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Multielectron oxidation in a ferromagnetically coupled dinickel(II) triple mesocate†

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Triple-stranded dinuclear nickel(II) complexes of the meso-helicate type have been obtained from the new N,N’-1,3-phenylenebis(pyrazine-2-carboxamidate) ligand; they possess a multielectron redox behaviour featuring up to four stepwise, one-electron oxidations of the two ferromagnetically coupled NiII ions to afford the putative high-valent dinickel(III) and dinickel(IV) species, as supported by theoretical calculations. Metallacyclic complexes containing multiple ligand- and/or metal-based, spin containing electrophores are of large interest as potential electronic and magnetic devices in the emerging field of molecular spintronics.1–3 Toward this goal, we are developing new multifunctional exchange-coupled polynuclear metallacyclic complexes with new pyrazineamidate-substituted aromatic bridging ligands that would possess a rich metal-centred electrochemical activity. In fact, high-valent nickel(III) and nickel(IV) mononuclear complexes with related pyridineamidate chelating ligands were isolated by Mukherjee due to the strong σ-donor ability (basicity) of the amidate donor groups, that reduce the oxidizing character of high-valent complexes and therefore increase the stability of themselves.4 More recently, Colacio and co-workers have obtained ferromagnetically-coupled, triple-stranded dinuclear nickel(II) complexes with the N,N’-1,3-phenylenebis(pyridine-2-carboxamidate) bridging ligand, but their electrochemical activity has not been investigated.6

Here we report the synthesis, structural and spectroscopic characterization, magnetic and electrochemical properties, and Density Functional (DF) and Complete Active Space (CAS) calculations of novel triple-stranded dinuclear nickel(II) complexes with the N,N’-1,3-phenylenebis(pyrazine-2-carboxamidate) (L) bridging ligand. To our knowledge, they constitute the first members of a novel class of exchange coupled dinuclear triple meso-helicates (“mesocates”), exhibiting multistep metal-based redox behaviour. Based on these experimental and theoretical exploratory studies, we suggest that dinickel(II) mesocates can act as effective multielectron reservoirs for charge storage applications.

The proligand H2-L was synthesized from the straightforward reaction of 1,3-phenylenediamine and 2-pyrazinecarboxylic acid under the presence of triphenyl phosphite (1:2:2 molar ratio) in pyridine solution in very good yields (90%) (see ESI†). The anionic dinuclear nickel(II) complex, [NiII2L3]2−, was synthesized from the reaction of the proligand and the nitrate salt of the Ni2+ ions (3:2 molar ratio) in basic methanol solution by using either potassium or n-tetrabutylammonium hydroxide as base, and it was isolated as its corresponding salts of formula K2[NiII2L3] · 3MeOH · 3H2O (1a) and (nBu4N)2[NiII2L3] · 4MeOH (1b) respectively, in moderate to good yields (70–75%) (see ESI†).

The crystal structure of 1a consists of dinickel(II) triple mesocate anions of the metallacyclopentand-type with approximate C3h molecular symmetry, [NiII2(µ-η2:η2-L)3]2− (Fig. 1), coordinated potassium cations, together with crystallization methanol and water molecules (see ESI†). The two crystallographically independent Ni(1) and Ni(2) atoms adopt a trigonally distorted octahedral Ni6 coordination environment with alternating helical chiralities (named RS-stereoisomers) (Fig. 1). The values of the trigonal twist angle (τ) of 50.12(2) and 51.1° at Ni(1) and Ni(2) respectively, deviate appreciably from that of an ideal octahedral geometry (τ = 60°), as previously reported for the related dinickel(II) triple mesocates with...
the parent N,N′-1,3-phenylenebis(pyridine-2-carboxamidate) bridging ligand. The NiN₆ environment at each metal ion is formed by the coordination in a fac disposition of three amide and three pyridine nitrogen atoms belonging to three different bridging ligands [Ni-N₆_mide = 2.063(4)–2.096(4) Å and Ni-N₆_py = 2.091(4)–2.128(5) Å]. Within the Ni₈(m-N₆_C₆H₄)₄ metallacryptand core of 1a, the aromatic groups are disposed edge-to-face, with a weak C–H⋯π interaction between neighbouring benzene rings. The average torsion angle around the Ni–N–C–C bonds (φ) in 1a is 94.9(1)°, a value which is slightly closer to that of 90° than those reported for the aforementioned pyridine analogues (φ = 95.7–96.0°).

The cyclic voltammogram (CV) of 1b reveals a reversible oxidation wave at negative potentials up to –2.0 V (see Fig. 1). Within the NiN₆-mide coordination polymers of hexagonal-type topology (Fig. S1, ESI†). The value of the intramolecular Ni(1)–Ni(2) distance (r) across the triple m-phenylene diamidate bridge in 1a is 6.900(1) Å, while the shortest intermolecular Ni(2)–Ni(1) separation is 9.513(3) Å [symmetry code: (1) = ½+x, ½−y, −½+z].

The binding of these heterochiral metallacryptand-type Ni₃⁺,₂ metal mesocates to the two crystallographically independent K(1) and K(2) atoms through the free carbonyl-oxygen atoms of the carboxamidate groups leads to heterometallic potassium(II)nickel(II) 2-D coordination polymers of hexagonal-type topology (Fig. S1, ESI†). The value of the intramolecular Ni(1)–Ni(2) distance (r) across the triple m-phenylene diamidate bridge in 1a is 6.900(1) Å, while the shortest intermolecular Ni(2)–Ni(1) separation is 9.513(3) Å [symmetry code: (I) = ½+x, ½−y, −½+z].

The cyclic voltammogram (CV) of 1b in acetonitrile at 25 °C shows up to four reversible oxidation waves grouped in two pairs at E₁ = 0.31 V, E₂ = 0.47 V, E₃ = 0.89 V, and E₄ = 1.10 V vs. SCE (Fig. 2), with anodic to cathodic peak separation values (ΔEₚ,₁ = ΔEₚ,₂ = ΔEₚ,₃ = ΔEₚ,₄ = 70 mV) which are similar to that of the ferrocene under the same conditions [ΔEₚ,Fc/Fc⁺ = 70 mV (CH₃CN, 0.1 M n-Bu₄NPF₆)]. So, an almost linear plot of the peak current against the square root of the scan rate is obtained for all redox waves (see Fig. S8, ESI†), which are then stated to be pseudo-reversible on the voltammetric time-scale. Complex 1b does not show any reduction wave at negative potentials up to –2.0 V vs. SCE.

The first pair of closely spaced oxidation waves of 1b (ΔE₁₂ = E₁ −E₂ = 160 mV) would correspond to the stepwise one-electron oxidation of the metal centres to afford the dinickel(II,III) and dinickel(III,III) species. The second pair of oxidation waves (ΔE₁₄ = E₃ −E₄ = 210 mV) would then correspond to the further stepwise one-electron oxidation of the resulting dinickel(III,III) intermediate to give the corresponding dinickel(III,IV) and dinickel(IV,IV) species. The small splitting of each pair reflects on the weak but non-negligible electronic interactions between the metal centres through the triple m-phenylene diamidate bridge in the resulting mixed-valent species. The calculated values of the individual comproportionation constant along this electron transfer series, however, clearly reflect the higher thermodynamic stability of the homovalent Ni₃⁺ complex (log K₃⁺ = ΔE₃⁺/59 = 7.12) when compared with those of the heterovalent Ni₃⁺,₂ and Ni₃⁺,IV ones (log K₃⁺ = ΔE₃⁺/59 = 2.71 and log K₃⁺ = ΔE₃⁺/59 = 3.56).

Variable-temperature (2.0–300 K) magnetic susceptibility measurements for 1a and 1b in the form of the χₐ and χₐT plots (χₐ being the molar magnetic susceptibility per dinuclear unit and T the absolute temperature) are shown in Figure S2 and S3 respectively (ESI†). At room temperature the χₐT values of 2.11 (1a) and 2.10 cm³ mol⁻¹ K⁻¹ (1b) are close to that expected for two magnetically non-interacting high-spin Ni₃⁺ ions. Upon cooling, χₐT continuously increase for 1a and 1b revealing the presence of moderately weak intradimer ferromagnetic coupling between the high-spin Ni₃⁺ ions. In fact, since the large intermolecular metal-metal separation of ca. 10 Å, the interdimer magnetic interactions through the diamagnetic K⁺ ions in 1a are certainly negligible. However, 1a and 1b show a maximum χₐT value of 2.90 and 2.86 cm³ mol⁻¹ K at 3.5 and 4.7 K, respectively, and then they slightly decrease down to 2.81 cm³ mol⁻¹ K at 2.0 K, which is a consequence of a non-negligible zero-field splitting (zfs) of the six-coordinate, octahedral high-spin d⁶ Ni₃⁺ ions ($^3A_g$).

The magnetic susceptibility and magnetization data of 1a and 1b were analysed in unison through a spin Hamiltonian [eqn. (S1), ESI†] for a dimer model which takes into account the local axial (D) and equatorial (E) zfs of a triplet Ni₃⁺ ions (Sₐ = 1), a magnetic coupling between them (J), and a Zeeman effect through the Landé factor for Ni₃⁺ ion (g₀ₐ). A good fit for 1a/1b is obtained through the applicable analytical expression with J = +3.3/3.5 cm⁻¹, D = –3.1/–3.1 cm⁻¹, E/D = 0.004/0.007, g = 2.040/2.035, and F = 3.1 x 10⁻⁵/1.5 x 10⁻⁵ (where F is the agreement factor defined as $\Sigma [(\chi exp − \chi calc)^2]/\Sigma (\chi exp)^2$), where $\chi$ is the physical property under study (solid lines in Fig. S2 and S3, ESI†). The experimental J and D values for 1a and 1b are similar to those reported earlier for related...
dinickel(II) triple mesocates with the ligands $N,N'$-1,3-phenylenebis(oxamate) and $N,N'$-1,3-phenylenebis(pyridine-2-carboxamidate) ($J = 3.2$–$3.6 \text{ cm}^{-1}$ and $|D| = 0.5$–$3.5 \text{ cm}^{-1}$).8

The observed net intramolecular ferromagnetic coupling in 1a and 1b is supported by DF calculations on a molecular model based on the experimental geometry and including the K$^+$ ions and their surroundings, which provide a calculated $J$ value of $+3.9 \text{ cm}^{-1}$ (see Computational details, ESI†). Similar calculations on a more simple model, where K$^+$ ions are excluded, give the same result ($J = +3.9 \text{ cm}^{-1}$) or very close ($J = +4.2 \text{ cm}^{-1}$) for its optimized geometry. From the spin density map of the quintet state of the Ni$^{112}$ unit shown in Figure 3a, it can be observed that a spin delocalization occurs from the $e_d(z^2, x^2-y^2)$ magnetic orbitals of the metal ions to the coordinated amidate nitrogen atoms. The spin density on these nitrogen atoms is then pumped in the $\pi$ pathway of the organic skeleton by a spin polarization mechanism leading to the alternating atomic spin densities on the exchange pathway.9 Thus, according to the McConnell II mechanism, a ferromagnetic coupling is found because of an odd number of atoms exists through the pathway.10

The stable doubly oxidized dinickel(III,III) species was prepared by both electrochemical and chemical oxidation of 1b with nBu$_4$NPF$_6$ as supporting electrolyte in acetonitrile and an applied voltage of $+0.50 \text{ V}$ (under a constant current of 0.35 $\mu$A for three days) and excess of bromine in acetonitrile, respectively [$E(Br_2/Br^-) = +0.47 \text{ V vs. SCE}$] (see ESI†). Up to now, all our attempts to characterize the quadruple oxidized dinickel(IV) species obtained either by chemical or electrochemical oxidations were unsuccessful, probably because of its partial decomposition under our experimental conditions.

On the contrary, the Q-band EPR spectrum at 8 K of 1b in acetonitrile solution shows a complicated spectral pattern similar to that reported in a previous paper for [Ni$_2$(μ$_{2}$-OH$_2$)(μ$_{2}$-O$_2$CBu)$_2$(O$_2$CBu)$_2$(py)(3-Mepy)]$^{11}$ (py = pyridine and 3-Mepy = 3-methylpyridine) (see Figure S5). In such case, $D$, an probably also $g_z$, $g_x$, $g_y$ for each nickel(II) metal ion and $J$ magnetic coupling constant between Ni$^{1111}$ ions are not very different from those found for us (see above), what justify the resemblance between the Q-band EPR spectra. Such as it is told by Walsh et al., “due to a very limited number of transitions falling within the available magnetic field range, … and a significant $z_J$ is acting on weakly coupled non-Kramer ions” an interpretation of the spectra is extremely difficult. The complexity arises because of the two Ni$^{111}$ ions are non-equivalents and their $D$ tensors are not collinear. The equivalent spectrum in solid state is richer and more defined, probably due also to the observation of the hyperfine coupling (see Figure S5).

On the other hand, CAS calculations on a more simple molecular model, where one of the high-spin Ni$^{111}$ ions was replaced by a diamagnetic Zn$^{111}$ ion, allowed to calculate the local magnetic anisotropy parameters of the nickel(II) centre [$D = –6.0 \text{ cm}^{-1}$ and $E/D = 0.07$ for centre Ni(1) and $D = –6.6 \text{ cm}^{-1}$ and $E/D = 0.12$ for centre Ni(2)]. It is worthy to say, that the $|D|$ value obtained above from the best-fit corresponds to a minimum value since a perfectly alignment of the local $D$ tensors was considered, which is not the case. Indeed, a larger value is found by CAS calculations in agreement with an angle between $z$-axis of ZFS equal to 57.7°.

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On the contrary, the Q-band EPR spectrum at 8 K of the doubly oxidized species obtained by either electrochemical or chemical oxidation of 1b in acetonitrile solution is characteristic of a doublet from a Ni$^{1111}$ species ($S_{\text{ni}} = 1/2$) and with $g_1 = 2.05$, $g_2 = 2.07$ and $g_3 = 2.20$ (see Figure S6). A similar spectrum was registered on a crystalline sample obtained from electrocrystallization ($g_1 = 2.05$, $g_2 = 2.05$ and $g_3 = 2.30$), unfortunately any good single-crystal was obtained (see Figure S7). However, the experimental spectra is more complicated than the theoretical ones obtained with these $g_i$ values and some signals at lower magnetic field are also observed, which correspond to an anisotropic spin state generated from a weak ferromagnetic coupling between the two Ni$^{111}$ ions. The stabilization of the trivalent oxidation state of nickel in 1b is explained in terms of the well known strong electron donating character of the amidate groups, as reported earlier for the dicopper(II) metallacyclophane with the innocent ligand $N,N'$-2-methyl-1,3-phenylenebis(oxamate) ($E_1 = +0.43$ and $E_2 = +0.65 \text{ V vs. SCE}$).$^{10}$

Usually in coordination chemistry, DF calculations provide a correct description of the electronic structure but it is not possible in an easy way to correlate the obtained molecular orbitals with those usually used in simplified but useful schemes. In such cases, the formal magnetic orbitals are split into several molecular orbitals and any physical information cannot be directly extracted from them, e.g. their energies. An answer can be found in the natural orbitals that allow us to find a composition and shape of the magnetic orbitals. As an approach, it is possible to find an estimation of their energies carrying out a calculation using frozen natural orbitals, as illustrated in Figure S4 (ESI†). In 1a, the energy gaps between pairs of the magnetic orbitals are very small ($125$ and $173 \text{ cm}^{-1}$), i.e., they are
nearly degenerated and following the Hay-Thiebault-Hoffman mechanism a ferromagnetic is expected, in agreement with our calculations. In fact, these orbitals should be symmetric and antisymmetric combinations of the local magnetic orbitals, but as in some ferromagnetic diradical species, they are non-bonding in the skeleton, avoiding the mixture of them, what support the ferromagnetic nature of the interaction.

It is very usual thinking that oxidation processes occur by removing electrons of the HOMO, i.e., the highest occupied molecular orbital, but, sometimes, in modern coordination chemistry this is not the case, because a reorganization of the molecular orbitals occurs after removing one electron, what can stabilize an oxidation from a more intern orbital. Thus, following the description in the preceding paragraph, an oxidized \( \text{Ni}^{III} \) complex should be expected, but the only way to rule out a radical form is looking for the most stable of them. So, from the optimized molecular geometry of the simple model of 1a we removed two electrons and optimized the molecular geometry. Evidently, an oxidation of one electron in each metal centre to reach a \( \{\text{Ni}^{III}\}^2 \) configuration were studied, but also other where the electrons were removed from the organic bridge to arrive at \( \{\text{Ni}^{III}\}^2 \) species with different arrangements of the local spin moments on \( \text{Ni}^{II} \) and \( \text{L}^\ast \) paramagnetic centres. A double oxidation in only one of the metal ions to generate a \( \text{Ni}^{IV}:\text{Ni}^{III} \) specie was logically discarded. The radical species were all placed above to nearly 3400 cm\(^{-1}\) from the most stable \( \{\text{Ni}^{III}\}^2 \) configuration and above to nearly 2600 cm\(^{-1}\) for a configuration, \( \{\text{Ni}^{III}::\text{Ni}^{II}::\text{LL}^\ast \} \), where the oxidized is mixed between a metal ion and one organic bridge.

DF calculations on the \( \{\text{Ni}^{III}\}^2 \) species showed that a weak ferromagnetic coupling \( (J = +20.4 \text{ cm}^{-1}) \) mediates between doublet \( (S = \frac{1}{2}) \) \( \text{Ni}^{III} \) ions, being, in agreement with the EPR study, a triplet as a spin ground state. As in 1a, the McConnell mechanism makes possible a ferromagnetic coupling in the oxidized species, such as it is shown in Figure 3b. However, three phenyl ring are operative to transmit the magnetic coupling in 1a, but now only one of them is pertinent because the \( x^2-y^2 \) magnetic orbital is empty. Indeed, a lost of spin density is observed in the basal plane of the \( \text{Ni}^{III} \) ion that leads to a spin polarization instead of a delocalization on the nitrogen atoms of two pyrazineamidate ligands, but the spin polarization on the pathway is conserved but its magnitude is largely decrease. On the other hand, as in 1a, the larger spin density on the \( z \) axis is delocalized on the amidate nitrogen atoms and then polarized through the pathway being effective the McConnell mechanism, observing hence a net ferromagnetic coupling. Comparing the \( n_\alpha n_\beta J \) parameter, where \( n_\alpha \) and \( n_\beta \) are the unpaired electrons in each centre, closed values are found for 1a (16.8 cm\(^{-1}\)) and its oxidized species (20.4 cm\(^{-1}\)) showing that the magnetic coupling in both compounds is similar.

Conclusions

The self-assembly of the novel \( N,N'-1,3\)-phenylenebis(pyrazine-2-carboxamidate) ligand with \( \text{Ni}^{II} \) ions renders a unique example of ferromagnetically coupled dinickel(II) metallacrypt and of the triple mesocate-type. Interestingly, the two metal centres function as electron reservoirs to impart a multielectron (charge storage) oxidation behaviour to this electroactive magnetic molecule with several chemically accessible oxidation levels at the exchange-coupled spin carriers that can store and deliver an electric charge by the application of the appropriate electric potential.

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Notes and references