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Regularities of One-Electron reduction of Acenaphthene-1,2-Diimine Nickel(II) Complexes

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Abstract: New Ni-based complexes 1,2-bis[(2,6of diisopropylphenyl)imino]acenaphtene (dpp-bian) with halides as coligands and BF₄ counterion were synthesized in THF and MeCN. The Ni^I complexes were obtained using two approaches: electrochemical reduction of Ni^{II} precursors or a chemical comproportionation reaction. Their structural features and redox properties were determined by means of single crystal X-ray diffraction. cyclic voltammetry, EPR, and UV/Vis spectroelectrochemistry. The influence of temperature and solvent nature on the structure of the Ni¹ complexes was studied in detail, namely an uncommon reversible solvent-induced monomer-dimer transformation of the Ni^l complexes was observed. In the case of fluoride complex, the unpaired electron was found to be localized on the dpp-bian ligand, whilst all the other nickel complexes consist of neutral dpp-bian.

Introduction

The great interest to metal complexes with redox non-innocent ligands, such as α -diimines, is caused by their ability to be a donor or an acceptor of one or more electrons.¹⁻¹¹ Nickel complexes with bis-iminoacenaphtenes (bians) are known as utterly active catalysts for the conversion of ethylene and α -

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Electronic Supplementary Information (ESI) available: The crystallographic data for the investigated structures have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1846515, 1846519, 1846520, 1846521, 1846522 and 1846523.

olefins into high molecular weight polymers.¹²⁻¹⁹ The mechanistic data available to date assumed that cationic divalent LNi^{II}-alkyl complexes can be considered as active species in the catalytic systems.²⁰⁻²² According to the known common mechanism, the main role of diimine ligands is providing for a steric effect. 13,15,16 However, it was shown that electron transfer may take place during catalysis, which results in the formation of diimine radical anions that dramatically influence on the polyethylene branching system.¹⁴ Some previous reports^{23,24} also demonstrate that real catalyst systems considerably differ from the model system described by Brookhart and coworkers.¹³ Namely, cationic complexes of Ni^{II} formed in real catalytic systems LNiBr₂/MAO or LNiBr₂/MMAO (where L = 1,4-bis-2,4,6-dimethylphenyl-2,3dimethyl-1,4-diazabuta-1,3-diene, MMAO = AlⁱBu₃-modified methylalumoxane) were studied in situ by ¹H NMR spectroscopy at temperatures below -20°C.23 At the same time, the conversion of these complexes to EPR active species at warming and predominating of paramagnetic compounds in the reaction solution at room temperature were found.²⁴ This once again emphasizes the importance of establishing the location of an unpaired electron in reduced nickel complexes for the best understanding of the catalyst mechanism. Furthermore, despite the widespread use of Ni-based catalysts with different bians, only a few examples of structurally characterized complexes with a formal nickel oxidation state of +1 are known.^{12,25}

The importance of low-valent nickel for catalysis and redox diversity of bian complexes induced us to investigate oneelectron reduction products of Ni¹ complexes with 1,2-bis[(2,6diisopropylphenyl)imino]acenaphtene (dpp-bian) with different suitable techniques, such as electrochemical approaches, EPR, UV/Vis spectroscopy, which could facilitate the establishment of the nature of metal complexes in solutions. As a result, complexes with unpaired electron localization on a metal or a ligand were found depending on halide type. Moreover, an uncommon reversible solvent-induced monomer–dimer transformation of the Ni¹ complexes was observed.

Results and Discussion

Synthesis and structure of nickel(II) complexes with dppbian

In this report nickel(II) complexes with dpp-bian were obtained with yields up to 90% by the treatment of the corresponding anhydrous nickel(II) salts with one equivalent of dpp-bian in THF or MeCN by analogy with previously reported methods.¹⁵⁻¹⁷ The ratio of dpp-bian to Ni in all the complexes was 1 : 1. In this work the complexes were named as **I–IV**, where **I** is the complex with

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 the complexes were named as I–IV

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a BF₄⁻ counter ion; II, III, and IV are the complexes with I, Br,

and CI anionic co-ligands, respectively (Scheme 1).



Scheme 1 Synthesis of nickel(II) complexes with dpp-bian

The molecular structures of I and III were determined by single crystal X-ray diffraction. According to these data, compound I proved to be octahedral nickel(II) cationic complex [(dpp-bian)Ni(NCMe)_4]²⁺ with two isolated BF₄⁻ anions (Figure 1a). As shown in Figure 1b, compound III represents a four-coordinate neutral nickel(II) complex: two dpp-bian nitrogen atoms and two bromide ligands form a tetrahedral coordination environment around the metal center. Selected bond distances in I and III are listed in the caption and close to those values found in the other Ni^{II} complexes with neutral diimine ligands.¹⁹

At the same time, dpp-bian nickel(II) complex with fluoride ligand cannot be prepared using NiF₂ directly due to poor solubility of the latter in organic solvents. Although desired complex (dpp-bian)NiF₂ was able to be prepared by treating of complex I with Me₄NF, low solubility of the product prevented its investigation.





Figure 1. ORTEP projections of complexes I (a) and III (b) showing anisotropic displacement ellipsoids at the 50 % probability level. Hydrogen atoms, minor disordered components, and solvent molecules are omitted for clarity. Selected interatomic distances for I [Å]: Ni1–N1 2.1300(12), Ni1–N2 2.1184(12), Ni1–N3 2.0633(14), Ni1–N4 2.0710(14), Ni1–N5 2.0570(14), Ni1–N6 2.0870(14), N1–C1 1.2807(19), N2–C2 1.2830(18), C1–C2 1.5161(19). Selected interatomic distances for III [Å]: Br1–Ni1 2.3301(6), Br2–Ni1 2.3373(6), Ni1–N1 2.027(3), Ni1–N2 2.020(3), N1–C1 1.286(4), N2–C2 1.279(4), C1–C2 1.501(5).

Electrochemical properties of Ni(II) complexes with dppbian

The redox properties of nickel(II) complexes **I–IV** were studied by cyclic voltammetry (CV) in MeCN solutions using Bu₄NBF₄ as a supporting electrolyte. Complexes **I–IV** demonstrated similar behaviour. Four reversible or quasi-reversible one-electron reduction peaks from –0.77 to –0.97, from –1.45 to –1.52, from – 1.72 to –1.76, and at –2.50 V were observed on the CVs of Ni^{II} complexes in MeCN (Figure 2). The first two peaks are related to the couples Ni^{IV1} and Ni^{IV0} reductions, which is confirmed by further EPR studies. The other reduction peaks correspond to dpp-bian^{0/1–} and dpp-bian^{1–/2–} couples, respectively.^{26,27} Reduction potentials referenced vs. Fc⁺/Fc couple for all the complexes in MeCN were summarized in Table 1. In general, the potentials of the Ni^{II/IV0} couples are shifted toward more negative values in the series BF₄⁻, I, Br, CI.

Table 1. Electrochemical data for Ni^{II} complexes I–IV in MeCN ($\Delta E = E_a-E_c$, mV, is shown in brackets). Potentials were measured vs. Fc⁺/Fc, Bu₄NBF₄ was used as a supporting electrolyte

		-		
Complex	E ^p _{red} (Ni ^{II/I}), V	${\sf E}^{\sf p}_{\sf red}({\sf Ni}^{\sf I/0}),{\sf V}$	E ^p _{red} (BIAN ^{0/1−}), V	E ^p _{red} (BIAN ^{1-/2-}), V
I	-0.77 (200)	-1.45 (80)	-1.74 (90)	-2.50 (200)
П	-0.80 (240)	-1.46 (75)	-1.76 (90)	-2.50 (190)
ш	–0.81 (160)	-1.47 (70)	-1.72 (70)	-2.50 (200)
IV	-0.97 (270)	–1.52 (130)	-1.74 (90)	-2.50 (210)

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Figure 2. Cyclic voltammogramms for a 1.5 mM solution of complex I in MeCN. Conditions: a working electrode was glassy carbon; an auxiliary electrode was Pt; Bu₄NBF₄ was used as a supporting electrolyte (SE).

Synthesis of reduced nickel complexes and their spectroelectrochemical investigation

Two pathways for the synthesis of the one-electron reduced nickel complexes, namely complexes 1-4 with a BF₄⁻ anion and I, Br, and Cl co-ligands, respectively, were performed (Scheme 2). First, following the cyclic voltammetry data, bulk electrolysis of a 1.5 mM solution of Ni^{II} complexes I-IV in anhydrous acetonitrile or THF solutions was carried out at the Ni^{II/I} couple potentials. Under spectroelectrochemical conditions, appearance and increase of intensity of new absorption bands for one-electron reduced nickel complexes 1-4 were detected in both solutions in the UV/Vis spectra. Interestingly, the UV/Vis spectra of the 1-4 in MeCN and THF were found to be notably different. Spectra of MeCN solutions of 1-4 demonstrated strong bands at 800 and 550 nm with a shoulder at 480 nm (Figure 3a). In the spectra of THF solutions of 1-4, two bands at 750 and 850 nm were observed in the long-wave region, while only one band was registered at 550 nm (Figure 3b). The mentioned differences in the UV/Vis spectra are most probably caused by the structural differences of the complexes in the two different solvents, namely in the Ni¹ environment since the longwave bands can be assigned to d-d Ni¹ transitions.²⁸



Scheme 2. Schematic representation of two synthetic approaches

Reversible or quasi-reversible peaks corresponding to the oxidation of the Ni^{VII} couple at the peak potentials from -0.42 to -0.76 V (vs. Fc⁺/Fc) were observed for electrochemically reduced nickel complexes **1-4** on CVs in MeCN and THF solutions (Figure 4, See ESI). In the case of transition from the iodide through bromide to chloride co-ligand, the oxidation potentials of the Ni^{VII} pair are also shifted to the cathodic region resembling the precursor Ni^{II} complexes (see ESI). The reversible reduction peak for the Ni^{VI0} is observed at potentials from -0.58 to -0.78 V (See ESI) in both solutions. In general, the reduced nickel complexes in THF are oxidized more difficult than corresponding complexes in MeCN.



Figure 3. Absorption spectra recorded in the course of electrochemical reduction of **III** in MeCN (a) and THF (b) (SE is Bu₄NBF₄). In both cases black curves correspond to the starting complex **III** prior electrochemical reduction.



Figure 4. Cyclic voltammogramms for a 1.5 mM solution of **3** in MeCN. Conditions: a working electrode was glassy carbon; an auxiliary electrode was Pt; Bu₄NBF₄ was used as supporting electrolyte (SE).

Chemical pathway to the one-electron reduction products

In order to isolate the one-electron reduction products, the chemical pathway was performed. Thus, a comproportion reaction between 1 equiv. of Ni^{II} salt, 1 equiv. of Ni(COD)₂ and 2 equiv. of dpp-bian in MeCN and THF led to the one-electron reduced nickel complexes with the simplified formula [(dppbian)Ni(X)]_n {where n = 1, 2; X = BF₄ (1), I (2), Br (3), CI (4)}. The complexes obtained in MeCN and in THF were named as 1a-4a and 2b-4b, respectively. The single crystals of the one-electron reduced nickel complexes 2a-3a and 2b-3b were grown by slow diffusion of diethyl ether into acetonitrile or THF solutions at -33 °C, respectively. It turned out that compounds 2a and 3a (Figure 5) represent monomeric molecular complexes with the nickel atom being tetrahedrally coordinated. It should be mentioned that one MeCN molecule was coordinated by the nickel center. The complexes 2b and 3b are halogen-bridged binuclear complexes (Figure 6).¹² Both metallocycles in 2b and 3b are approximately planar with the nickel atoms having a distorted tetrahedral geometry. Selected interatomic distances for the complexes in the solid state are listed in the caption of Figures 5 and 6. The lengths of bonds N1-C1, N2-C2, and C1-C2 of dpp-bian in the complexes should have indicated the presence of monoanionic radical in complexes 2a, 3a, 2b, and 3b.29 Similar regularity was also observed earlier for complex dpp-bianNi-Cp.25 However, the EPR spectrum of the complexes indicated the presence of Ni¹ state and showed no signal corresponding to a dpp-bian radical-anion. Details of our EPR



investigation for all the synthesized complexes are discussed

below.

Figure 5. ORTEP projections of complexes 2a (a) and 3a (b) showing anisotropic displacement ellipsoids at the 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances for 2a [Å]: I1–Ni1 2.5507(5), Ni1–N1 1.955(3), Ni1–N2 1.952(3), Ni1–N3 1.965(3), N1–C1 1.309(4), N2–C2 1.309(4), C1–C2 1.448(4). Selected interatomic distances for 3a [Å]: Br1–Ni1 2.3651(6), Ni1–N1 1.958(3), Ni1–N2 1.964(3), N1–N3 1.970(3), N1–C1 1.317(4), N2–C2 1.307(4), C1–C2 1.440(5).

Interesting, stepwise re-dissolution of the solid samples, which were obtained after solvent removal, in THF, MeCN, and again in THF led to predictable changing in the UV/Vis spectra. Initially, the spectra with bands at 480, 550, and 800 nm were observed in MeCN. After removing MeCN and dissolution of the solid residue in THF, the new bands at 550, 750, and 800 nm appeared. Then, removing THF and dissolution of the solid in MeCN led to returning the initial spectra (Figure 7). These experiments indicate reversible solvent-induced monomer to

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dimer conversions for Ni¹ complexes. Further EPR experiments also confirmed this observation.

Ni1

C

а

Figure 6. ORTEP projections of complexes 2b (a) and 3b (b) showing anisotropic displacement ellipsoids at the 50 % probability level. Hydrogen atoms and solvent molecule are omitted for clarity. Selected interatomic distances for 2b [Å]: Ni1–Ni1⁴ 3.4282(5), I1–Ni1 2.5842(3), I1–Ni1⁴ 2.5985(3), Ni1–N1 1.9527(10), Ni1–Ni⁴ 1.9526(10), N1–C1 1.3103(14), C1–C1[#] 1.4542(2); equivalent atoms are labeled by the superscripts i (-x+1, -y, -z+1) and ii (x, y, -z+1). Selected interatomic distances for 3b [Å]: Ni1–Ni1⁴ 3.2996(6), Br1–Ni1 2.4091(4), Br1i–Ni1 2.4118(4), Ni1–N2 1.9427(18), Ni1–N1 1.9500(18), N1–C1 1.308(3), N2–C2 1.318(3), C1–C2 1.449(3); equivalent atoms are labeled by the superscript i (-x+1, -y+1).

Br

Ni







Electronic paramagnetic resonance study

The signals in the EPR spectra corresponding to the Ni¹ state, namely complexes with the metal-centered unpaired electron localization¹⁰ were observed for **1-4** in MeCN and THF (Table 2). At 295 K the isotropic spectra of **1** (both in MeCN and THF) are characterized with g-value of 2.20 (Figure 8).³⁰ The anisotropic spectra with three lines were observed at 215 K (g^{II}=2.13 and g[⊥] = 2.27; g_{average}=2.20) in both solvents.





The halogen-bridged dimers **2b-4b** in THF at room temperature were characterized with a single EPR signal with the g-factor of 2.26 and ΔH of 30-50 G (see ESI). The mentioned value is also typical and corresponds to Ni¹ state.³⁰⁻³⁴ At the temperature of the frozen solution, the intensity of EPR was decreased, that is consistent with the dimeric form of complexes. The anisotropic spectra were complicated by additional signals with g_{average} of 2.36.³⁴

In MeCN complexes with the halogenide co-ligands were characterized by two signals with g-factors of 2.20 and 2.26 and Δ H of 40-50 G at room temperature (Figure 9) Thus, it can be assumed that two types of complexes with the monomeric (g-factor = 2.20) and halogen-bridged dimeric (g-factor = 2.26) structures are in equilibrium in MeCN solution at room temperature. The intensity of the signal for dimer complex decreases at lowering temperature, whereas the signal for monomer complex raises. In case of the iodide co-ligand the monomeric form in MeCN is predominant (See ESI). The EPR spectra of halogenide complexes in MeCN measured in the solid state (195 K and lower) gave a single broad line (Δ H = 150 G) with g = 2.189 (See ESI).³⁵

Similarly to the above-mentioned UV/Vis experiments, one EPR signal with g-factor of 2.26 transformed into two signals with g-factors of 2.20 and 2.26 and vice versa after stepwise redissolution of the solid samples, which were obtained after removing a solvent, in MeCN and then in THF.



Figure 9. EPR spectra of 3 in MeCN at room temperature.

Table 2 Magnetic resonance parameters for 1-5 in MeCN and THF							
Osmalau	295 K		175 K				
Complex	g value	ΔH (G)	g value				
1	2.200	30-40	2.27, 2.19, 2.13				
2-4 in MeCN	2.200; 2.260	30-40; 60	2.26				
2-4 in THF	2.260	70-80	2.36, 2.30, 2.15				
5 in MeCN	2.200; 2.003	35-40; 10	2.27, 2.19, 2.13; 2.003				
5 in THF	2.003	10	2.003				

One-electron reduced nickel complex with the fluoride coligand

Complex 5 with the fluoride co-ligand was prepared by a comproportion reaction between 1 equiv. of NiF₂, 1 equiv. of Ni(COD)₂ and 2 equiv. of dpp-bian in both THF and MeCN.

Interesting features for fluoride complexes were observed in EPR spectra. So, expected two signals in EPR spectra were observed at room temperature for the MeCN solutions (Table 2, Figure 10). The first signal with g-factor of 2.20 obviously corresponds to monomer complex with metal-centered unpaired electron localization similarly to other halide complexes with dpp-bian. The second signal is a multiline pattern with g-factor of 2.003 and ΔH of 10 G corresponding to the dpp-bian anion radical in nickel complexes (See ESI).^{11,12} Two forms are also in equilibrium at room temperature. But no shift of equilibrium from one form to another was registered during changing the temperature. At low temperatures, anisotropic spectra with gaverage=2.20 and anion radical signal were found. In the EPR spectra of fluoride nickel complex in THF only one multiline signal with g-factor of 2.003 and ΔH of 10 G (Figure 10) corresponding to the complex with ligand-centered unpaired electron localization was observed.11,12



Figure 10. EPR spectra of 5 in MeCN (red) and THF (blue) at room temperature

The values of the effective moment for the solid reduced nickel complexes 2-5 were measured. Supposing the presence of two non-interacting Ni-Hal (Hal = I, Br, CI, F) ions, then to calculate effective moments per dimer we have to divide μ_{eff} by $\sqrt{2}$. Thus, the values μ_{eff} for 2-4 were found to be in the range from 2.1 to 2.3 at 2 K that close to the effective moment of spin S=1/2 (μ_{eff} = 1.7) and support by EPR data. In case of complex 5 with the fluoride co-ligand, the value μ_{eff} was found 4.6 at 2 K and 4.4 at 300 K. Both Ni ions and the ligand are supposed to have a nonzero magnetic moment. Ni^{II} ions have S = 1 and the ligand S =1/2. Therefore it is difficult to estimate their particular contribution to the total effective magnetic moment. Thus, it is clearly established that the electronic structures of paramagnetic fluoride nickel complexes and other halide nickel complexes are different. Thereby the detailed investigation of magnetic properties of obtained complexes is the focus of our further investigations.

Computations

For deeper understanding of experimental results quantum chemical computations were carried out. For all the complexes three variants of spin and electron density distribution can be envisaged: (i) BIAN⁰, Ni⁺ with $S_{Ni} = 1/2$, and multiplicity for the whole complex m = 2; (ii) BIAN with $S_{BIAN} = 1/2$, Ni^{2+} with S = 0, m = 2; and (*iii*) BIAN⁻ with S_{BIAN} = 1/2, Ni^{2+} with S_{Ni} = 1, m = 4. To model these cases, monomeric complexes 2a-5a were optimized with two different multiplicities: m = 2 (S = 1/2) and m = 4 (S = 3/2).

Optimization of the structures of complexes 2a-4a with m = 2 led to geometries with a tetrahedral environment of the Ni center, whereas the optimized structure of 5a had an almost squareplanar geometry (Figure 9). Attempts to optimize a squareplanar structure for **2a-4a** (corresponding to Ni⁺ with $S_{Ni} = 1/2$ or Ni^{2+} with S = 0) as well as a tetrahedral structure for **5a** were unsuccessful. According to literature data C-N bond lengths can be used as indicators of bian charge: in a neutral ligand they amount to 1.28-1.29 Å, whereas in a monoanionic form they increase to 1.34 Å.29

The computed C-N distances in complexes 2a-4a are equal to 1.31-1.32 Å, whereas in 5a they slightly decrease to 1.29-1.30 Å. For complexes 2a-4a spin density at Ni ions is predicted to be 1.5, and at the NCCN fragments it amounts to -0.5 (Figure 11). The corresponding values computed for complex 5a equal to 0.8 and 0.2, respectively. Thus, when m = 2 is defined, both the spin density distribution and C-N bond lengths suggest that in 5a the ligand is neutral and one unpaired electron is localized at Ni⁺ ion, i.e. variant (i) (vide supra) is realized. On the same ground, we can conclude that in the case of 2a-4a the computations suggest a variant intermediate between cases (i) and (ii), in other words in these complexes partial electron density transfer from nickel to bian is expected.



Figure 11. Optimized structures of the monomeric and dimeric complexes with m=2 and m=3, respectively: 2a - 4a,b (a) and 5a,b (b). X is Cl, Br or I; R is 2,6 -di-isopropylphenyl.

In the case of m = 4, optimization of the structures of complexes 2a-5a led to a tetrahedral Ni environment, similar to that shown in Figure 11a. For all the complexes spin density is close to 1.7 at Ni centers and to 0.9 at the NCCN part of bian. Both the spin



predict the form with higher multiplicity to be more stable by 8

Thus, according to quantum chemical computations, in the case

of complex 5a variant (iii) of spin and electron density

distribution is realized with one unpaired electron at bian¹⁻ and high-spin state of Ni^{2+} (S_{Ni}\!=\!1). This corresponds to EPR experiments, demonstrating that unpaired electron in 5a is

delocalized at the ligand. High-spin Ni2+ ion is very difficult to

observe in the spectra as it appears as a very broadened signal.

In the case of complexes 2a-4a computations predicted spin

density mostly localized on metal center, however partly shifted

to bian, which is corroborated by EPR experiments. Moreover,

this explains why C-N bond lengths found in X-ray diffraction

analysis are intermediate between values typical for bian⁰ and

for bian¹⁻. The difference in electronic structures of **5a** compared

to the other complexes in the series is also confirmed by analysis of IR spectra of bian and complexes 1-5 in THF (see ESI). Unfortunately, THF has its own spectrum which masks

region below 1500 cm⁻¹. Nevertheless, in the THF transmission

window IR spectra of complexes 1-4 contain the band at 1533

cm⁻¹, which is absent in the spectra of the ligand and complex **5**.

Computations show that this band is associated with

asymmetrical C-N stretching vibrations and predicted at 1553

cm⁻¹ for the most stable form of complex **3a** with m=2, whereas

in the spectrum of the most stable form of complex 5a with m=4

it is shifted to low-frequency range (1510 cm⁻¹) and mixed with

CH deformations, and in the spectra of bian it is predicted at

1770 cm⁻¹. Thus the corresponding band in the spectrum of 5 in

THF is apparently masked by THF absorbance.

kcal mol⁻¹.

Figure 12. Spin density distribution in the most stable structures of 3a (m = 2) and 5a (m = 4).

Similar tendencies are predicted also for dimeric forms, calculated only for species with bromide and fluoride ligands (3b and **5b**, respectively). For these complexes, multiplicities m = 3

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(S = 1) and m = 7 (S = 2) were considered. Again optimization of complex **5b** structure at m = 3 resulted in the almost squareplanar environment of the metal center, whereas in **3b** it remained in a tetrahedral form. Relative energies of various forms are predicted to be also similar to the monomeric case: for **3b** the state with m = 3 is more stable than the form with m = 7 by 12 kcal mole⁻¹, whereas for **5b** the high-spin state is more energetically advantageous by 12 kcal mole⁻¹. Thus, according to computations for both monomeric and dimeric complexes, fluoride ligand stabilizes forms with higher multiplicity and with spin density being localized not only at the Ni ion but also at the bian ligand. For all the other co-ligands, the forms with lower multiplicity and spin density localized mostly on the Ni ions are more energetically stable.

For the most energetically stable high-spin form of dimeric complex **5b** with spin density localized both on Ni and bian fragments the following broken-symmetry (BS) states were also considered: (a) antiparallel spins at bians and parallel spins at Ni ions, m = 5; (b) antiparallel spins at Ni ions and parallel spins at bians, m=3; and (c) antiparallel spins both at Ni ions and bians, m=1. All these cases are energetically very slightly less stable compared to m=7 state, indicating very weak ferromagnetic interactions of less than 2 cm⁻¹.

On the example of complexes **3a** and **3b** the energies of dimerization ($\Delta E = E_{dimer} - E_{monomer} + 2E_{MeCN}$) in the gas phase and in MeCN and THF solutions were estimated for the more stable spin states with m = 2 for **3a** and m = 3 for **3b**. Computations predicted the monomeric form to be more advantageous both for THF and MeCN solutions: $\Delta E = 7.5$ kcal mole⁻¹ for MeCN and 6 kcal mole⁻¹ for THF. For the gas phase, the dimeric form was predicted to be slightly more stable: $\Delta E = -0.6$ kcal mole⁻¹. Similar computations for the high-spin forms of complexes **5a** and **5b** with m=4 and 7 in gas-phase have shown that dimeric species are more stable by 9 kcal mole⁻¹.

CONCLUSIONS

In summary, we have successfully prepared a series of the new one-electron reduced nickel complexes 1-5 with dpp-bian and BF₄⁻ or various halide ligands by two different pathways, namely by chemical and electrochemical procedures. It was found that varying the conditions makes possible to control the reversible solvent-induced transitions between the monomeric and dimeric complexes. Both EPR experiments and magnetic data showed that electron localization at the nickel center occurs in the case of the complexes 1-4 with a BF₄ anion and the iodide, chloride and bromide co-ligands and leads to the Ni¹ complexes with neutral bian. In the case of the fluoride co-ligand, anion-radical complex 5 with an unpaired electron on the ligand was found. The observed trends were reproduced by computations: for complexes 2a-4a and 2b-4b computations predicted spin density mostly localized on the metal center, however, slightly shifted to bian. In the case of 5a and 5b, the form with one unpaired electron at bian¹⁻ and high-spin Ni²⁺ ($S_{Ni} = 1$) is realized. The discovered features about structural and electronic diversity of reduced nickel complexes may be useful tool for analysis and planning the catalytic systems based on them.

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Keywords: nickel • dpp-bian • reduction • electrochemistry • cyclic voltammetry

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FULL PAPER

The one-electron reduction reaction of nickel(II) complexes with dpp-bian has been studied. Monomeric and dimeric Ni¹ complexes have been obtained with a BF₄⁻ anion, iodide, bromide and chloride anionic co-ligands. For fluoride nickel complexes, unpaired electron localization on dpp-bian moiety was found.



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