 means that the resonance structure **B** predominates over the structure **A** (Figure 2).

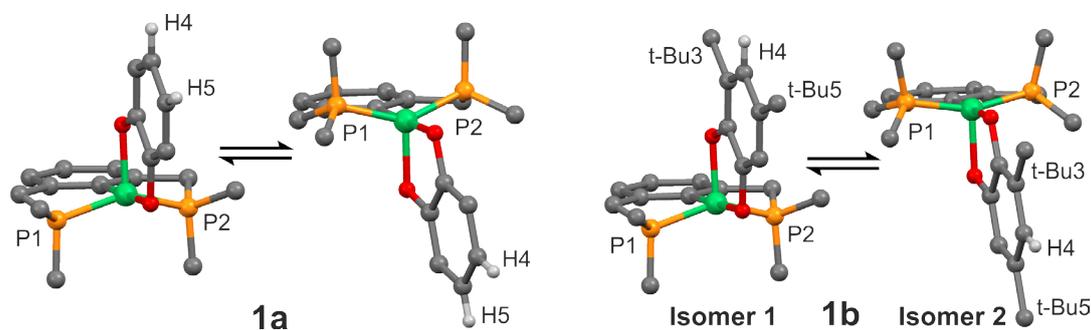


**Figure 2.** The resonance structures responsible for protonic HFC splitting

The temperature rising results in averaging of protonic HFC constants (Table 1) via fast (in EPR timescale) “swing” oscillations (Figure 4) [3]. It should be noted that the phosphoruses remain equivalent with temperature variations.



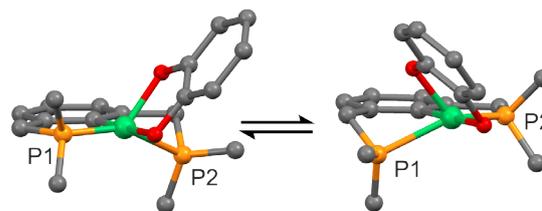
**Figure 3.** Structures of **1a-3a** (a) and their core (b), selected bonds lengths (Å) and angles (°).



**Figure 4.** “Swing” oscillations in **1a** and **1b** (without non-relevant atoms).

For complex **1b** at low temperature the superposition of two spectra is observed (Table 1). These spectra can be attributed to different structural isomers (Figure 4). Temperature rising leads to averaging of the spectral parameters (Table 1) which is a result of fast isomers interconversion via “swing” oscillations (Figure 4).

Complexes **2a-c** demonstrates another scheme of dynamics which we have called “fan” oscillations (Figure 5) [3]. The temperature dependences of EPR spectra of all three complexes are similar (Table 1). So, at low temperature the splitting on two non-equivalent phosphorus is observed. Such unequivalence is a result of “sloped” configuration of chelate fragments in molecule (Figures 3, 5).



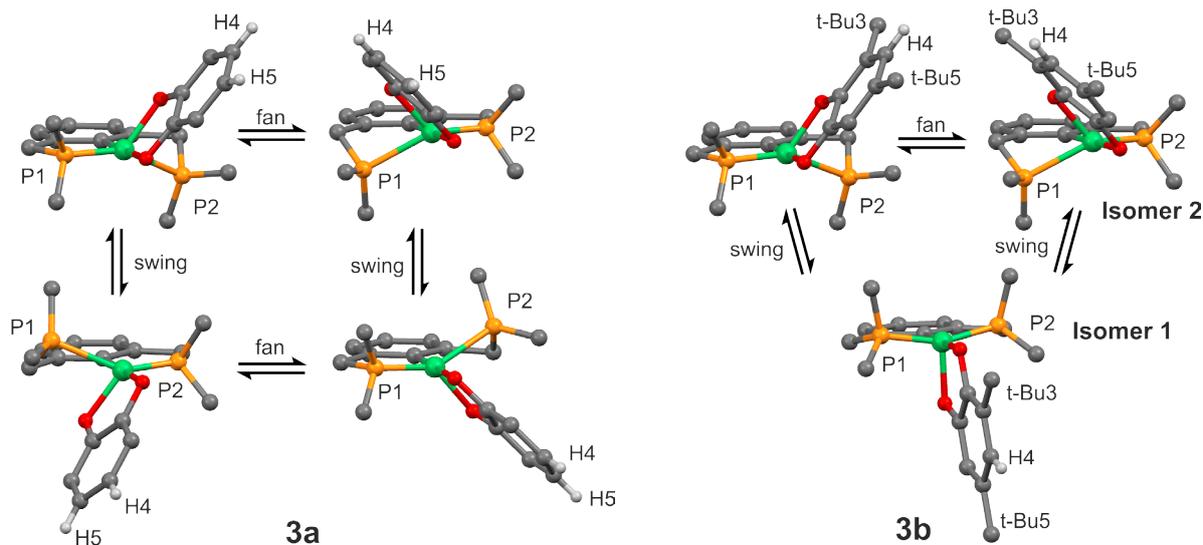
**Figure 5.** “Fan” oscillations in **2a-c** (hydrogens and substituents are omitted for clarity).

In general, HFC constant on the magnetic nuclear of ligand (<sup>31</sup>P) bonded to the metal-*o*-semiquinone fragment can appear due to two mechanisms [5]: spin polarization of  $\sigma$ -bonds O-Ni-P and direct interaction of group Ni-P orbital with  $\pi^*$ -orbital of *o*-semiquinone containing unpaired electron. The second path is quite more effective and in the case of pincer-*o*-semiquinonato-nickel complexes it determines the phosphorus splitting constants. As the consequence this value is very sensitive to geometrical features and particularly to the angle between Ni-P axis and *o*-semiquinonic plane [4] (particularly to the normal to this plane). Phosphorus HFC constant is the largest when this angle is close to 90° [4]. Examination of inner coordination core (Figure 3) show that the angles P1-Ni1-O2 in the complexes **2a** and **2b** are closer to right angle (89.39° in **2a** and 87.86° in **2b**) comparing with the P2-Ni1-O2 (124.54° in **2a** and 111.03° in **2b**) whereas in **1a** both angles are closer one to another (115.70° and 101.58°). It is the reason of the larger

difference between phosphorus HFC constants  $a_{P1}/a_{P2}$  for **2a** and **2b** comparing with the same value for **1a** ( $a_{P1}/a_{P2} = 27.8/14.7$  G in **2a**,  $25.3/15.7$  G in **2b** and  $25.6/25.6$  G in **1a**). The angles P1-Ni1-O2 and P2-Ni1-O2 (both relative to O2) are especially preferred in examination of phosphorus HFC constants because O2 has an excess of spin density comparing with O1 (vide supra).

Heating averages all HFC constants (Table 1). It should be noted that for **2a** protonic HFC constants become different already below 260 K. Moreover, no isomers interconversion is observed for **2b** (in contrast with **1b**). These facts are the direct evidence of the absence of “swing” oscillations for these complexes.

In the case of **3a** and **3b** the coordination sphere dynamics is more complicated. For these complexes both kinds of oscillations are observed simultaneously. So, for **3a** at low temperature in EPR spectrum the hyperfine splitting on two nonequivalent phosphorus and two nonequivalent protons is observed (Table 1). With the temperature rising the averaging of the phosphorus constants is observed (like for **2a**), but the same process is observed for protonic constants too (like for **1a**). It means that both “swing” and “fan” oscillations take place simultaneously (Figure 6). For **3b** the similar transformation of EPR spectrum is observed (Table 1). The superposition of two signals at low temperature transforms into averaged spectrum with the heating. So, the structural isomers interconversion via “swing” oscillations (as for **1b**) is observed as well as “fan” oscillations (Figure 6). It should be noted that only one of isomers (Isomer 2 at Figure 6) has different phosphorus constants and correspondingly demonstrates the “fan” oscillations (like for **2b**). It means that the presence of bulky *t*-Bu group in *ortho*-position to basal oxygen is relevant for “fan” oscillations appearance.



**Figure 6.** Simultaneous “fan” and “swing” oscillations in **3a** and **3b**

For **4b** neither “fan” nor “swing” oscillations were observed [3]. So, it can be concluded that “swing” oscillations are driven by steric properties of the phosphorus substituents of the pincer fragment. For “fan” oscillations the driving force is not so clear. Most probably, the mechanism of these oscillations is related with the absence of axial symmetry along P-C axis in Cy and *i*-Pr substituents.

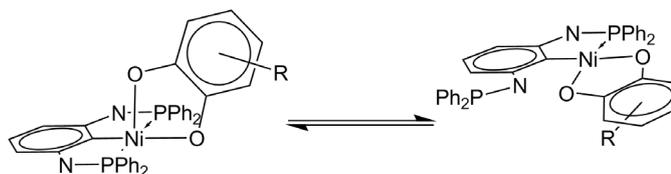
EPR spectra of **5a** and **1a** are similar (Table 1) as well as their temperature dependences. So, the “swing” oscillations are observed for **5a** as well as for **1a**.

Surprisingly, in the case of **5b** the EPR spectrum is drastically distinct (Table 1). It looks as superposition of two signals: one contains two large equal phosphorus constants ( $a_{P1} = a_{P2} = 16.7$  G) and another containing only one small phosphorus constant ( $a_P = 3.1$  G). Such low HFC constants on phosphorus nuclei ( $a_P \sim 0\text{--}3$  G) are typical for four-coordinated square-planar and related

complexes [5]. So, in our case we propose the decoordination of one of phosphano group of pincer fragment and forming of corresponding four-coordinated product (Figure 7).

Most probably the reason of this decoordination is a presence of bulky *t*-Bu group in *para*-position to *o*-semiquinonato oxygens together with rigid –NH– linker in pincer fragment. This proposal is confirmed in the case of **5c**. In its EPR spectrum (Table 1) at

ambient temperature only one signal with only one small phosphorus constant ( $a_P = 4.1$  G) is observed, which can be attributed to four-coordinated product (Figure 7). With temperature decreasing this signal disappears, and another one with two larger phosphorus constants ( $a_{P1} = a_{P2} = 16.4$  G) appears. So, low-temperature signal can be attributed to five-coordinated product (Figure 7).



**Figure 7.** Isomerization of **5b-c**.

#### 4. Summary

Several kinds of dynamics are possible in the PCP-pincer *o*-semiquinonic complexes: “swing” or “fan” oscillations, their combinations or reversible decoordination of one of pincer “arms”.

“Swing” oscillations possibility is defined by steric bulkiness of phosphorus substituents whereas “fan” ones are defined by specific interactions of these substituents with *o*-semiquinonato ones. Reversible decoordination of one of “arms” is caused by rigidity of pincer core together with specific interactions between pincer and *o*-semiquinonato substituents.

#### Acknowledgments

This work was supported by Russian President (grants NSH-1113.2012.3 and MK-474.2011.3), Russian Foundation for Basic Research (grants 10-03-00788-a and 12-03-31087-mol) and FSP “Scientific and scientific-pedagogical cadres of innovation Russia” for 2009-2013 years (GK-P839 from 25.05.2010).

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