**Synthesis and Characterization of Catalytically Active Ni(II) Complexes with Bis(phenol)diamine Ligands**

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**Abstract**

 Two N,N'-dimethylethylenediamine derivatives of substituted bis(phenol)diamine ligands (2-(*tert-*butyl)-4-methylphenol in H2L1 and 2,4-di-*tert-*butyl phenol in H2L2), respectively were synthesized by a convenient green procedure. Nickel)II) complexes [NiL1] **1** and [NiL2] **2** have been synthesized and characterized by various methods along with crystal structures determined. Ni(II) coordination centers of both mononuclear complexes are surrounded by two phenolate oxygen atoms and two amine nitrogen atoms of the ligand in a square planar arrangement. The magnetic susceptibility of both title complexes indicates a paramagnetic behavior above 150 K, while strong ferromagnetism below 100 K. Furthermore, the cyclic voltammetry studies show the ligand-centered oxidation of phenolate group to phenoxy radical and metal-centered reduction of Ni(II) to Ni(0) in both cases. On the other hand, the Glaser coupling reaction of phenylacetylene was studied only for NiL1 **1**. A strong catalytic activity at room T in THF solvent is observed in the presence of zinc powder as a reducing agent. The DFT analysis corroborates with the square-planar NiO2N2 chromophore of **1** being reduced in catalytically active Ni(0) by applied Zn. With Gibbs free energy of the reaction leading to the formation of the substrate Ni-complex being favorable endothermic.

**Keywords:** Bisphenoldiamine; Nickel complexes; Glaser reaction; Coupling of phenylacetylene; Ferromagnetism: Green procedure

**Introduction**

Coordination compounds play an essential role in life processes. Depending on the ligands, different properties of formed complexes can be obtained. Among ligands, amine (or diamine)-bis(phenolate) ligands play an increasingly important role in transition-metal catalyst design [1-3]. Such compounds initially included late transition metals [4-10] and more recently also early transition metals [11-13] of Group 3 (Sc, Y), Group 4 (Ti, Zr, Hf) and Group 5 (V, Ta). Thesy have been particularly applied in olefin and cyclic esters polymerizations [14-17], epoxidation [18,19], and sulfoxidations [20-22]. The C-C coupling reactions are divided into different types [23], such as Heck [24], Suzuki [25], Negishi [26], Sonogashira [27], and Glaser [28,29].

The late transition metal nickel(II) ion in such complexes exists in different coordination environments. Its octahedral, trigonal-bipyramidal, square-pyramidal, and tetrahedral complexes are typically paramagnetic, showing most often green or blue colors. The square-planar nickel(II) complexes are mostly yellow, red, or brown colored. Regarding Lewis acidity, Ni(II) is considered a borderline metal ion, binding to both soft and hard ligands and sometimes, albeit rarely, to both in the same complex [7,8]. Due to different coordination environments and two lone electrons, Ni(II) is a potent redox agent and magnetic center.

Our intention is to synthesize and characterize nickel complexes of bis(phenol) diamine ligands and apply them typically in the Glaser coupling reaction, which is a synthesis of symmetric or cyclic bisacetylene units via terminal alkynes (Scheme 1).

**Scheme** **1**.

**Experimental**

**Materials, physical measurements and theoretical calculations**

 Unless noted otherwise, all the chemicals and solvents were obtained from commercial sources and were used as supplied. The principal bis(phenol)diamine ligands H2L1 (2-(*tert-*butyl)-4-methylphenol) and H2L2 (2,4-di-*tert-*butyl phenol in H2L2), were synthesized according to the described procedure (Scheme 2) [30]. The identity and purity of the ligands were checked with NMR measurements.

Elemental analyses (CHN) were carried out on Thermo Finnigan-Flash 1200. The NMR spectra were recorded on Bruker DRX 400 MHz spectrometer, with external tetramethylsilane (TMS) as reference. FT-IR spectra were recorded on Shimadzu FT-IR 8300 infrared spectrophotometer with KBr pellets. UV-Vis measurements in CH2Cl2 solution were carried out on Perkin-Elmer (LAMBDA 2) UV-Vis spectrophotometer equipped with a LAUDA-ecoline-RE 104 thermostat at different temperatures.

Single crystals were obtained from 1:1 CH2Cl2**–**CH3CN solution for **1** and **2**, respectively. The X-ray diffraction experiments were performed with an Oxford Sapphire CCD diffractometer using Mo *K*α radiation λ = 0.71073 Å, at 293(2) K, by ω-*2θ* method. The structures were solved by direct methods and refined with full-matrix least-squares on *F*2 with the use of SHELX program package [31]. Analytical absorption corrections were applied (CrysAlis) [32], giving the minimum and maximum transmission of 0.912 and 0.778, respectively. Hydrogen atoms were located from the electron density maps and their positions were constrained in the refinement with appropriate AFIX command, as implemented in SHELX software. The *tert*-butyl groups in **2** show some disorder, seen in larger thermal ellipsoids. This structure of **2** has already been reported, though with the 150 K dataset [7]. Due to a lower T data, the *tert*-butyl groups were there determined without disorder.

Magnetic susceptibility data were measured from powder samples of solid material in the temperature range of 2–300 K using a SQUID susceptometer with a field of 0.1 T (MPMS-XL-5, Quantum Design. These measured data were corrected for the temperature independent Larmor diamagnetic susceptibility obtained from the Pascal's tables and for the sample holder contribution [33].

The room temperature cyclic voltammograms (CV) were measured with 1.5**×**10**-3** M CH2Cl2 solutions containing 0.10 M tetrabutylammonium perchlorate as a supporting electrolyte. Scan rates were 20 to 500 mV/s within the potential range 1.00 -1.00 V.

The experiment for the Glaser coupling reaction included reagent phenylacetylene (1 mmol) in THF (2 mL), KOH (2 mmol) and a catalyst, namely **1** (0.02 mmol). Additionally, Zn powder (1 mg), air or argon atmosphere were applied as well as temperature change. 1H NMR spectrum was applied for the checking of the catalytic reaction product 1,4-(diphenyl)-buta-1,3-diyne (Figure S5).

**Scheme** **2**.

Detailed density functional theory (DFT) calculations of the C-C coupling reaction mechanism, taking place with the Ni-complex (**1** and **2**) which are depicted in Scheme 4 (phenylacetylene coupling reaction to 1,4-(diphenyl)-buta-1,3-diyne), were performed. These calculations were done at the B3LYP/6-31G(d) level of theory using a spherical basis set and all heavy atoms having (5d, 7f) functions [34,35]. All calculations were performed in Gaussian 16 [36].

To reduce the calculations computational cost, smaller versions of the catalyst molecule (as in **1** or **2**, with the phenyl rings replaced by a bridging methylene moiety), reactants and products (acetylene coupling to buta-1,3-diyne), were used. With these reductions, the mechanism is estimated to be similar enough, although various reactions’ barriers may differ.

**Preparations**

#### **Synthesis of****[NiL1]** **1**

The procedure was similar and analogous as already described (Scheme 3) [7,30]. Triethylamine (0.28 mL, 2.00 mmol) was added to a solution of H2L1 (0.44 g, 1.00 mmol) in ethanol in a 100 mL flask under continuous stirring. Ni(OAc)2 (1.60 g, 1.00 mmol) was added to this solution after 30 min, and the resulting mixture was refluxed for 2 h, giving an intense purple solution. The solvent was removed, and the solid dark red compound **1** was collected.

 (0.41 g, 83 % yield). Elemental Analysis, Found (Calc.), %: C28H42N2O2Ni, (MW = 497.34 g/mol) C: 67.29 (67.62); H: 8.52 (8.51); N: 5.15 (5.63). FT-IR, cm-1: 3438 n(O-H), 2943 n(C-H), 1602, 1460 d(C-H), 1208, 900,703. UV-Vis, nm: 380 LMCT, 525 d-d.

**Scheme** **3.**

**Synthesis of [NiL2] 2**

An analogous synthesis procedure for dark purple compound **2** was used as for **1**, with another ligand (0.55 g, 67 % yield). This compound has already been reported and partly characterized [7]. Elemental Analysis, Found (Calc.) %:C34H54N2O2Ni, (MW = 580.69 g/mol) C: 69.19 (69.83); H: 9.73 (9.29); N: 5.92 (5.82). FT-IR, cm–1: 3443 n(O-H), 2953 n(C-H), 1613, 1470 d(C-H), 1254, 1086, 876, 745. UV-Vis, nm: 385 LMCT, 530 d-d.

**Results and Discussion**

**Crystal structure of** **[NiL1] 1**

The central nickel(II) ion in **1** is surrounded with one tetradentate *N,N’,O,O’* ligand L1, being double deprotonated at the coordinated two hydroxy phenolate oxygen atoms (Figure 1). The mononuclear coordination sphere shows slightly distorted square planar geometry, completed by two amine nitrogen atoms. The selected bond lengths and angles are given in Table 1, while the diffraction experiments data and the refinement data are summarized in Table 2. The compound crystallizes in the orthorhombic space group *P*2**1**2**1**2**1.** The ligand is found in the (*R*, *R*)-N1,N2 absolute configuration.

Within the coordination sphere, the shortest bonds are formed by both phenolate oxygen atoms, with Ni1-O1 and Ni1-O2 distances of 1.848(3) Å and 1.859(3) Å, respectively. The amino nitrogen coordination bonds Ni1-N2 and Ni1-N1 are significantly longer (1.923(4) Å and 1.935(4) Å, respectively). The internal strain caused by that type of coordination is manifested by the shortest Ni-O and Ni-N bonds positioned *trans* to each other in the observed geometry. In the ligand conformation detected, the N1-C8-C9-N2 torsion angle is 51.5(6)°, and the N-Me groups are positioned on the opposite sides of the ethylenediamine bridge plane.

The intramolecular C-H···O interactions are found involving O1 phenolate and C18, C19 groups of *t*Bu, as well as O2 and C26 and C28 of *t*Bu, with distances ranging from 2.977(7) Å to 3.010(6) Å. The C-H···π intermolecular interactions are found between the phenyl C1···C6 ring, and methylene C8-H8A and methyl C20-H20B groups. Thus, the distances to the ring gravity centers (Cg) being H8A···Cg[1-x,-1/2+y,3/2-z] and C20B···Cg[2-x,1/2+y,3/2-z] 2.71 Å and 2.92 Å, respectively (Figure 2).

**Figure** **1**.

**Table 1.**

**Table 2.**

**Figure 2.**

**Crystal structure of [NiL2] 2**

The crystal structure of **2** has already been reported, though with the 150 K dataset [7] and is analogous to the one found for **1**, with one tetradentate *N,N’,O,O’* ligand, herein in **2** being L2. Square-planar coordination sphere NiN2O2 in **2** has almost identical bond distances as found in **1**. The effect of the internal strain related to the four-coordinated ligand is also detected, with the shortest Ni-O2 bond in the *trans* position to the shorter Ni1-N1 bond (Table 1). Complex **2** crystallizes in the orthorhombic centrosymmetric *Pbca* space group (Table 2). Herein, the coordination molecule of [NiL2]is found in the asymmetric unit of the structure.

The strain in **2** caused by two *t*Bu phenolate moieties on positions 2 and 4 seems to be more pronounced than that in **1** (with one Me and one *t*Bu), resulting in the *trans* angles more deviated from the ideal 180° (O2-Ni1-N1 **1**/**2** 175.54(17)°/172.31(10)°, O1-Ni1-N2 175.39(18)°/173.11(10)°). Additionally, this pronounced intramolecular strain is visible in the displacement of atoms from the coordination plane (O1,O2 **1**/**2** 0.078/0.123 Å, N1,N2 **1**/**2** 0,072/0.117 Å), which is also significantly larger than observed for **1**.

Intermollecularly, the methyl ethylene C25-H25A···π phenolate interaction C1···C6 [1/2-x,-1/2+y,z] and C26-H26B···π to C11···C16[1/2-x,1/2+y,z] are found, with the H···Cg distances being 2.84 Å and 2.82 Å, respectively. The coordination molecules in **2** are packed in pseudo dimers, showing a weak association within pairs, though without any stronger bonds. No such association is seen in **1** (Figure 2).

Significant diminishing or disappearance of O-H stretching band for the complexes at around 3400 cm-1, compared to the free ligands IR spectra, is in agreement with the conversion of the phenol to phenolate moiety and its coordination to Ni(II) center. The other IR bands for **1**, **2**, H2L1 and H2L2 are very similar, corroborating with their similar structures.

**Magnetic susceptibility**

The molar susceptibility for **1** and **2** decreases with the increasing temperature, according to Curie 1/T law, which indicates a paramagnetic behavior of complexes above 150 K (Fig. 3a).

**Figure 3.**

The effective magnetic moments (*µ*eff) for **1** and **2** are nearly constant ≈ 2.3 µB in the temperature range 100–300 K (Figure 3b), which is lower than the value of the magnetic moment for two unpaired electrons in Ni(II) ion with a spin quantum number S = 1 (spin-only *μ*eff = 2.82 μB) [37]. Nevertheless, two unpaired electrons are present in the complex.

The steep increase of magnetic moment at low temperatures and the splitting between zero-field and field cooled susceptibilities confirm a relatively strong ferromagnetic behavior in both complexes (Figure 3). A considerable ferromagnetic coupling between Ni(II) centres of neighboring complexes is thus assumed. The interaction parameter *J* was calculated from the Curie-Weiss temperature (inset in Fig. 3b) in a mean-field approximation [38], *J* = 3 kB θ/(z S (S+1)), where z = 6 is the number of nearest magnetic neighbors, S = 1, and kB the Boltzmann constant. It results in *θ* = 25 K (J = 4.3 cm-1) and *θ* = 19 K (J = 3.3 cm-1) for **1** and **2**, respectively. The shortest metal to metal distance is 8.197 Å and 5.626 Å for **1** and **2**, respectively. This is related to the packing of both compounds, as in **2** the molecules are seen in pseudo dimers, while in **1** no obvious connection between the molecules is noticed (Figure 2). Although the shortest M…M distance in **1** is significantly longer than in **2**, the ferromagnetism in **1** seems to be stronger (Figure 3) Therefore, the mentioned ferromagnetic coupling seems not to take the direct space path, but rather trough the weaker structural interactions or jointly as a bulk phenomenon.

The ferromagnetic ground state of the complexes is additionally confirmed by isothermal magnetization and ac susceptibility measurements. Figure 4 shows the isothermal magnetization of the sample measured between -50 kOe and 50 kOe at 2 K. Both magnetization curves M(H) exhibit the clear hysteresis loops, which suggests ferromagnetic behavior. The ac susceptibility measured at different frequencies of the applied magnetic field exhibits a maximum at about 14 K (Figure S3). The position of the maxima is almost independent of frequency, which is consistent with the proposed long-range ferromagnetic order at low temperature.

**Figure 4**

**Electrochemistry**

Obtained CV measurements reveal two oxidation peaks for **1** and **2** with a similarly small difference in their redox potentials (Figures 5, S4). The similarity of *E*ox values for two complexes by ~0.1 V suggests the same oxidation mechanism. The +0.8 V redox process might be tentatively attributed as ligand-centered, in which the phenolate group yields phenoxy radical PhO → PhO•⁺ within the complex, while the -0.7 V process as metal-centered Zn(II) → Zn(0). Some minor differences of the oxidation potentials of both complexes suggests that anodic oxidation processes are sensitive to the changes involved in the steric and electronic effect of substituents on phenolate moieties of the ligands (Figure 5).

**Figure 5**

**The Glaser coupling reaction**

The Glaser coupling was initially investigated for complexes **1** and **2**, both showing similar reactivity. As described later on, only **1** was tested and similar results are expected also for **2**. The coupling reaction of phenylacetylene giving 1,4-(diphenyl)-buta-1,3-diyne (Scheme 1) was selected as a model for a C…C coupling catalysis reaction, and various parameters were checked to find optimum conditions (see Experimental data and Table 3).

**Table 3**

Traces of the coupling product were obtained already in the absence of Zn powder after 14 h (Table 3a,b). An increased T enables better conversion rate. With reductive Zn powder employed, the conversion rate rises toward maximum earlier and already at room T. The necessity of air oxygen and catalyst was confirmed by their absence in the control experiments, where no conversions were noticed (Table 3).

The proposed catalytic reaction mechanism is shown in Scheme 4. As suggested therein, the Zn(0) powder reduces Ni(II) to Ni(0) within the catalyst species in the process (**A** to **B**). By consequent removal of the hydrogen atom from phenylacetylide in the alkaline conditions and with the air oxygen, the reaction proceeds by the oxidative addition of two phenylacetylide radicals bonding onto the Ni(0) center in *trans* orientation giving Ni(II) (**B** to **C**). The next step is reductive elimination of the coupling product (1,4-(diphenyl)-buta -1,3-diyne) (**C** to **B**) which leads to the formation of the phenylacetylide free Ni(0) species. The reactions can now circulate between positions **B** and **C** with the catalyst restored.

**Scheme 4**.

**Computational DFT analysis of reactions mechanism**

The theoretically calculated mechanism, with reduced catalyst molecule as well as with reduced substrate (see experimental), corroborates with the experimental observations. Though position **A** with a calculated tetrahedral configuration of the Ni(II) complex differs from those found in **1** and **2** with square-planar Ni(II), the Zn reduction enables the same square-planar Ni(0) at calculated catalytically active **B**. We did that to enable full optimization and no rigid ligand was enforced as it is in **1** and **2**.

The theoretically added acetylene substrate reacts with KOH forming a substrate acetylide radical, whichare very reactive nucleophiles, and they coordinate at the axial position of the catalyst metal center **C**. This reaction may be stepwise on two Ni axial positions.

Then, the two *trans* positioned acetylides in **C** join in one step forming buta-1,3-diyne, via the *trans* complex transformation through a temporary *cis* intermediate, the latter being at a higher energy level. A nickel metal is suitable for this transformation due to possible varieties of its coordination sphere. The two released electrons of such reductive elimination are meanwhile accepted by the Ni(II) metal center that is consequently reduced to the square-planar **B** Ni(0). This is also the rate-determining step of the whole reaction mechanism. The final catalytic product buta-1,3-diyne is released here and a catalytically active position **B** is restored.

 In Figure 6 we present the Gibbs free energy of the reaction leading to the formation of the acetylide Ni-complex. The Gibbs free energy is endothermic by 87 kJ/mol, which suggests that the energy requirement for the formation of the complex is not very demanding.

**Figure 6**

Conclusions

Two nickel(II) complexes of tetradentate square planar [ONNO]-type diamine bis(phenolate) ligands have been synthesized and characterized by IR, UV–Vis, CHN, MAGSUS and CV techniques. The single crystal X-ray diffraction revealed comprehensive information about the effect of phenolate ring substituents on the structure of complexes. In both complexes, the Ni(II) centers are surrounded by two phenolate oxygen atoms and two amine nitrogen atoms. The magnetic susceptibility of both complexes decreases with the increasing temperature, according to Curie 1/T law, which indicates a paramagnetic behavior of complex above 150 K. A strong ferromagnetic coupling is noticed below 100 K enabling ferromagnetic ground state of each herein investigated compound

In the electronic absorption spectra of the two complexes, the position of LMCT bands shows the phenolate (π) to Ni(II) anti-bonding orbital charge transfer at 380 nm, while d-d at 525 nm. The cyclic voltammetry studies show the ligand-centered oxidation of phenolate group to phenoxy radical and metal-centered reduction of Ni(II) to Ni(0) suggesting that such ligand may also participate in the metal catalytic activity.

Furthermore, the catalytic activity of phenylacetylene coupling reaction to 1,4-(diphenyl)-buta-1,3-diyne was studied. A full conversion was achieved in the alkaline solution with Zn powder at 25 ◦C in THF solvent. Additionally, a catalytic cycle redox mechanism is proposed. A DFT analysis suggests not very demanding energy requirement for such a reaction. It̕̕s noteworthy that the coupling reactions are mostly performed at high temperatures using Cu, Pt, and Pd catalysts. On the contrary, the herein investigated Ni(II) complexes are able to catalyze the coupling reaction at mild conditions with low amount of catalyst.

**Appendix A.**

 The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are 2013762 and 2013764 for **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](https://imp.umk.pl/horde/imp/message.php?mailbox=INBOX&index=5418).

**CRediT authorship contribution statement:** Za. J.: Writing – original draft, Investigation (synthesis, preparations of samples, basic method measurements), Catalysis analysis; E. S.: Supervision, Conceptualization, Writing – review & editing, Electrochemistry analysis, Funding acquisition; A. W. Writing – editing, Structural analysis, Funding acquisition; C. D. Z.-Y.:DFT analysis, Writing – review & editing; B. K.:Writing – review & editing, Conceptualization; Zv. J.:Writing – editing, Magsus analysis, Funding acquisition.

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