



# Tracking of the formation of binuclear nickel complexes of $[\text{Ni}_2(\mu\text{-O}_2\text{PR}^1\text{R}^2)_2(\text{bpy})_4]\text{Br}_2$ type by ESI and MALDI mass spectrometry

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## ABSTRACT

The formation of binuclear nickel complexes of type  $[\text{Ni}_2(\mu\text{-O}_2\text{PR}^1\text{R}^2)_2(\text{bpy})_4]\text{Br}_2$ , where  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{phenyl (Ph)}$ , 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp) or  $\text{R}^1\text{R}^2 = \text{-OCH}_2\text{CH}(\text{Et})\text{NHCH}(\text{Ph})\text{-}$ ; bpy = 2,2'-bipyridine, in solution and their fragmentation behavior have been investigated by ESI and MALDI mass spectrometry. It was found that binuclear cationic fragments  $[\text{Ni}_2(\mu\text{-O}_2\text{PR}^1\text{R}^2)_2(\text{bpy})_2\text{Br}]^+$  are characteristic ions displaying the formation of binuclear nickel(II) complexes in solution.

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## 1. Introduction

Transition metal complexes containing two or more interconnected metal coordination centers are of high practical interest for different areas of applied chemistry, molecular biology and pharmacology [1–4]. Presently bi- and polynuclear complexes formed by bridging  $\{\mu\text{-O}_2\text{CR}\}^-$  ( $\text{R} = \text{H, Alk, Ar}$ ) ligands are the most studied systems [2]. However, very restricted number of polynuclear transition metals complexes containing in its structure  $\{\mu\text{-O}_2\text{PR}_2\}^-$  bridging fragments is currently known [2,5]. It should be noted that the creation of new types of materials based on polynuclear compounds with organic phosphorus derivatives as the bridging ligands are of high particular interest due to the fact that electronic properties of carbon and phosphorus atoms are different. In this regard, the development of new methods for the synthesis and investigation of the properties of bi- and polynuclear species formed by bridging  $\{\mu\text{-O}_2\text{PR}_2\}^-$  fragments are very important from the view point of the creation of magnetically active

materials [5,6] and new active catalysts for biological processes [7]. Indeed binuclear complexes of nickel, zinc, cobalt and manganese were found to be important intermediates in biological systems which catalyze the hydrolysis of a range of peptide and phosphate ester bonds via formation of  $\{\mu\text{-O}_2\text{PR}_2\}^-$  bridged derivatives [8]. These species play a central role in biological processes of oxidative phosphorylation [9,10], oxidative decarboxylation [11], and energy transfer [12–14]. Recent examples include the use of binuclear nickel(II) complexes as high efficient antibacterial reagents capable for cleavage of DNA [15].

From the viewpoint of materials chemistry, organic–inorganic hybrids are an important class of compounds in advanced materials design [16–21]. Some nickel diphosphonates [22] and nickel pyrophosphates [23] showed antiferromagnetic properties and slow relaxation behavior. As a variant of polymetallic nickel complexes with  $\{\mu\text{-O}_2\text{PR}_2\}^-$  bridges, some nickel phosphonate–carboxylate cages bearing twelve nickel centers were synthesized [24]. Interestingly, a number of pentacoordinate nickel(II) complexes doubly bridged by phosphate ester or phosphinate ligands were synthesized and investigated [25].

However, it should be noted that the monitoring of the binuclear nickel complexes formation in solution is very difficult especially in case of paramagnetic behavior of high spin state nickel derivatives. In this respect mass spectrometry analysis is

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