

An EPR Monitoring of Isomerism and Coordination Sphere Dynamics in Five-Coordinated Pincer Nickel Complexes

K.A. Kozhanov, M.P. Bubnov, V.K. Cherkasov, G.K. Fukin,
N.N. Vavilina, L.Yu. Efremova, G.A. Abakumov*

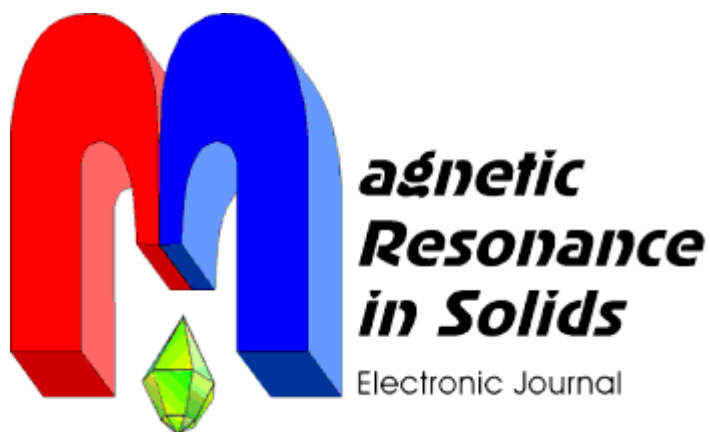
Institute of Organometallic Chemistry of RAS, 603950,
Tropinina str, 49, Nizhny Novgorod, Russia

* *E-mail*: kostik@iomc.ras.ru

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K.A. Kozhanov*, M.P. Bubnov, V.K. Cherkasov, G.K. Fukin, N.N. Vavilina,
L.Yu. Efremova, G.A. Abakumov

*G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603950,
Tropinina str, 49, Nizhny Novgorod, Russia*

** E-mail: kostik@iomc.ras.ru*

A number of five-coordinated paramagnetic pincer nickel complexes have been obtained and investigated by X-band EPR spectroscopy. In general, these complexes can exist in solution as a pair of interconverting structure isomers. Activation parameters of this interconversion were estimated for several complexes.

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Keywords: Electron paramagnetic resonance, o-semiquinonic complexes, pincer nickel complexes

Pincer complexes consist of a metal center and a pincer skeleton. The pincer skeleton is a tridentate ligand which is connected to the metal *via* a metal-carbon σ -bond and two coordinative bonds. The most common type of pincer skeleton is an aryl fragment having two arms as substituents in aryl 2,6-positions. Due to the rigid chelating skeleton providing excess electron density on the metal, this class of complexes determines its specific properties. First discovered in the early 1970s, the chemistry of pincer complexes has been extensively developed over the last ten years. This class of compounds has found application in wide range of organic syntheses as catalysts [1, 2] and is fundamental to the creation of new materials such as gas sensors, switches, self assembling dendrimers, *etc.*[3].

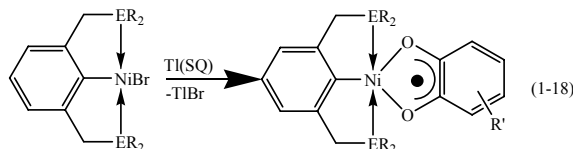
o-Semiquinone ligand is a radical anion of *o*-quinone containing an unpaired electron in π -aromatic system. It coordinates to metal through two oxygen atoms forming five-membered chelate ring. It has already been used as a spin label for EPR spectroscopy [4]. In many cases it has allowed us to study structural features and dynamic processes occurring in the inner coordination sphere of complexes in solution [4, 5]. It is also a useful tool to investigate thermodynamic and kinetic parameters of inner-sphere dynamics [6]. Tautomeric interconversions of *o*-semiquinonic complexes were studied as well [7].

Here we report a new five-coordinated spin-labeled *o*-semiquinonic, *o*-iminosemiquinonic, catecholate and di-halogen PCP- and NCN-pincer nickel complexes.

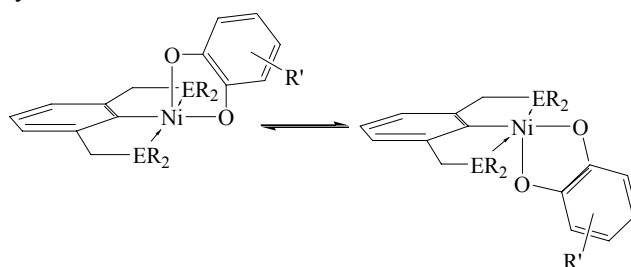
Table 1. The notation of complexes 1-18.

Complex	ER ₂	SQ	Complex	ER ₂	SQ	Complex	ER ₂	SQ
1	PPh ₂		7	PPh ₂		13		
2	PPh ₂		8	PPh ₂		14		
3	PPh ₂		9	PPh ₂		15		
4	PPh ₂		10	PPh ₂		16		
5	PPh ₂		11	PPh ₂		17		
6	PPh ₂		12	PPh ₂		18	NMe ₂	

o-Semiquinonic and catecholate nickel complexes with different pincer ligands have been obtained using exchange reaction of nickel organohalogenides with corresponding thallium salts:



It was found using EPR spectroscopy and X-ray diffractometry that complexes 1-17 have a structure of square pyramid [8, 9]. Complexes 4, 5, 7 - 11, 14 with asymmetrical *o*-semiquinones exist in solution in a form of two interconverting geometry isomers:

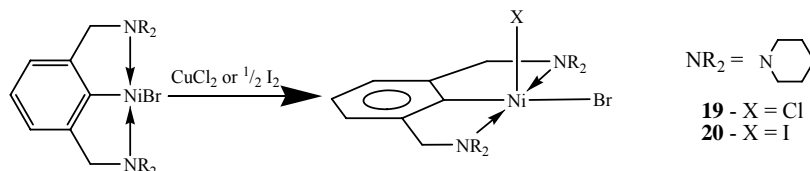


The equilibrium of isomers is controlled by entropy factor. For **7**, **8**, **10**, **11** an activation parameters (ΔH^\ddagger and ΔS^\ddagger) have been estimated [9].

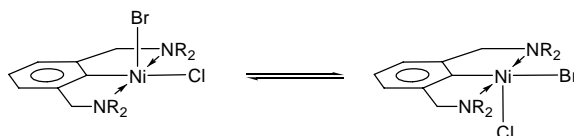
In the case of NCN complexes **13** – **17** [10] the spin density is shifted from *o*-semiquinone to the metal fragment in a great extent that this one in **1**, **7**, **4**, **6**, **5**. Also, the mesomeric donor groups in **2** - **5**, **15**, **17** decrease such shift whereas withdrawal substituent in **6** and **16** increase this shift [8-10]. In complex **16** spin density is even localized on metal forming catecholate of nickel(III) [10].

Complex **18** has a square plane structure with the bidental coordination of pincer fragment. Most probably, it is caused by sterical reasons.

The mixed halogen NCN-pincer complexes **19** and **20** have been obtained by oxidation of monohalogen precursor by appropriate compounds:



It was found by X-ray diffractometry that complex **19** have a square pyramid structure. It was shown by EPR that this complex exists in solution as a mixture of two isomers as the *o*-semiquinonic complexes:



In opposite site, complex **20** exists in a form of only one of isomers, with apical iodine atom. Most probably, it is caused by sterical reasons.

Acknowledgements

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