A Square-Planar Dinickel(II) Complex with a Noninnocent Dinucleating Oxamate Ligand: Evidence for a Ligand Radical Species

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The new bimetallic nickel(II) compound $(PPh_4)_4[Ni_2(\mathbf{2})]\cdot 6H_2O$ (**3**), where $H_8[\mathbf{2}]$ stands for *N*,*N'*,*N''*,*N'''*-1,2,4,5-benzenetetrayltetrakis(oxamic acid), has been synthesized and its crystal structure determined by single-crystal X-ray diffraction. The structure of **3** consists of $[Ni_2(\eta^4{:}\eta^4\text{-}\mathbf{2})]^{4-}$ anions, tetraphenylphosphonium cations, and water molecules. Facile one-electron oxidation of the square-planar diamagnetic dinickel(II) complex $[Ni_2(\eta^4{:}\eta^4\text{-}\mathbf{2})]^{4-}$ generates the metallo-radical species $[Ni_2(\eta^4{:}\eta^4\text{-}\mathbf{2}^{\cdot+})]^{3-}$ with characteristic *intra*-ligand π-cation radical transitions in the visible region (475–550 nm) as well as a typical quasi-isotropic EPR signal at $g \approx 2.0$.

Interest in the chemistry of metal coordination compounds with organic ligands of a radical nature (radical ligands) is rapidly increasing in several areas ranging from bioinorganic chemistry to solid-state physics.[1][2] Radical ligand complexes are currently being studied as biomimetic catalysts, because experimental evidence is accumulating about the involvement of organic radical species in the active sites of diverse metalloproteins.[3][4] Likewise, mixed materials incorporating organic radicals coordinated to metal ions have been extensively investigated with the aim of generating molecular-based magnets.[5][6] The development of these new classes of compounds relies on the firm understanding of factors that influence the ligand's innocence or noninnocence in describing of the electronic structure of metal complexes. This plays a pivotal role in the coordination chemistry field in connection with the formal oxidation state assignment of the metal centre and, particularly, in high-valent transition metal complexes where the coordinated ligand contains an extended delocalized system.[7]

Recently, we have shown that substituted oxamato ligands like $H_4[\mathbf{1}]$,[8] the parent acid of the tetraanionic polychelating ligand *N*,*N'*-1,2-phenylenebis(oxamate), can stabilize unusual high oxidation states of first-row transition metal ions, ranging from manganese to copper.[8−11] We have found that the resulting square-planar four-coordinated copper(II) and nickel(II) complexes, $[M(\mathbf{1})]^{2-}$, oxidise at relatively low potentials, i.e. 0.41 and 0.60 V vs. SCE, respectively[10][11] (CH_3CN, 25 °C, 0.1 $mol\cdot dm^{-3}$ NBu_4PF_6). For the nickel complex, however, a second electron can be removed but at a higher potential (1.10 V vs. SCE). Since this particular ligand $H_4[\mathbf{1}]$ contains a benzenediamido-N unit with potential π-noninnocent character, these oxidation processes may involve the metal ion as well as the ligand. Thus, the electronic distribution in a given oxidised complex can be described by any one of the three redox isomers depicted in Scheme 1, for which the formal oxidation states of the metal centre are different (resonance forms **I** to **III**). Our observations clearly indicate that, at least the one-electron-oxidised species, $[M(\mathbf{1})]^-$ (M = Cu, Ni), are genuine copper(III) and nickel(III) complexes of form **I**.[10][11] Metal-radical ligand species (form **II**) can be ruled out as might be expected on the basis of the strong σ field of the tetradentate planar ligand (high σ-donor capacity of the amido-N group[12−15]).

Hence, in the scope of our continuous research in this field we have extended our studies to the related ligand $H_8[\mathbf{2}]$, the parent acid of the ligand *N*,*N'*,*N''*,*N'''*-1,2,4,5-benzenetetrayltetrakis(oxamate) (Scheme 2). Potentially, this dinucleating ligand possesses a noninnocent character, as its mononucleating counterpart, because the benzenetetraamido-N fragment is also a putative oxidation site.[16] We report herein the synthesis, general physical and structural characterisation together with the electrochemical properties of the tetraphenylphosphonium salt of the dinickel(II) complex of formula $(PPh_4)_4[Ni_2(\mathbf{2})]\cdot 6\,H_2O$ (**3**), as well as a preliminary ab initio theoretical study of its electronic structure.

The ^{1}H-NMR spectrum of **3** shows a sharp singlet corresponding to the two magnetically equivalent phenylene protons of the ligand at $\delta = 8.35$, along with the signals from the aromatic protons of the PPh_4^+ cations located in the region $\delta = 7.7-8.0$. The sharpness of these NMR peaks, as well as the small shift of 0.50 ppm for the benzene proton

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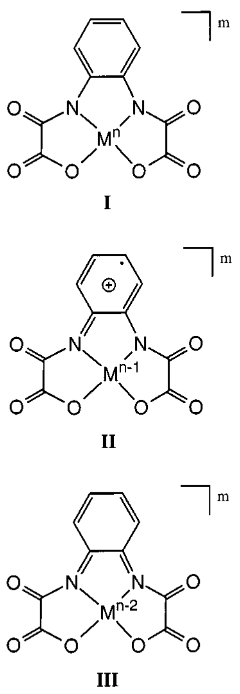
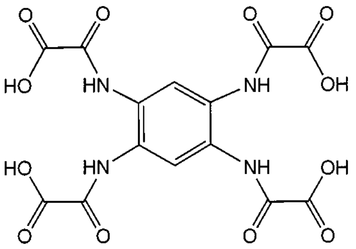


Scheme 1. Resonance structures of the metal complexes with the noninnocent *N,N'*-1,2-phenylenebis(oxamato) ligand



H$_8$[**2**]

Scheme 2. *N,N',N'',N'''*-1,2,4,5-Benzenetetrayltetrakis(oxamic acid)

signal relative to that of the free ligand Et$_4$H$_4$[**2**] (δ = 7.85) are indicative of a diamagnetic nickel(II) complex. That is to say, the Ni^{II} ion is in a square-planar coordination geometry (low-spin d^8-electronic configuration for Ni^{II}). This spectroscopic observation was further confirmed by a single-crystal X-ray structure analysis.

The structure of **3** includes centrosymmetric dinuclear nickel(II) complex anions, [Ni$_2$(**2**)]$^{4-}$ (Figure 1), tetraphenylphosphonium cations and water molecules of crystallisation. As expected, the coordination environment of each nickel atom is essentially square-planar, formed by two deprotonated amide-N and two carboxylate-O atoms of the bis-tetradentate chelating ligand [largest deviations from the plane of the four donor atoms are 0.002(1) Å with the metal ion 0.018(1) Å out of the mean basal plane]. The average Ni−N and Ni−O bond lengths (1.82 and 1.89 Å, respectively) are identical to those found for the monomeric nickel(II) complex (PPh$_4$)$_2$[Ni(**1**)],[11] but significantly shorter than those of the copper(II) complex, (PPh$_4$)$_2$[Cu(**1**)] (1.91 and 1.95 Å, respectively).[10b] The entire ligand skeleton is nearly planar [maximum deviation from the mean molecular plane of 0.264(2) Å for O(5)] (Figure 1, top). All the bond lengths are identical, within the 3σ criterion, to those of the related mononucleating ligand in the isostructural complexes (PPh$_4$)$_2$[Cu(**1**)][10b] and (PPh$_4$)$_2$[Ni(**1**)].[11] The observed C−C *intra*-ring benzene distances in **3** are almost equivalent and are intermediate between those of single and double bonds (average 1.40 Å), whereas the C−N bond lengths between the benzene ring and the amide nitrogen atoms are characteristic of single bonds (average 1.42 Å), thereby reflecting complete π delocalisation mainly within the benzene ring.

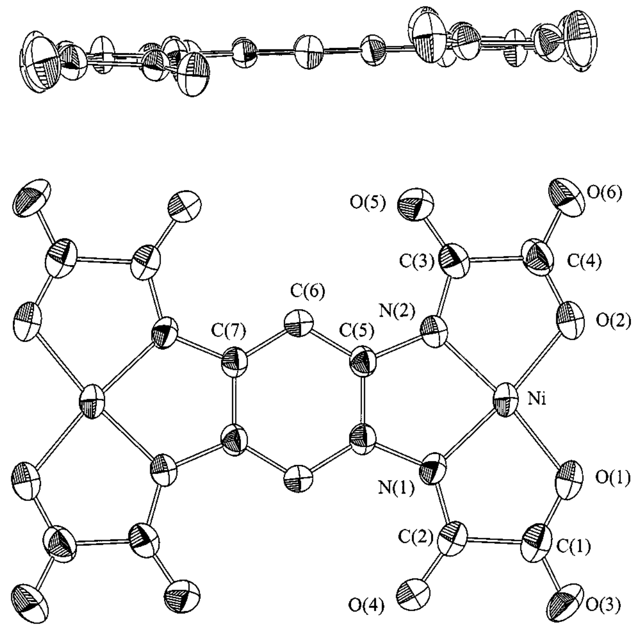


Figure 1. Perspective views of the anionic dinuclear unit of **3** with the atom-numbering scheme; thermal ellipsoids are drawn at the 30% probability level (hydrogen atoms have been omitted for clarity); selected bond lengths [Å] and angles [°] with standard deviations in parentheses: Ni−N(1) 1.822(2), Ni−N(2) 1.823(2), Ni−O(1) 1.879(2), Ni−O(2) 1.889(2); N(1)−Ni−N(2) 86.36(10), N(1)−Ni−O(1) 86.76(10), N(1)−Ni−O(2) 172.74(10), N(2)−Ni−O(1) 173.06(10), N(2)−Ni−O(2) 86.47(10), O(1)−Ni−O(2) 100.39(10)

The cyclic voltammogram of **3** in dry acetonitrile shows two well-separated one-electron reversible oxidation waves at the remarkably low potentials of 0.05 and 0.40 V vs. SCE (25 °C, 0.1 mol·dm^{-3} NBu$_4$PF$_6$). The one-electron nature of both waves was confirmed by coulometric measurements. A comparison of the potentials of the [Ni$_2$(**2**)]$^{3-/4-}$ and [Ni$_2$(**2**)]$^{2-/3-}$ redox couples with that of [Ni(**1**)]$^{-/2-}$ (0.60 V vs. SCE), where both ligands have the same set of donor atoms, reveals that both oxidised dinuclear complexes [Ni$_2$(**2**)]$^{3-}$ and [Ni$_2$(**2**)]$^{2-}$ are much more easily accessible than the corresponding mononuclear complex [Ni(**1**)]$^{-}$. A survey on the kinetic stability of the oxidised species obtained after bulk electrolysis of **3** in dry acetonitrile (−40 °C, 0.2 mol·dm^{-3} NBu$_4$PF$_6$, 0.24 and 0.60 V vs. SCE, respectively), indicates that the complex [Ni$_2$(**2**)]$^{3-}$ is stable over several days under nitrogen at room temperature. However, the doubly oxidised species, [Ni$_2$(**2**)]$^{2-}$, rapidly decomposes under these same conditions, being stable only on the time-scale of the cyclic voltammetry measurement. Preliminary electrochemical studies by combined UV/Vis and EPR techniques have been carried out in order to determine the nature of the chemically stable one-electron-oxidised species of **3**.

The electronic absorption spectrum of the orange complex **3** in acetonitrile [Figure 2, curve (a)] consists of two intense asymmetric bands in the UV region centred at 425 and 370 nm, corresponding to the π-π* *intra*-ligand charge transfer. A third, less intense band appears in the visible region at 560 nm, which corresponds to a d−d transition of a low-spin d^8-Ni^{II} ion.[17] The most remarkable feature of the spectrum of the electrochemically generated red complex $[Ni_2(\mathbf{2})]^{3-}$ is the appearance of new absorption bands on the high- and low-energy side of the visible region [Figure 2, curve (b)]. The first group of transitions are formed by two rather sharp and intense bands located at 555 and 515 nm, along with additional bands at 540 (sh), 500 (sh), and 475 nm. All these bands, which are not present in the spectrum of the nickel(III) complex $[Ni(\mathbf{1})]^-$, are similar in both shape and intensities to those observed for the "Wurster's Blue" salts containing the 1,4-bis(dimethylamino)-benzene radical cation.[16] The absorption intensities and energies of these bands are dependent on the substitution pattern on the benzene ring. This observation can therefore be assigned to a ligand-centred one-electron oxidation process of **3** rather than the nickel centre. Accordingly, the second group of bands in the Vis/NIR region comprising one broad, intense band at 1230 nm with two distinct shoulders at 1030 and 900 nm probably originates from metal-to-ligand charge-transfer (MLCT) transitions. The presence of this rather low-energy MLCT transition on the spectrum of $[Ni_2(\mathbf{2})]^{3-}$ at 1230 nm (8130 cm^{-1}) indicates that there is a relatively small energy separation between the ground and excited states (corresponding to the two opposed situations where the locus of oxidation is the ligand and the metal ion, respectively). Consequently, a small portion of mixing can occur between both electronic states.

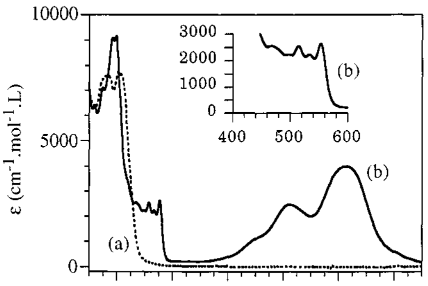
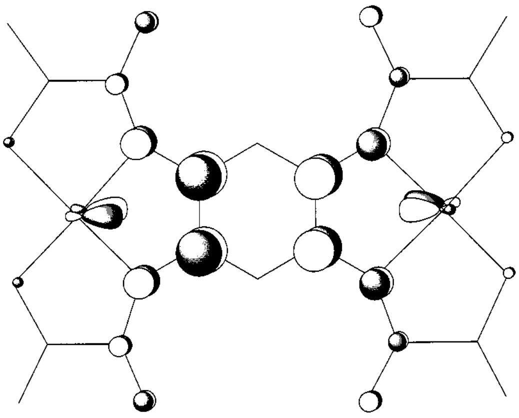


Figure 2. Electronic absorption spectra in acetonitrile solution of the dinickel(II) complex $[Ni_2(\mathbf{2})]^{4-}$ (a) and the electrochemically generated complex $[Ni_2(\mathbf{2})]^{3-}$(b)

Theoretical calculations have been performed on both dinuclear ($[Ni_2(\mathbf{2})]^{4-}$) and mononuclear ($[Ni(\mathbf{1})]^{2-}$) species at the DFT-B3LYP level with the Gaussian 94 package.[18−20] Preliminary calculations have been carried out on unsubstituted, 1,2-diamido- and 1,2,4,5-tetraamidobenzene molecules. The HOMO is of π-type in both cases and rises in energy from −6.7 (benzene) to −6.0 (diamide) and to −5.6 eV (tetraamide). These calculations indicate, as expected, that the π-donating ability of the ligand is enhanced with the number of amide substituents.

The electronic structure of $Na_4[Ni_2(\mathbf{2})]$[19] shows that the HOMO is essentially located on the organic moiety of the complex. Coefficients of the d orbital are small (about 0.03) whereas those of the p orbitals on the ligand atoms are considerably larger (0.10−0.16). The HOMO is strongly polarised on the benzene ring and results from the antibonding combination of the tetraamidobenzene HOMO with the d_{xz} of the nickel atoms as illustrated in Scheme 3. Due to the high energy of the ligand orbital, the contribution from the metallic moiety in this combination is very weak. Similar calculations on the mononickel complex $Na_2[Ni(\mathbf{1})]$ give rather different results and show that the three highest molecular orbitals are mainly of d character.



Scheme 3. Shape of the HOMO of $[Ni_2(\mathbf{2})]^{4-}$ moiety

The EPR spectrum at 4.4 K of the electrochemically generated complex $[Ni_2(\mathbf{2})]^{3-}$ exhibits an almost unique and narrow resonance band g close to 2.0 having a linewidth of only 50 G [Figure 3, curve (a)], typical of an isotropic radical species. This observation further supports the hypothesis of ligand rather than metal oxidation. Once again, this is in clear contrast with the observed EPR spectrum of the nickel(III) complex $[Ni(\mathbf{1})]^-$, where a nearly axial signal with apparent g at 2.230 and 2.006 is observed [Figure 3, curve (b)]. In that case, the large anisotropy and the average g value of 2.155 for $[Ni(\mathbf{1})]^-$ unambiguously indicate that the oxidation is located on the metal centre. Moreover, the fact that $g_{\perp} > g_{\parallel} \approx 2.0$ clearly establishes a d_{z^2}-electronic ground-state configuration for the Ni^{III} ion.[14b,15b] However, the situation for $[Ni_2(\mathbf{2})]^{3-}$ is somewhat more complicated; actually, the EPR signal is slightly anisotropic with $g_1 = 2.037$, $g_2 = 2.012$ and $g_3 = 1.998$. The result can primarily be interpreted as an Ni^{II}_2 complex containing a ligand-based π-cation radical; this feeble anisotropy observed on the EPR signal being due to the partial delocalisation of the unpaired electron onto the d_π-type orbitals of the nickel centres.

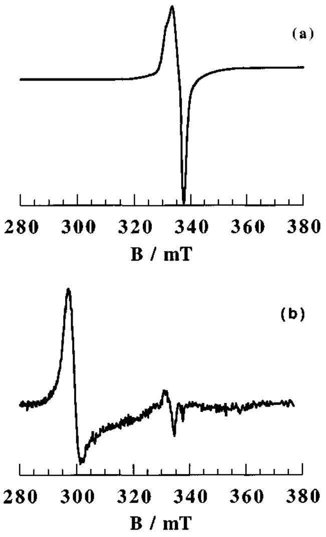


Figure 3. X-band EPR spectrum in frozen acetonitrile solution of the electrochemically generated complex [Ni$_2$(**2**)]$^{3-}$ (a) compared to that of complex [Ni(**1**)]$^-$ (b) at 4.4 K

In summary, compound **3** represents an interesting example of radical-ligand bimetallic complex precursor when oxidised to the π-cation radical species. In one, we have shown that the dinucleating ligand provides a ready locus of oxidation due to its larger π-electron donor properties than those of the mononucleating ligand analogue. Secondly, it also shifts the oxidation potentials of the metal ions to values beyond those of the aromatic π system because of its smaller σ-electron donor properties,[17] thus precluding metal oxidation. Substitution of diamagnetic nickel(II) ions by paramagnetic ones, such as copper(II), is a promising strategy to electrochemically control the magnetic exchange coupling in dimetallic complexes.[21] On the other hand, it may always be expected that these dinickel and dicopper complexes readily bind additional paramagnetic ions to the terminal carbonyl oxygen atoms giving oxamato-bridged polymetallic compounds, as is the case for the mononuclear analogues.

Experimental Section

Synthesis of H$_8$[2]: The proligand H$_8$[**2**] resulted from the condensation of 1,2,4,5-tetraaminobenzene and ethyl oxalyl chloride in *N*,*N*-dimethylformamide under inert atmosphere, and it was isolated as its tetraethyl ester derivative Et$_4$H$_4$[**2**]: To a solution of 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.84 g, 10 mmol) in DMF (250 mL) was added ethyldiisopropylamine (14 mL, 80 mmol). This solution was then added dropwise, by using a dropping funnel, to ethyl oxalyl chloride (4.7 mL, 40 mmol). The resulting mixture was stirred for 1.5 h at 50°C and the solvent removed in a rotatory evaporator. The remaining oil was dissolved in a minimum amount of methanol and treated with diethyl ether to give a white solid, which was collected by filtration and dried under vacuum (3.76 g, 70%). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.29 (t, 12 H, CH$_3$), 4.24 (q, 8 H, CH$_2$O), 7.82 (s, 2 H, *p*-H of C$_6$H$_2$N$_4$), 10.45 (s, 4 H, NH). − IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (NH), 1770, 1743, and 1702 cm^{-1} (C=O). − C$_{22}$H$_{26}$N$_4$O$_{12}$ (538): calcd. C 49.07, H 4.87, N 10.40; found C 49.24, H 5.26, N 10.21.

Synthesis of 3: The sodium salt of the dinickel(II) complex was obtained by reaction of the tetraethyl ester Et$_4$H$_4$[**2**] with Ni^{2+} in basic aqueous media: To a suspension of Et$_4$H$_4$[**2**] (1.1 g, 2.0 mmol) in water (50 mL) was added an aqueous solution (10 mL) of NaOH (0.68 g, 17 mmol). After stirring for 15 min at room temperature until complete dissolution, an aqueous solution (25 mL) of Ni(NO$_3$)$_2$ · 6 H$_2$O (1.16 g, 4.0 mmol) was added dropwise. The orange solid that formed was collected by filtration, washed with ethanol and air-dried (90%). Then, the tetraphenylphosphonium salt of complex **3** was obtained by metathesis of the sodium salt through the intermediacy of the silver salt: To a suspension of Na$_4$[Ni$_2$(**2**)] (0.95 g, 1.5 mmol) in water (100 mL) was added an excess of AgNO$_3$ (1.36 g, 8 mmol). After 30 min of stirring, the orange solid was collected by filtration, washed with water and ethanol, and air-dried (1.3 g, 90%). To a suspension of Ag$_4$[Ni$_2$(**2**)] (0.97 g, 1 mmol) in water (25 mL) was added a solution of PPh$_4$Cl (1.5 g, 4 mmol), dissolved in a minimum amount of water (10 mL). A white precipitate of AgCl formed and was removed by filtration after 15 min of stirring. Well-shaped large crystals of **3** suitable for X-ray diffraction were obtained from slow concentration of the mother liquor. − ^{1}H NMR ([D$_6$]DMSO): δ = 8.35 (s, 2 H, *p*-H of C$_6$H$_2$N$_4$), 7.71−8.10 (m, 80 H, C$_6$H$_5$ of PPh$_4$$^+$). − IR (KBr): $\tilde{\nu}$ = 1661 and 1617 cm^{-1} (C=O). − C$_{110}$H$_{82}$Ni$_2$P$_4$N$_4$O$_{12}$ · 6 H$_2$O (2001): calcd. C 65.96, H 4.70, N 2.80; found C 65.90, H 4.64, N 2.88.

X-ray Crystallographic Study of 3:[23] Crystal data: C$_{55}$H$_{47}$NiP$_2$N$_2$O$_9$, *FW* = 1000.6, triclinic, space group $P-1$, a = 13.558(1) Å, b = 13.799(2) Å, c = 14.604(1) Å, α = 78.43(1)°, β = 73.01(1)°, γ = 67.33(1)°, V = 2399.1(5) Å^3, d = 1.385 g cm^{-3}, Z = 2. − Data collection: Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, 293 K, ω-2θ, Lorentz and polarization effects and absorption correction, μ = 0.532 mm^{-1}, 2.0° ≤ θ ≤ 22.5°, crystal size 0.1 × 0.1 × 0.1 mm. 6280 unique reflections, and 6259 assumed as observed with $I > 2\sigma(I)$. − Structural analysis and refinement: standard Patterson methods with subsequent full-matrix least-squares method refinement on F^2, SHELX93.[24] The hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter. Refinement of 811 variables with anisotropic thermal parameters for all nonhydrogen atoms gave R = 0.035 and R_w = 0.079 with S = 1.029.

Acknowledgments

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[17] The electronic absorption spectrum of the nickel(II) complex (PPh$_4$)$_2$[Ni(**1**)] in acetonitrile shows a similar pattern to that of **3**, consisting of an intense band in the UV region located at 350 nm and a less intense band in the visible region at 420 nm. The significant red shift observed in the visible d−d absorption maximum of the orange dinickel complex [Ni$_2$(**2**)]$^{4-}$ related to the yellow nickel complex [Ni(**1**)]$^{2-}$, in spite of the presence of the same chromophor NiN$_2$O$_2$, clearly indicates the weaker ligand field associated with the ligand [**2**]$^{8-}$ than with [**1**]$^{4-}$. Likewise, the *intra*-ligand UV bands in the spectrum of [Ni$_2$(**2**)]$^{4-}$ corresponding to intraligand π-π* transitions within the aromatic benzene ring are also red-shifted with respect to the analogous band in [Ni(**1**)]$^{2-}$. The higher aromaticity of the 1,2,4,5-tetrasubstituted benzene ring of [**2**]$^{8-}$ than of the 1,2,-disubstituted benzene ring of [**1**]$^{4-}$ is presumably responsible for this bathochromic effect. These differences in the spectroscopic properties between the dinuclear nickel(II) complex and the mononuclear analogue already announce their dramatically different electrochemical behaviour.

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