DOI: 10.1002/ejic.201100232

A Dianionic Dinickel(II) Complex and Its Oxidised Phenoxyl Radical States

Laurent Benisvy*[a][‡] Riccardo Wanke,[a] M. Fátima C. Guedes da Silva,[a,b] and Armando J. L. Pombeiro*[a]

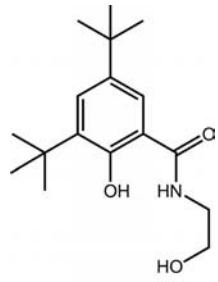
Keywords: Nickel / Polyanionic ligands / Redox chemistry / Anions / Radicals

The new dianionic dinickel(II) complex $[NBu_4]_2[Ni_2(L)_2]$ {L^{3-} = trianionic form of 3,5-di-*tert*-butyl-2-hydroxy-*N*-(2-hydroxyethyl)benzamide} has been synthesised and characterised by ^1H, ^{13}C NMR and IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. The X-ray structure of $[NBu_4]_2[Ni_2(L)_2]\cdot EtOH\cdot CH_3CN$ reveals a quasiplanar dinickel(II) dianionic complex, each of the Ni^{II} ions possessing a NO_3 planar coordination sphere that results from the ligation of L^{3-} in a NO_2 fashion through the *N*-amidate, *O*-phenolate and O-bridging alcoholate donor atoms. The cyclic voltammogram of $[Ni_2(L)_2]^{2-}$ reveals two one-electron reversible oxidation processes at relatively low potentials. The EPR and UV/Vis spectroscopic characterisations of the electrochemically generated one-electron- and two-electron-oxidised products are consistent with two ligand-based oxidation processes leading to the formation of relatively stable mono- and diphenoxyl radical complexes, $[Ni_2(L^{\cdot})(L)]^-$ and $[Ni_2(L^{\cdot})_2]$, respectively.

Introduction

The properties of transition metal complexes of phenoxyl radicals have recently attracted considerable attention.[1] This interest has been stimulated by the discovery of so-called "radical enzymes" in nature,[2] as illustrated by the galactose oxidase (GO) active site that contains a unique catalytically active Cu^{II}-tyrosyl radical moiety.[3] Recently, mononuclear nickel(II)-phenoxyl radical complexes have emerged in the literature that were prepared by using mainly suitably protected Salen-type ligands.[4] Combined spectroscopic studies have shown that the one-electron oxidation of square-planar $[Ni^{II}(L)]$ complexes {where L is $(Salen)^{2-}$ with varying bridging 1,2-diamine backbones} produces relatively stable Ni^{II}-phenoxyl radical complexes,[4g–4m] as confirmed by recent structural characterisations.[4i,4m] Interestingly, the groups of Yamauchi and Thomas independently reported that some of these radical complexes could exhibit temperature-dependant valence tautomerism, that is, at low temperature (below 190 K) the compounds are best described as Ni^{III} complexes.[4f,4g] In contrast, when axially coordinating ligands (such as pyridine) are present, the oxidation is metal-based and always leads to stabilised octahedral Ni^{III} species.[4g] In recent studies, Thomas et al. have introduced an amide function in place of the Schiff base in the Salen framework, producing Ni^{II} complexes of salicylamidate and demonstrating that the strong donating ability of the *N*-amidate donors stabilise Ni^{II}-radical oxidised species.[4g] Apart from these studies and earlier pioneering work by Collins and co-workers, the use of salicylamide ligands has been very limited, though Collins et al. had clearly demonstrated that *N*-amidate donors are crucial for the stabilisation of complexes with high oxidation states.[5]

In this respect, herein we report the coordination behaviour towards Ni^{II} ions of a new potentially trianionic salicylamide NO_2-ligand, 3,5-di-*tert*-butyl-2-hydroxy-*N*-(2-hydroxyethyl)benzamide (LH_3) (Scheme 1), comprising *O*-phenoxy, *O*-alkoxy and *N*-amidate donors. We show that the one- and two-electron oxidations of the dianionic di-Ni^{II} complex obtained, $[Ni_2(L)_2]^{2-}$, lead to mono- and diphenoxyl radical complexes, respectively.



LH_3

Scheme 1.

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon,
Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Fax: +351-218464455
E-mail: pombeiro@ist.utl.pt
[b] Universidade Lusófona de Humanidades e Tecnologias, ULHT Lisbon,
Campo Grande 376, 1749-024 Lisbon, Portugal
[‡] Current address: Laboratory of Biomimetic Chemistry, Department of Chemistry, Bar-Ilan University,
Ramat Gan 52900, Israel
E-mail: benisvl@mail.biu.ac.il

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100232.

Results and Discussion

The pro-ligand LH_3 has been synthesised in two steps as described previously.[6a] The reaction of LH_3 with $Ni^{II}(OAc)_2$ in the presence of a base ([NBu_4]OH) in a 1:1:3 ratio affords the salt $[NBu_4]_2[Ni_2(L)_2]$ (designated as $[NBu_4]_2$[**1**]). An acetonitrile solution of $[NBu_4]_2$[**1**] at –20 °C affords, after several days, pink single crystals that are suitable for X-ray crystallography and have the structure $[NBu_4]_2[Ni_2(L)_2]\cdot EtOH\cdot CH_3CN$ (Figure 1).

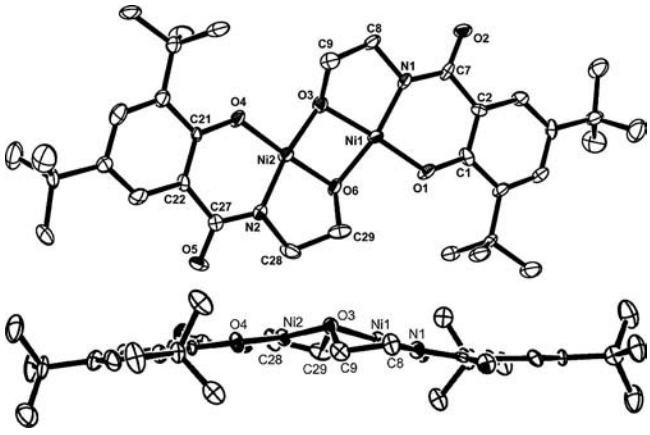


Figure 1. ORTEP representations of the dianion $[Ni_2(L)_2]^{2-}$ ($\mathbf{1}^{2-}$) in $[NBu_4]_2$[**1**]·EtOH·CH_3CN, shown with 50% thermal ellipsoids; (top) view along the *b*-axis, (bottom) view along the *a*-axis. The hydrogen atoms, the $[NBu_4]^+$ cations, and the solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–N1, 1.833(5); Ni1–O1, 1.824(4); Ni1–O3, 1.872(4); Ni1–O6, 1.885(4); Ni2–N2, 1.847(5); Ni2–O4, 1.829(4); Ni2–O6, 1.866(4); Ni2–O3, 1.890(4); Ni1···Ni2, 2.780(2). O1–Ni1–N1, 96.5(2); N1–Ni1–O3, 87.7(2); O1–Ni1–O6, 94.97(18); O3–Ni1–O6, 80.82(17); O4–Ni2–N2, 96.6(2); N2–Ni2–O6, 87.8(2); O4–Ni2–O3, 94.71(17); O6–Ni2–O3, 80.86(17)°. Torsion angles [°]: N1–C8–C9–O3, 43.54; N2–C28–C29–O6, 44.46; Ni1–O3–O6–Ni2, 152.88; O3–Ni1–Ni2–O6, 149.23°.

The molecular structure of $[NBu_4]_2$[**1**] consists of a dinuclear dianionic complex $[Ni_2(L)_2]^{2-}$ as indicated by the presence of two tetrabutylammonium cations per molecule of complex. Both ligands are present in their fully deprotonated trianionic form, L^{3-}, and bind both Ni^{II} ions in a NO_2-fashion, through the phenolate and alcoholate O-donor atoms and the amidate N-donor atom. Each metal possesses a Ni^{II}-NO_3 type square-planar coordination sphere, in agreement with the geometry generally preferred by the Ni^{II} ions in a strong ligand field. The two metals ions are bridged by two alcoholate O-donor atoms to form a bis(μ-alkoxido) Ni_2O_2 diamond core. The Ni···Ni separation of 2.780(2) Å is comparable to those in other related complexes.[7–9] Only a few similar dianionic complexes having ligands that are salicylamide derivatives have been reported with Cu^{II}[8,10,11] and with Ni^{II}.[9] The average bond length around each inequivalent Ni^{II} centre of 1.853 Å [Ni1] and 1.858 Å [Ni2] is in good agreement with those of Ni^{II}-salicylamidate compounds.[9] The lengths of the Ni–O [ranging from 1.824(4) to 1.890(4) Å] and Ni–N [1.833(5) and 1.845(5) Å] bonds are in agreement with those of few salicylamidate complexes of Ni^{II} reported to date.[9] Dinuclear complex $\mathbf{1}^{2-}$ is distorted from planarity with a slight concave shape [i.e. the angle between the N1–O1–Ni1 and N2–Ni2–O4 planes is 24.3°, Figure 2] imposed by the alkyl chains that bend out of the plane [i.e. the N2–C28–C29–O6 and O3–C9–C8–N1 torsion angles are 44.46° and 43.54°, respectively, Figure 2 bottom]. The crystal packing of **1** benefits from the high planarity of the dinuclear anion $[M_2(L)_2]^{2-}$, forming ionic alternating planes where the dianionic units are interspersed with the tetrabutylammonium cations (Figure S1).

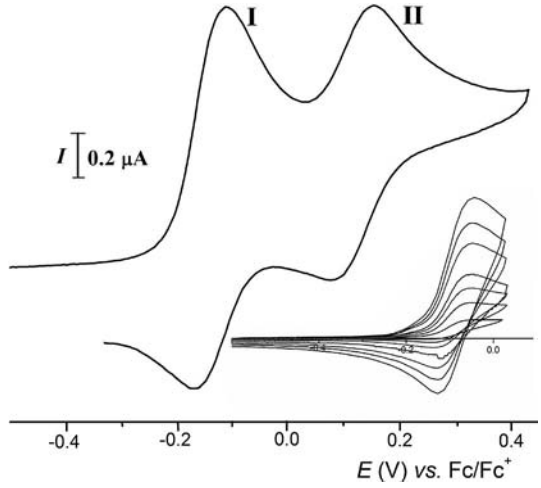


Figure 2. Cyclic voltammogram of $[NBu_4]_2$[**1**] (ca. 1 mM) in CH_3CN at 298 K containing $[NBu_4][BF_4]$ (0.2 M) as supporting electrolyte, at a scan rate of 120 mV/s, at a platinum disc electrode (d = 0.5 mm). The inset shows the first oxidation process at scan rates 20–900 mV/s.

Spectroscopic Characterisation of $[NBu_4]_2$[1]

As expected for a d^8, low-spin, square-planar Ni^{II} complex, $\mathbf{1}^{2-}$ is diamagnetic. Thus, $\mathbf{1}^{2-}$ is EPR-silent at room temperature or at 77 K in the liquid or frozen solution (in acetonitrile) states. Consequently, $\mathbf{1}^{2-}$ exhibits a well-resolved ^1H NMR spectrum in CD_3CN, displaying all expected resonance peaks, that is, the four resonances of the $[NBu_4]^+$ cations, two *t*Bu singlets, two methylene resonances and the two *meta*-protons of each phenol ring. Neither OH nor NH resonance peaks were observed. Interestingly, the two methylene resonances occurring as a broad multiplet at 2.32–2.54 ppm, are drastically shifted upfield as compared to the corresponding peaks for the free LH_3 [3.86 (broad, 2 H, CH_2-OH), 3.46 (q, 2 H, CH_2-NHCO)] and LH_2^- [3.58 (m, 2 H, CH_2-OH), 3.42 (m, 2 H, CH_2-NHCO)].[6a] Similarly, the two doublets at δ = 6.83 and 7.84 ppm assigned to both *meta*-H atoms of the phenol group are considerably shifted from the corresponding signal of LH_3 (7.49 and 7.41 ppm) or LH_2^- (7.63 and 7.13 ppm).[6a] These NMR

spectroscopic data clearly indicate that the ligand is in its fully deprotonated form and that the di-Ni^{II} complex is preserved in CD_3CN solution. Variable-temperature ^1H NMR spectroscopic experiments (298–235 K) did not reveal any significant changes, presumably indicating the absence or the presence of slight conformational changes in $\mathbf{1}^{2-}$.

The IR spectrum of the solid state of $\mathbf{1}^{2-}$ displays an amide C=O vibration frequency at 1604 cm^{-1}, at much lower frequency than that of the corresponding peak for the free ligand (1624 cm^{-1}), confirming the amidate form of the ligand with decreased π-character of the CO-bond through the resonance form. The negative electrospray mass spectrum of $[NBu_4]_2$[**1**] shows negative peaks, revealing the presence of the anions $[\mathbf{1}]^{2-}$ and $[\mathbf{1} + NBu_4]^-$, confirming thus the stability of the dinuclear complex in solution. The UV/Vis spectrum of $[NBu_4]_2$[**1**] in acetonitrile at room temperature displays a band at 500 nm (525 $M^{-1}cm^{-1}$), which can be tentatively assigned to a phenolate-to-Ni^{II}-charge-transfer transition.

Electrochemistry Studies

The cyclic voltammogram of $[NBu_4]_2$[**1**], in CH_3CN at 298 K, containing $[NBu_4][BF_4]$ (0.2 M), displays two reversible one-electron oxidation processes (Figure 2) associated with the formation of the corresponding oxidised compounds $\mathbf{1}^-$ and **1**, respectively. These oxidation processes occur at $E_{1/2}$ values of –0.120 and 0.110 V vs. the ferrocene/ferrocenium couple ($Fc^{+/0}$). The reversibility of the oxidation processes indicates that the oxidised species of $\mathbf{1}^{2-}$, that is $\mathbf{1}^-$ and **1**, are stable on the timescale of the cyclic voltammetry experiments.

Generation and Characterisation of the Oxidised Species $\mathbf{1}^-$ and **1**

The one-electron oxidation of $\mathbf{1}^{2-}$ performed by controlled potential electrolysis in CH_3CN at 243 K under a nitrogen atmosphere yields the oxidised species $\mathbf{1}^-$, which is sufficiently stable, under these conditions, to allow characterisation by UV/Vis and EPR spectroscopy. The X-band EPR spectrum of $\mathbf{1}^-$ in a frozen solution (at 100 K) exhibits an unresolved isotropic signal centred at g_{iso} = 2.0032 with a peak-to-peak line width of 11.2 G (Figure 3). In fluid solution at 273 K, the spectrum displays a well-resolved doublet signal (Figure 3) that was successfully simulated with the inclusion a hyperfine coupling constant of 4.73 G. The *g* value of the signal of $\mathbf{1}^-$ (as well as its isotropic properties) is typical of that observed for free or coordinated phenoxyl radicals,[6,12,13] which is usually close to the free electron value (g_e = 2.0023). The doublet observed for $\mathbf{1}^-$ is tentatively assigned to an interaction of the unpaired electron with one *meta*-proton of the aromatic ring; alternatively a successful simulation was obtained with the inclusion of two hyperfine couplings with both *meta*-H, that is, a_{H1} = 1.5 G and a_{H2} = 4.5 G (line width 2 G). Attempts to increase the a_{H1} or decrease the a_{H2} coupling constants would lead to triplet or multiple patterns. In contrast, the room-temperature X-band EPR spectrum of the corresponding H-bonded phenoxyl radical $LH_2^{\cdot}$ gives rise to a usual triplet signal that is successfully simulated with two quasi-equal hyperfine couplings with two *meta*-H nuclei (a_{H1} = 1.45 G and a_{H2} = 1.60 G).[6a] This difference most likely indicates that, in $\mathbf{1}^-$, the electron density of the unpaired electron of the phenoxyl radical is polarised presumably because of the delocalisation of the radical through both phenoxyl rings via the di-Ni^{II} core. The presence of the phenoxyl radical is further evidenced by the appearance of new absorptions at 439 (ε = 955) and 670 (ε = 290) nm in the visible spectrum of $\mathbf{1}^-$ (Figure 4), which are characteristic of phenoxyl radical transitions.[1e]

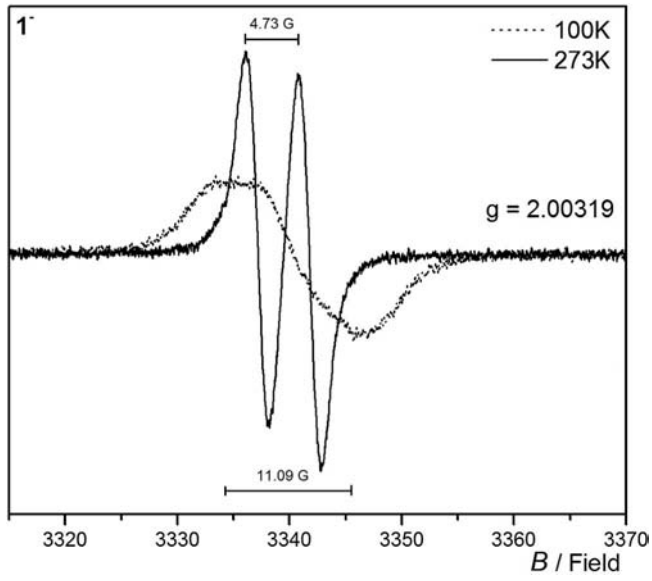


Figure 3. X-band EPR spectrum of electrochemically generated $\mathbf{1}^-$ recorded at 100 and 273 K (dotted and solid lines, respectively).

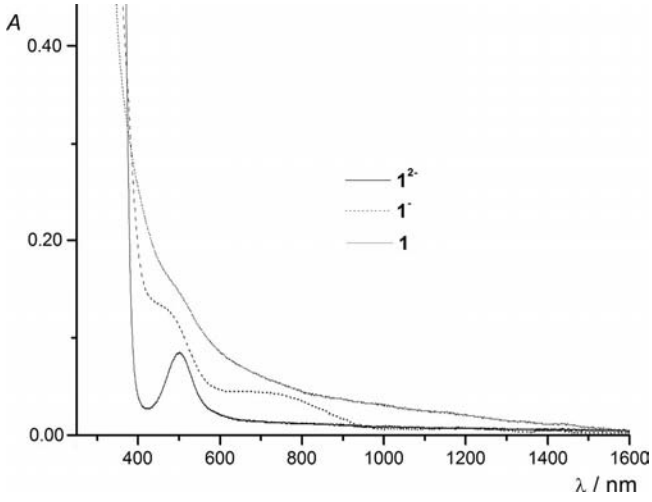


Figure 4. UV/Vis/NIR spectra of $\mathbf{1}^{2-}$ (solid) and $\mathbf{1}^-$ (dashed) and **1** (dotted) in CH_3CN at 273 K (all spectra are normalised to 1 mM concentration).

Thus, clearly, the one-electron oxidation of $\mathbf{1}^{2-}$ does not yield the mixed-valence Ni^{II}-Ni^{III} complex, but rather leads to a di-Ni^{II}-phenoxyl radical complex. The closeness of the *g* value for $\mathbf{1}^{-}$ to that of a free radical and the lack of anisotropy seem to indicate that the phenoxyl radical is not necessarily bound to Ni^{II} and could be weakly interacting with the metal ion; however, the polarisation of the spin density may arise from the delocalisation of the unpaired electron through both phenoxy rings.

The two-electron oxidation of $\mathbf{1}^{2-}$ produced the oxidised species **1**, which shows a UV/Vis spectrum that is similar to that of the analogous mono-oxidised $\mathbf{1}^{-}$ (i.e. 374, 492, 750 nm, Figure 4), confirming the presence of the phenoxyl radical moieties.[1e]

However, in contrast to $\mathbf{1}^{-}$, the EPR spectrum of **1** was found to be silent in the 90–298 K temperature range. These data correlate well with the presence two magnetically coupled phenoxyl radical moieties and suggest that **1** is a di-Ni^{II}-diphenoxyl radical complex. A similar EPR-silent di-Ni^{II}-diradical complex has been reported with iminobenzosemiquinone radical ligands.[14]

Conclusions

The new dianionic di-Ni^{II} complex, $[Ni_2(L)_2]^{2-}$ ($\mathbf{1}^{2-}$), bearing a trianionic N_2O-tridentate bridging ligand (L^{3-}) comprising *N*-amidate, *O*-alcoholate and *O*-phenolate donor atoms, has been synthesised. Each metal possesses a Ni^{II}-NO_3 square-planar coordination sphere. Electrochemical studies have revealed that two one-electron-oxidised species are accessible at relatively low potentials. Electrochemical, EPR and UV/Vis spectroscopic characterisation of both oxidised species, $\mathbf{1}^{-}$ and **1**, have indicated that these oxidation processes are both ligand-based, leading to the formation of relatively stable Ni_2-phenoxyl ($\mathbf{1}^{-}$) and Ni_2-diphenoxyl (**1**) radicals. To the best of our knowledge, these are the first dinickel(II) complexes bearing phenoxyl radical ligands. These results also confirm that salicylamide polyanionic ligands are suitable to stabilise phenoxyl radical complexes.

The chemical synthesis and isolation of these oxidised species are underway, as well as the exploration of their reactivity towards oxidation reactions. These complexes are relevant to metalloenzymes in nature using the combination of metallic redox centres coupled with organic redox cofactors; as exemplified by the Cu^{II}-phenoxyl radical moiety of the galactose oxidase active site or the RNase active site in which a tyrosyl radical has been identified in the proximity of a di-Fe^{III} core.[2] In addition, one should note that dianionic complexes such as $\mathbf{1}^{2-}$ may find promising use as "complex-ligand" building blocks for the construction of new 3d/3d and/or 3d/4f magnetic and luminescent materials.[15]

Experimental Section

General Remarks: C, H and N analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded with a BIO-RAD FTS 3000MX instrument by using KBr pellets (abbreviations: first letter s/m/w = strong/medium/weak; second letter s = sharp). Frequencies are expressed in cm^{-1}. UV/Vis/NIR spectra (1600–200 nm) were recorded with a Shimadzu UV-3101PC UV/Vis NIR spectrophotometer. ^1H, ^{13}C NMR spectra were measured with Bruker 300 and 400 UltraShield™ spectrometers. ^1H and ^{13}C NMR chemical shifts are expressed in ppm relative to $Si(Me)_4$. Coupling constants are in Hz (abbreviations: s, singlet; d, doublet; m, complex multiplet).

$[NBu_4]_2$[1]: To a pale green solution of $[Ni(OAc)_2]\cdot(H_2O)_4$ (424 mg, 1.70 mmol, 1 equiv.) in ethanol (60 mL) was added dropwise a solution of LH_3 (500 mg, 1.70 mmol, 1 equiv.) in ethanol (35 mL). The resulting solution was stirred under dinitrogen at room temperature for 30 min, whereupon a solution of $[NBu_4]OH$ in methanol (5.1 mL, 5.11 mmol, 1.0 M, 3 equiv.) was added dropwise. The solution turned pink/red and was stirred for 1 h at room temperature. The solvent was evaporated in vacuo, and an orange/pink oil was obtained. This residue was partially dissolved in dry acetonitrile (45 mL) and filtered through a cannula. The resulting filtered solution was stored under a dinitrogen atmosphere at –20 °C for 2 d. The solvent was decanted, leaving a pink crystalline solid of $[NBu_4]_2$[**1**] that was washed with cold acetonitrile (5 mL) and dried (412 mg, 41%). $C_{66}H_{120}N_4Ni_2O_6$ (1183.09): calcd. C 67.00, H 10.22, N 4.74; found C 66.26, H 10.32, N 4.71. ^1H NMR (CD_3CN): δ = 7.62 (d, J^4 = 2.4 Hz, 2 H, ArH), 6.90 (d, J^4 = 2.5 Hz, 2 H, ArH), 3.11 (m, 16 H, -CH_2-N, [NBu_4]), 2.54–2.32 (br. m, 8 H, CH_2-OH + CH_2-NHCO), 1.66–1.56 (m, 16 H, -CH_2-, [NBu_4]), 1.42–1.33 (m, 16 H, -CH_2-, [NBu_4]), 1.20 (s, 18 H, *t*Bu), 1.16 (s, 18 H, *t*Bu), 0.96 (t br, 24 H, CH_3-, [NBu_4]) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 175.84 (CO), 159.29 (*C*-OH, Ar), 135.06 (C-*t*Bu, Ar), 134.95 (C-*t*Bu, Ar), 124.01 [HC(Ar)], 123.54 [HC(Ar)], 117 (*C*-CO, Ar), 63.98 (CH_2-OH), 59.36 (-CH_2-N, [NBu_4]), ca. 43 (br., CH_2-NH), 35.26 (C-, *t*Bu), 35.08 (C-, *t*Bu), 32.21 (CH_3, *t*Bu), 29.85 (CH_3, *t*Bu), 24.42 (-CH_2-, [NBu_4]), 20.35 (-CH_2-, [NBu_4]), 13.85 (-CH_3, [NBu_4]) ppm. MS [EI (+)]: *m*/*z* = 242 $[NBu_4]^+$, 1423 $[M + NBu_4]^+$; [EI (–)]: *m*/*z* = 348 $[M - 2NBu_4]^{2-}$, 696 $[M - 2NBu_4 + H]^-$, 938 $[M - NBu_4]^-$. IR (KBr pellets): $\tilde{\nu}$ = 2960 (s s), 2903 (m s), 2875 (m s), 1637 (w s), 1604 (m s, C=O), 1555 (s s), 1479 (m s), 1431 (s s), 1282 (m s), 1254 (m s), 1064 (m s), 800 (w s), 663 (w s) cm^{-1}. UV/Vis/NIR: λ (ε, $M^{-1}cm^{-1}$) = 500(525), 338(7550) nm.

Electrochemistry: The electrochemical experiments were carried out with an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry studies were undertaken in a two-compartment three-electrode cell, with platinum disk working (*d* = 0.5 mm) and counterelectrodes. A Luggin capillary connected to a silver-wire pseudo-reference electrode was used to control the working electrode potential. The solutions were saturated with N_2 by bubbling this gas before each run and were 10^{-3} M in the test compound and 0.2 M in $[NBu_4][BF_4]$, used as supporting electrolyte. The *E* values given are relative to that of the oxidation of ferrocene ($Fc^{0/+}$), but to avoid overlapping of redox couples with that of the ferrocene internal standard, $[Fe(TpmPy)_2](BF_4)_2$ {TpmPy = 4-[(tris-2,2,2-pyrazolyl-1-ylethoxy)-methyl]pyridine}[16] was used as the internal standard, and the potentials of redox process(es) observed were referenced to the $Fc^{0/+}$ couple by an independent calibration, that is, $E_{1/2}[Fc]^{0/+}$ – $E_{1/2}[Fe(TpmPy)_2](BF_4)_2^{0/+}$ = 0.642 V. Controlled potential electrolyses (CPE) were carried out in a two-compartment, three-electrode cell with platinum-gauze working and counterelectrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The solutions were saturated with N_2 by bubbling this

gas before each run and were 0.2 M in $[NBu_4][BF_4]$, used as supporting electrolyte, and ca. 10^{-3} M in the test compound.

Electrochemical data for $[NBu_4]_2$[1]: Redox process I: ${}^{I}E^{ox}_{1/2}$ = –0.120 V (ΔE = 89 mV at 120 mV s^{-1}). ΔE = 76–95 mV (scan rate = 20–900 mV s^{-1}); $i_p^{ox}/i_p^{red} = 1 \pm 0.3$; (scan rate)$^{1/2} \propto i_p^{ox}$ (and i_p^{red}). Redox process II: ${}^{II}E^{ox}_{1/2}$ = +0.110 (ΔE = 102 mV at 120 mV s^{-1}). ΔE = 99–109 mV (scan rate = 20–900 mV s^{-1}); $i_p^{ox}/i_p^{red} = 1 \pm 0.2$; (scan rate)$^{1/2} \propto i_p^{ox}$ (and i_p^{red}). For ferrocene oxidation (Fc/Fc^+): ΔE = 77–89 mV (scan rate = 20–900 mV s^{-1}). Thus, these processes are considered to be reversible. Controlled potential coulometry performed in CH_3CN at 253 K, for process I at (0.340 V vs. Ag/AgCl) and for process II at (0.589 V vs. Ag/AgCl), indicated the transfer of 1.01 and 1.92 electrons per molecule, respectively. Thus, each of these processes concerns a one-electron oxidation.

X-ray Crystallographic Data for $[NBu_4]_2$[1]·EtOH·CH_3CN: Crystal data: $C_{70}H_{128}N_5Ni_2O_7$, pink plate, Fw = 1269.19, triclinic, space group $P\bar{1}$, a = 12.085(3) Å, b = 16.345(4) Å, c = 20.368(5) Å, α = 69.892(10)°, β = 80.773(11)°, γ = 84.246(11)°, V = 3724.8(15) Å^3, d = 1.131 g cm^{-3}, Z = 2, T = 150(2) K, $F(000)$ = 1388, μ(Mo-K_α) = 0.556 mm^{-1}. Single crystals of $[NBu_4]_2$[**1**]·EtOH·CH_3CN were obtained as indicated above. Intensity data were collected at 150 K with a Bruker AXS-KAPPA APEX II diffractometer having graphite monochromated Mo-K_α (λ = 0.71073) radiation. Data were collected by using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved by using Bruker SMART software and refined by using Bruker SAINT[17] on all the observed reflections. Absorption corrections were applied with SADABS.[17] The structure was solved by direct methods by using the SHELXS–97 package[18] and refined with SHELXL–97.[19] Calculations were performed with the WinGX System–Version 1.80.03.[20] All hydrogen atoms were inserted in calculated positions. PLATON/SQUEEZE[21] was used to correct the data. The final refinement agreement factors are R_1 = 0.0667 for 5194 data with $F > 4\sigma(F)$ and wR_2 = 0.1440 for 13085 data. CCDC-815769 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

EPR Spectroscopy: EPR spectra were recorded with a Bruker ESP 300E X-band spectrometer equipped with an ER 4111 VT variable-temperature unit; g values were calculated from the formula ν = 1.39962gB', where ν is the frequency measured (GHz) and B' is the corrected value of field (kGauss). The field correction (ΔB) was calculated from the difference of theoretical and experimental values of the field ($B' - B^{exp}$) of our reference compound (i.e. perylene radical in conc. sulfuric acid) with known g value (i.e. 2.002569): $B' = \nu^{exp}/(1.39962g)$. Sample solutions of electrochemically generated $\mathbf{1}^-$ (see above) were rapidly transferred under exclusion of dioxygen into an X-band quartz tube (4-mm inner diameter), which was immediately frozen and stored in liquid nitrogen. The measurements were performed at temperatures from 90 to 298 K; the temperature was regulated with an Oxford ESR 900H cryostat. The microwave power supplied to the resonator was varied in the range 0.2–2 mW; a 100-kHz magnetic field modulation with a peak-to-peak amplitude of 0.5 mT was used.

$\mathbf{1}^-$ (in CH_3CN at 90–298 K): centre field: 3350.9832; modulation frequency: 100 KHz; modulation amplitude: 1.0–0.2 Gpp; receiver gain: 4.48×10^{-4}; conversion time: 40.96 ms; time constant: 81.92 ms; ST: 40 s. The 273 K spectrum was simulated with SIMPHONIA software.

Supporting Information (see footnote on the first page of this article): Packing diagram of $[Ni_2(L)_2]^{2-}$ ($\mathbf{1}^{2-}$) in $[NBu_4]_2$[**1**]·EtOH·CH_3CN.

Acknowledgments

This work has been partially supported by the Foundation for Science and Technology (FCT) and its PPCDT 2010 programme (FEDER funded), grant SFRH/BD/23187/2005 (R. W.), as well as by the Human Resources and Mobility Marie Curie Research Training Network (AQUACHEM project, CMTN-CT-2003-503864). L. B. thanks the EU for the provision of an ER (Experienced Researcher) fellowship within this project. We also acknowledge Dr. J. P. Telo and Dr. M. C. Oliviera for their assistance with EPR spectroscopy and mass spectrometry measurements.

[1] Recent reviews: a) B. A. Jazdzewski, W. B. Tolman, *Coord. Chem. Rev.* **2000**, *200–202*, 633–685; b) S. Itoh, M. Taki, S. Fukuzumi, *Coord. Chem. Rev.* **2000**, *198*, 3–20; c) P. Chaudhuri, K. Wieghardt, *Prog. Inorg. Chem.* **2001**, *50*, 151–216; d) P. Chaudhuri, K. Wieghardt, T. Weyhermüller, T. K. Paine, S. Mukherjee, C. Mukherjee, *Biol. Chem.* **2005**, *386*, 1023–1033; e) F. Thomas, *Eur. J. Inorg. Chem.* **2007**, 2379–2404.
[2] J. Stubbe, W. A. van der Donk, *Chem. Rev.* **1998**, *98*, 705–762.
[3] J. W. Whittaker, *Chem. Rev.* **2003**, *103*, 2347–2363.
[4] a) J. Müller, A. Kikuchi, E. Bill, T. Weyhermüller, P. Hildebrandt, L. Ould-Moussa, K. Wieghardt, *Inorg. Chim. Acta* **2000**, *297*, 265–277; b) Y. Shimazaki, S. Huth, S. Karasawa, S. Hirota, Y. Naruta, O. Yamauchi, *Inorg. Chem.* **2004**, *43*, 7816–7822; c) Y. Shimazaki, F. Tani, K. Fului, Y. Naruta, O. Yamauchi, *J. Am. Chem. Soc.* **2003**, *125*, 10512–10513; d) T. Glaser, M. Heidemeier, R. Fröhlich, P. Hildebrandt, E. Bothe, E. Bill, *Inorg. Chem.* **2005**, *44*, 5467–5482; e) O. Rotthaus, F. Thomas, O. Jarjayes, C. Philouze, E. Saint-Aman, J.-L. Pierre, *Chem. Eur. J.* **2006**, *12*, 6953–6962; f) Y. Shimazaki, T. Yajima, F. Tani, S. Karasawa, K. Fukui, Y. Naruta, O. Yamauchi, *J. Am. Chem. Soc.* **2007**, *129*, 2559–2568; g) O. Rotthaus, O. Jarjayes, F. Thomas, C. Philouze, C. Perez Del Vallee, E. Saint-Aman, J.-L. Pierre, *Chem. Eur. J.* **2006**, *12*, 2293–2302; h) L. Benisvy, R. Kannappan, Y.-F. Song, S. Milikisyants, M. Huber, I. Mutikainen, U. Turpeinen, P. Gamez, L. Bernasconi, E. J. Baerends, F. S. Hartl, J. Reedjik, *Eur. J. Inorg. Chem.* **2007**, 637–642; i) T. Storr, E. C. Wasinger, R. C. Pratt, T. D. P. Stack, *Angew. Chem.* **2007**, *119*, 5290; *Angew. Chem. Int. Ed.* **2007**, *46*, 5198–5201; j) O. Rotthaus, O. Jarjayes, C. Pérez Del Valle, C. Philouze, F. Thomas, *Chem. Commun.* **2007**, 4462–4464; k) A. Kochem, M. Orio, O. Jarjayes, F. Neese, F. Thomas, *Chem. Commun.* **2010**, *46*, 6765–6767; l) O. Rotthaus, O. Jarjayes, C. Philouze, C. Pérez Del Valle Carlos, F. Thomas, *Dalton Trans.* **2009**, 1792–1800; m) M. Orio, O. Jarjayes, H. Kanso, C. Philouze, F. Neese, F. Thomas, *Angew. Chem. Int. Ed.* **2010**, *49*, 2989–4992.
[5] F. C. Anson, T. J. Collins, T. G. Richmond, B. D. Santarsiero, J. E. Toth, B. G. R. T. Treco, *J. Am. Chem. Soc.* **1987**, *109*, 2974–2979.
[6] a) L. Benisvy, R. Wanke, M. L. Kuznetsov, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Chem. Eur. J.*, **2011**, submitted; b) C. Xie, P. M. Lahtie, C. George, *Org. Lett.* **2000**, *2*, 3417–3420.
[7] M. Koikawa, H. Yamashita, T. Tokii, *Inorg. Chem. Commun.* **2003**, *6*, 157–161.
[8] M. Koikawa, M. Nakashima, T. Tokii, *Inorg. Chim. Acta* **1998**, *277*, 134–137.
[9] T. C. Harrop, M. M. Olmstead, P. K. Mascharak, *Chem. Commun.* **2003**, 410–411.
[10] M. Koikawa, H. Okawa, N. Matsumoto, M. Gotoh, S. Kida, T. Kohzuma, *J. Chem. Soc., Dalton Trans.* **1989**, 2089–2094.
[11] J. P. Costes, M. Auchel, F. Dahan, V. Peyrou, S. Shova, W. Wernsdorfer, *Inorg. Chem.* **2006**, *45*, 1924–1934.

[12] L. Benisvy, E. Bill, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, G. McArdle, E. J. L. McInnes, J. McMaster, S. Ross, C. Wilson, *Dalton Trans.* **2006**, 258–267.
[13] a) T. Maki, Y. Araki, Y. Ishida, O. Onomura, Y. Matsumura, *J. Am. Chem. Soc.* **2001**, *123*, 3371–3372; b) F. Thomas, O. Jarjayes, H. Jamet, S. Hamman, E. Saint-Aman, C. Duboc, L. Pierre, *Angew. Chem.* **2004**, *116*, 604; *Angew. Chem. Int. Ed.* **2004**, *43*, 594–597; c) L. Benisvy, R. Bittl, E. Bothe, C. D. Garner, J. McMaster, S. Ross, C. Teutloff, F. Neese, *Angew. Chem.* **2005**, *117*, 5448; *Angew. Chem. Int. Ed.* **2005**, *44*, 5314–5317.
[14] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 2213–2223.
[15] M. Andruh, *Chem. Commun.* **2011**, *47*, 3025–3042.
[16] R. Wanke, M. F. C. Guedes da Silva, S. Lancianesi, T. F. S. Silva, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Inorg. Chem.* **2010**, *49*, 7941–7952.
[17] Bruker, *APEX2 & SAINT*. Madison, Wisconsin, USA, **2004**.
[18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[21] A. L. Spek, *Acta Crystallogr., Sect. C* **1990**, *46*, C34.

Received: March 6, 2011
Published Online: May 18, 2011

