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Novel structurally characterized *o*-semiquinonato PCP-pincer nickel complexes

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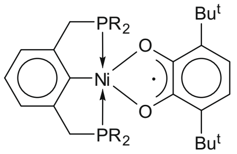
ABSTRACT

Structural study of dialkyl (PCP)-pincer *o*-semiquinonato nickel complexes indicated sloped relative positions of bi- and tri-dentate ligands. It became bright confirmation of propositions made on the base of their EPR spectra followed by molecular modelling.

1. Introduction

Previously we have communicated about new class of the spin labelled nickel compounds: the *o*-semiquinonato nickel complexes with the pincer ligands [1,2]. The structural study of 3,6-di-*tert*-butyl-*o*-semiquinonato nickel with 2,6-bis-(diphenylphosphinomethyl)phenyl (**1**) indicates a distorted square–pyramidal geometry of the inner coordination core [1]. Difference of the ligands occupying *trans*-positions towards oxygen atoms of the semiquinone causes an asymmetrical distribution of the spin density inside the *o*-semiquinonato ligand. The molecular motion which swaps oxygens being in the base of the pyramid and which is responsible for redistribution of the spin density in the *o*-semiquinonato fragment was called "swing" oscillation (Scheme 1). Similar rearrangements in the metal coordination sphere can be found as a stage of certain pincer complexes-catalyzed reactions, such as Heck coupling [3,4].

Using of pincer ligand with alkyl substituents (such as *cyclo*-hexyl (Cy), *iso*-propyl (*i*-Pr)) at the phosphorus atoms causes a difference of spin density on the pincer phosphoruses [5]. The molecular motion which is responsible for redistribution of spin density between the phosphorus atoms we have called "fan" oscillation (Scheme 1). We supposed that the complexes with the pincer ligands having alkyl substituents (*cyclo*-hexyl and *iso*-propyl having no axial symmetry along the P-alkyl bond) should have sloped relative positions of the planes of semiquinonato and pincer ligands (Scheme 1). This configuration should result in different spin density on the pincer phosphorus atoms. Here we report on structural investigation of two complexes of such type (**2** and **3**). Comparative analysis of two novel structures with previously published **1**, together with EPR data and results of molecular modelling, is presented here as well.



1 - R = Ph,

2 - R = Cy,

3 - R = *i*-Pr

2. Results and discussion

Structural study of **1** was carried out earlier [1]. Complexes **2** and **3** were obtained as previously described [5]. Slow evaporation of their pentane solutions gave X-ray quality single crystals. The X-ray diffraction study has shown that the Ni atom has a distorted square–pyramidal coordination mode in all three complexes (Fig. 1). In general, the bonds lengths and the angles in the chelate cycle of coordinated *o*-semiquinone are typical for the anion-radical coordination mode (Table 1).

It should be noted that the differences between C1–O1 and C2–O2 bonds lengths in the chelate cycles of the *o*-semiquinones, which reflect the asymmetry of the spin density distribution, in **2** and **3** are essentially larger than the same difference in **1** (Δ = 0.0154 Å in **2** and 0.0243 Å in **3** against 0.0085 Å in **1**). It causes the difference between HFC constants on semiquinonic pro-

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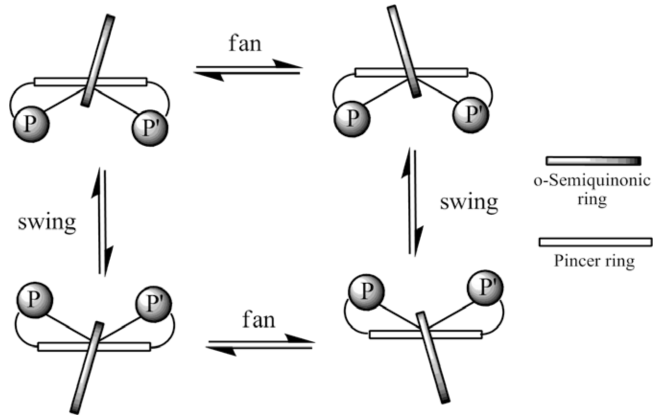
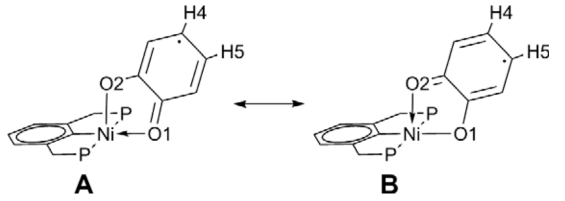


Scheme 1. “Swing” and “fan” oscillations (schematic view along basal O–Ni–C direction).

Table 1
Structural data of nickel-*o*-semiquinonato chelate cycles for complexes **1**, **2** and **3**.

Complex	1	2	3
Ni1–O1	1.9238(10)	1.9306(10)	1.9377(8)
Ni1–O2	2.0595(10)	2.0664(11)	2.2165(10)
C1–O1	1.2975(17)	1.3076(18)	1.3006(16)
C2–O2	1.2890(17)	1.2922(17)	1.2763(14)
O1–Ni1–O2	81.60(4)	81.16(3)	78.35(3)[a]

[a] Small deviation of the angle O1–Ni1–O2 in **3** comparing with the same one in **1** and **2** is the consequence of the elongation of the Ni1–O2 bond.



Scheme 2. Resonance structures responsible for hyperfine coupling with semiquinonic protons.

tons in EPR spectra of the complexes (a_{H4}/a_{H5} = 2.2/3.4 G in **1**, 2.2/3.6 G in **2** and 2.2/3.8 G in **3**) (Scheme 2, Table 2). It is known that spin density transfer from the *o*-semiquinone to the phosphorus magnetic nuclei of the pincer metallo-fragment can be realized by two independent mechanisms: by spin polarization of the σ-skeleton through Ni–O σ-bonds and by direct interaction of the group Ni–P orbitals with the corresponding oxygen p-orbitals containing unpaired electron. The last mechanism is quite more effective comparing with the first one, but its effectiveness strongly depends on the angles between Ni–P bonds and chelate plane of the *o*-semiquinone. Phosphorus HFC constant is larger when this angle is close to 90° [6,7]. Examination of inner coordination core describes that the angles P1–Ni1–O2 in the complexes **2** and **3** are close to right angle (89.39° in **2** and 87.86° in **3**) comparing with the P2–Ni1–O2 (124.54° in **2** and 111.03° in **3**) whereas in **1** 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 **2** and **3** comparing with the same value for **1** (a_{P1}/a_{P2} = 27.8/14.7 G in **2**, 25.3/15.7 G in **3** and 25.6/25.6 G in **1**). 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 [1]. The asymmetry of the spin density distribution inside the *o*-semiquinone follows from the difference of the bonds lengths in the chains Ni1–O1–C1 and Ni1–O2–C2 according to Scheme 2. The

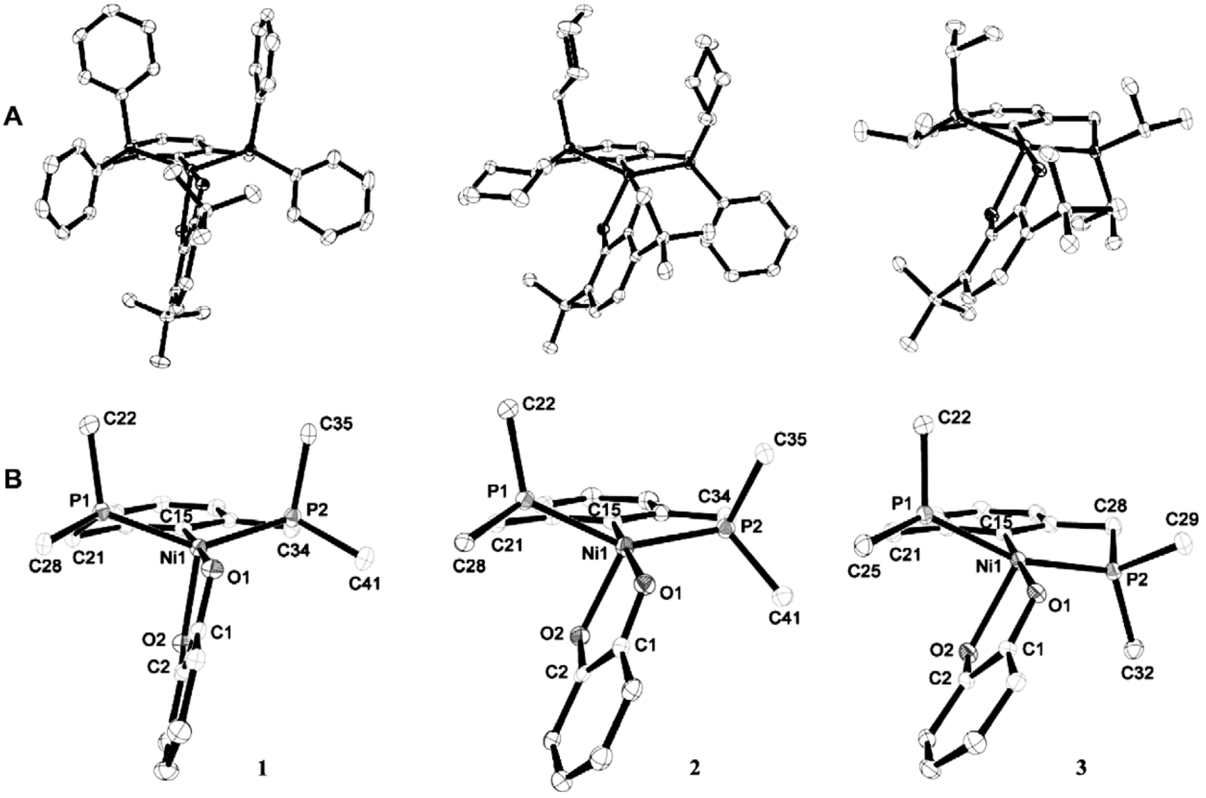


Fig. 1. ORTEP view of **1**–**3** with 50% thermal ellipsoids, hydrogen atoms are omitted for clarity. (a) With all substituents, (b) without substituents.