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PhenTAA: A Redox-Active N₄-Macroyclic Ligand Featuring Donor and Acceptor Moieties

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ABSTRACT: Here, we present the development and characterization of the novel PhenTAA macrocycle as well as a series of [Ni(RPhenTAA)] complexes featuring two sites for ligand-centered redox-activity. These differ in the substituent R (R = H, Me, or Ph) and overall charge of the complex n (n = −2, −1, 0, +1, or +2). Electrochemical and spectroscopic techniques (CV, UV/vis−SEC, X-band EPR) reveal that all redox events of the [Ni(RPhenTAA)] complexes are ligand-based, with accessible ligand charges of −2, −1, 0, +1, and +2. The o-phenylenediamide (OPD) group functions as the electron donor, while the imine moieties act as electron acceptors. The flanking o-aminobenzaldimine groups delocalize spin density in both the oxidized and reduced ligand states. The reduced complexes have different stabilities depending on the substituent R. For R = H, dimerization occurs upon reduction, whereas for R = Me/Ph, the reduced imine groups are stabilized. This also gives electrochemical access to a [Ni(R₂PhenTAA)]²⁻ species. DFT and TD−DFT calculations corroborate these findings and further illustrate the unique donor−acceptor properties of the respective OPD and imine moieties. The novel [Ni(RPhenTAA)] complexes exhibit up to five different ligand-based oxidation states and are electrochemically stable in a range from −2.4 to +1.8 V for the Me/Ph complexes (vs Fc/Fc°).

INTRODUCTION

The release and storage of electrons are intrinsic to many metalloenzymatic transformations. The prevalence of first row transition metals in such enzymes is often accompanied by redox-active ligands to impart multielectron reactivity. Inspired by nature, redox-active ligands have gained a significant foothold in inorganic chemistry, catalysis, and material sciences. Among numerous applications, the ability and application of redox-active ligands to function as redox shuttles have allowed the synthesis of first-row transition metal complexes featuring redox-active ligands to exhibit “noble-metal like” reactivity. The unique redox properties of these ligands, coupled with their high degree of synthetic versatility, allow for unexplored stoichiometric and catalytic reactivities. Consequently, the development of new redox-active scaffolds receives considerable interest. Popular motifs are ortho-substituted heteroaromatic systems (i.e., catechol, aminophenol, or o-phenylenediamine) and delocalized π-systems (i.e., diimines). Metal complexes bearing such building blocks can exhibit several ligand-based redox events, originating from the gain (or loss) of an electron onto (or from) the heteroaromatic system.

For instance, o-phenylenediamine initially experiences a 1e⁻ oxidation to the radical o-diamoiminoquinone, followed by another 1e⁻ oxidation to the fully oxidized benzoiminoquinone (Figure 1A). These ortho-substituted heteroaromatic systems are often employed as dianionic donor moieties, whereas π-systems are used as acceptor sites (Figure 1A). While examples of such motifs in multidentate ligands are abundant, examples of conjugated, redox-active macrocycles are not, despite the coordinating power imparted by the macrocyclic effect. This phenomenon enhances the stability of metal complexes, with the macrocyclic conjugation further stabilizing the buildup of charge and/or spin density. Nevertheless, a few examples of macrocyclic redox-active ligands have been reported thus far. A prominent group of conjugated macrocyclic ligands is the porphyrinoid family, consisting primarily of aromatic porphyrins and corroles, alongside antiaromatic norcorrole ligands (Figure 1B). Electrochemical investigations revealed that these porphyrinoid ligands can access both multiply reduced and oxidized forms, especially for the...
However, the structural dependency of global (anti)aromaticity for these macrocycles also limits their synthetic versatility. Therefore, we were interested in developing a conjugated macrocyclic ligand platform that derives its redox-active capability from independent moieties, in order to deviate from the reliance on a global (anti)aromatic electronic structure. The combination of independent redox-active groups within an overall conjugated macrocyclic structure should give rise to a unique electronic structure that features greater synthetic flexibility. We envision that the development of such a versatile platform can contribute to new modes of reactivity in catalysis, development of functional materials (i.e., redox-flow batteries), and replacement of expensive noble-metal driven processes.

Based on the aforementioned ortho-substituted heteroaromatic systems as electron donors and conjugated π-systems as electron acceptors, we report the synthesis of the novel conjugated macrocyclic tetraphenylene[b,e,i,m][1,4,8,11]tetrazagenanulene, $H_2(R_{2}PhenTAA)$, featuring a diaryl-α-phenylenediamine donor and an o-diiminophenylene acceptor moiety (Figure 1C). Nickel was employed as the first-row transition metal of choice, as the anticipated square planar Ni(II)-complexes are bereft of (readily accessible) metal-centered redox events. Additionally, the R-group at the imino group C-terminus was varied to probe the redox properties and/or stability of these Ni complexes. Through a combination of spectroscopic and electrochemical techniques (CV, spectroelectrochemical UV/vis, EPR) and computational methods (DFT), we characterized the redox properties of the various $[Ni(R_{2}PhenTAA)]$ complexes and determined whether redox events are either metal- or ligand-centered.

**RESULTS AND DISCUSSION**

### Synthesis of Ligands and Nickel Complexes

$[Ni(R_{2}PhenTAA)]$ complexes were synthesized via a gram-scalable divergent synthetic approach (Scheme 1). For the archetypical R = H, the starting point was the commercially available o-nitrobenzaldehyde, which was reduced to o-aminobenzaldehyde (1a) with iron powder according to a literature procedure. To prevent self-condensation, 1a was used immediately in the next step. Compounds 2a–c (R = H, Me, Ph, respectively) were synthesized using an Ullmann−Goldberg cross-coupling reaction between o-diiodobenzene and 1a–c (1b–c are commercially available starting materials) via a modified literature procedure. Condensation of o-phenylenediamine with dicarbonyl synthons 2a–c required a different route, depending on the R-group desired. For R = H, condensation of 2a with o-phenylenediamine in combination with a stoichiometric amount of Zn(OAc)$_2$:2H$_2$O as a Lewis acid afforded $[H_2(H_2PhenTAA)]$ (3a, 90% yield) in 90% yield.
as a bright orange-red precipitate. For R = Me, the condensation of 2b with o-phenylenediamine was achieved via reflux in toluene using 3 Å molecular sieves and NaHCO₃ as a mild base to afford [H₂[Me₂PhenTAA]] (3b) in 42% yield. Compounds 4a–b were synthesized via metalation of free-base ligands 3a–b with Ni(OAc)₂·4H₂O at reflux in DMF, with subsequent crystallization/precipitation affording complexes 4a and 4b in 88% and 90% yields, respectively. All attempts to obtain 3c proved unsuccessful, rationalized by the steric bulk imparted by the additional phenyl group in the benzophenone moiety. Therefore, a direct route toward [Ni(Ph₂PhenTAA)] was employed, using nickel as a template for square-planar complex formation. Subsequently, compound 2c, o-phenylenediamine, and Ni(OAc)₂·4H₂O were heated at reflux for 7 days in xylene using a Dean–Stark apparatus. [Ni(Ph₂PhenTAA)] (4c) was isolated in 32% yield after purification.

Characterization of the Free Base Ligands. The new compounds were characterized by ¹H, ¹³C, and 2D-NMR spectroscopy, HR–ESI–MS (positive mode), and UV/vis spectroscopy. Additionally, 3a was analyzed by in situ ATR–FT–IR and melting point analysis (see Supporting Information, page 8).

Single crystal X-ray diffraction (SC–XRD) studies (Figure 2A and B) showed that these macrocyclic structures have a distinct saddle-shaped geometry, akin to the tetramethyltetra[14]azaannulene macrocycle.⁰ Bond length analysis revealed a distinct deviation from the reference standard benzene for the o-aminobenzalimine phenyl rings 2 and 3 (Table S2, Supporting Information). The C–N and C₄₋₋C₅₋₋ bonds have significant double-bond character, whereas the adjacent C₄₋₋C₅ and C₅₋₋C₆ are lengthened with respect to benzene. This suggests significant delocalization across the o-aminobenzalimine moiety (Figure 2C).

Characterization of the Nickel Complexes. Upon metalation of 3a, the distinct signal of the NH hydrogens at δ = 12.20 ppm in ¹H NMR disappears, indicative of successful metalation. The imine (δ = 8.04 vs 8.73 ppm for 4a vs 3a, respectively) and Ar–H signals (see Supporting Information, pages 60 and 65) experience a significant upfield shift. 2D-NMR and mass spectrometry further support the composition of the expected complex. The diamagnetic nature of the complex (as per its NMR spectra) indicates that the complex does not possess an open-shell character, congruent with a square planar d⁸ geometry.¹⁸ UV/vis spectroscopy on the intensely dark-purple complex revealed the appearance of two new broad visible wavelength absorptions at 497 and 627 nm.
The UV absorption at 282 nm of 3a experienced a red-shift to 301 nm for 4a, with the bands at 307 nm and 394 nm disappearing completely for 4a. In situ ATR–FT–IR spectroscopy on the complex (suspended in \( \text{C}_3\text{H}_6 \) solution) reveals a shift of the characteristic C–N and o-aminobenzaldimine stretching modes between 3a (1587 and 1446 cm\(^{-1} \)) and 4a (1573 and 1457 cm\(^{-1} \)). Notably, the disappearance of the free N–H stretching band at 1638 cm\(^{-1} \) is consistent with metalation. SC–XRD confirmed the expected square-planar geometry of 4a, adopting a half-saddle shape, with the o-diminoophenylene moiety aligned with the two o-aminobenzaldimine moieties (Figure 3). This is in stark contrast to 3a, which featured a distinct saddle-shaped geometry. The increase in planarity upon metalation rationalizes the 10-fold decrease in solubility of 4a compared to 3a (1 vs 10 mg mL\(^{-1} \) in \( \text{C}_3\text{H}_6 \) respectively). Nickel complexes 4b–c exhibit comparable NMR spectra. These NMR spectra, together with mass spectrometry, confirmed their composition and structural and spin state changes upon oxidation/reduction as well as the spin density and overall electronic structure of the \( \text{R}_3\text{PhenTAA} \) complexes. Calculations were performed using the Karlsruhe de2-TZVPP basis sets using the TURBOMOLE 7.4.1. package (see Supporting Information, pages 77–85 and pages 133–139). To rule out any bias from the functional on the spin state of the complexes, all structures were calculated using the GGA BP86, the meta-GGA M06-L, and the hybrid B3LYP functionals. All three variants (\( R = \text{H, Me, and Ph or} \) 4a–c) were calculated in five different oxidation states (−2, −1, 0, +1, and +2). For integer spin systems, the closed-shell singlet (CSS), open-shell singlet (OSS), and triplet and quintet spin states were calculated. For noninteger spin states, the doublet, quartet, and sextet spin states were calculated. To include any implicit solvent effects that may be present during experimental conditions, all electronic structures were evaluated using single-point calculations with the conductor-like screening model (COSMO). As solvents, MeTHF (\( \epsilon = 6.97 \)) and MeCN (\( \epsilon = 38.8 \)) were chosen as these were the most apolar and polar used in X-band EPR measurements (vide infra). The results are displayed in the Supporting Information, Tables S12–S17. The calculated bond distances, angles, and overall geometry are in excellent agreement with experimental SC–XRD results for the neutral complexes. All three functionals (BP86, M06-L, B3LYP) yielded identical prediction of the ground spin state with the exception of the doubly reduced \( \text{4a}^{2-} \), for which B3LYP predicts an open-shell singlet (OSS) ground state. For all other complexes, the ground state was always the lowest possible spin state (i.e., closed-shell \( S = 0 \) or doublet \( S = 1/2 \)) for 4a–c and their five oxidation states (−2 to +2). Spin density plots (Table S44, Supporting Information) reveal a similar pattern for all three nickel complexes, indicating that the overall redox properties arise as a result of the unique \( \text{R}_3\text{PhenTAA} \) scaffold.

As such, for clarity, only the data for \([\text{Ni}(\text{Me}_3\text{PhenTAA})] \) is displayed from here on (Figure 5, vide infra). Upon single electron oxidation, significant spin density develops at the diaryl-o-phenylenediamine moiety, centered largely on the two nitrogen atoms as well as the central phenyl ring. A small amount of spin density (~10%) is also present on the phenyl \( \text{Ni(d}_{xy} \) orbital. Upon single electron reduction, the opposite occurs, and spin density develops on the \( \alpha \)-imino carbon and the neighboring phenyl rings. In contrast to the oxidized forms, reduction leads to some spin density in nearly empty \( \text{Ni(d}_{x2-y2} \) orbital (~13%). Interestingly, the resonance pattern on the o-aminobenzaldimine moiety is opposite to that obtained upon oxidation, where the \( \alpha \)-spin density follows an alternating pattern. This suggests that the peripheral \( \alpha \)-aminobenzaldimine phenylene rings have a stabilizing function and delocalize spin density for both the oxidized and reduced forms. Additionally, the reduced \( \text{4c}^{2-} \) exhibits spin density on the pendant phenyl rings as well (Table S44, Supporting Information).

**TD-DFT Calculations of Neutral Ni Complexes.** Time-dependent density functional theory calculations were performed at the B3LYP/de2-TZVPP level of theory with the Tamm–Dancoff approximation using the ORCA 4.2.1 software package. The CPCMC solvation model was used in accordance with experimentally used solvents for UV/vis–SEC monitoring (vide infra) (\( \text{CH}_3\text{Cl}_2 \) for oxidized species; THF for reduced species) (see Supporting Information, pages 86–132). A frontier orbital and Löwdin population analysis for 4a–c revealed a significant amount of ligand orbitals in between the

![Figure 4](https://example.com/figure4.png)

**Figure 4.** UV/vis spectra of Ni complexes 4a–c in CH\(_2\)Cl\(_2\) (1.0 mM, 4a–c, 20 °C, air, OTTLE cell (l = 0.2 mm)).
metal d-orbitals in the overall MO diagrams (Figures S107−S109, Supporting Information). The HOMO and HOMO−1 are centered on the diamide moiety, whereas the LUMO and LUMO+1 are centered on the α-imino carbon and neighboring phenyl rings. These findings are in line with the DFT-obtained spin density plots. While these four orbitals exhibit some intermixing with metal d-orbitals, the overall wave function is dominated by the ligand. Löwdin population analysis revealed that even for the doubly reduced and oxidized complexes, the oxidation state of the metal center is unchanged and retains its initial Ni(II) state (Figure 6). The redox chemistry is centered entirely on the HOMO and LUMO of the neutral complex and changes in the overall wave function of the frontier orbitals is negligible. The relative order of the d-orbitals also does not change upon reduction or oxidation, with the exception of the virtually degenerate d_{xz}−d_{yz} pair. TD−DFT calculations were performed with 100 roots to further elucidate the UV/vis spectra of Ni complexes 4a−c. The obtained spectra of the neutral complexes show that the excitations are dominated by ligand → ligand excitations.

Features II, III, and IV correspond to the same excitations for all three Ni complexes (Figure 7), whereas I is more affected by R group substitution (see Supporting Information, pages 90−92 (R = H); pages 106−108 (R = Me); pages 123−125 (R = Ph)). Feature II corresponds to an excitation from the HOMO to a high-lying orbital with global quinoidal character.

Feature III predominantly conforms to the HOMO → LUMO+1 excitation, and feature IV conforms to the HOMO → LUMO and HOMO−1 → LUMO excitations. As is evident from the MO scheme in Figure 6, the excitations for features III−IV correspond to excitations from the donor diaryl-α-phenylenediamine moiety to the acceptor diimino moiety (Figure 7), revealing a unique donor → acceptor relationship for the R₂PhenTAA macrocycle. These computational findings

Scheme 2. Schematic Representation of the Proposed Five Oxidation States of [Ni(R₂PhenTAA)] Complexes from Doubly Reduced to Doubly Oxidized (−2 to +2) (R = H, Me, Ph for 4a, 4b, and 4c, Respectively)

Figure 5. Spin density plots for (a) the singly oxidized (4b^1+) and (b) the singly reduced (4b^1−) forms of complex [Ni(Me₂PhenTAA)] (4b). α-spin density (purple); β-spin density (yellow). Isosurface value = 0.04. Calculated at the BP86/def2-TZVP level of theory.

Figure 6. Molecular orbital diagram for the oxidation states of [Ni(Me₂PhenTAA)] (4b) calculated with TD−DFT at the B3LYP/def2-TZVPP/CPCMC (CH₂Cl₂) level of theory using 100 roots. Visualized selected Hartree−Fock orbitals (left) for the neutral 4b form are representative for all other oxidation states. Metal d-orbitals shown in gray (from high- to low-energy: d_{x^2−y^2}, d_{z^2}, d_{xz} ≈ d_{xy}, d_{yz}) and color-coded selected ligand orbitals (L₁−L₄) were assigned via visual inspection and Löwdin population analysis.

Figure 7. Features II, III, and IV correspond to the same excitations for all three Ni complexes (Figure 7), whereas I is more affected by R group substitution (see Supporting Information, pages 90−92 (R = H); pages 106−108 (R = Me); pages 123−125 (R = Ph)). Feature II corresponds to an excitation from the HOMO to a high-lying orbital with global quinoidal character.

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show much promise for the potential redox-active nature of the R$_2$PhenTAA scaffold.

**Electrochemical Studies.** Having studied the [Ni-(R$_2$PhenTAA)] complexes computationally, we sought to corroborate the results experimentally via cyclic voltammetry (CV). To study any solvent effects and have a large voltaic window, measurements were conducted in CH$_2$Cl$_2$ and THF (Figure 8). The values for every redox event are noted in Table 1 (vs Fc/Fc$^+$. The three complexes 4a–c exhibit comparable voltammograms in CH$_2$Cl$_2$ and THF, and the oxidative

![Figure 7. Orbitals involved in the predominant excitations for features I–IV (A). Experimental (black) and simulated (red) spectra for complexes 4a–c with features I–IV labeled. The relative energy and oscillator strength of each excitation are represented in red bars and were fitted to the experimental spectra (B).](image1)

![Figure 8. Cyclic voltammograms of complexes 4a–c in CH$_2$Cl$_2$ and THF. Measurements were performed at 200 mV s$^{-1}$ at room temperature in a 0.1 M TBAPF$_6$ solution. WE = glassy carbon, CE = Pt wire; RE = Ag/AgCl (3.5 M KCl). All scans were collected within the accessible solvent windows. Potentials are reported vs Fc/Fc$^+$.](image2)

<table>
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<th>Table 1. All Redox Events for [Ni]-Complexes 4a–c Based on Differential Pulse Voltammetry$^b$</th>
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$^a$Based on CV due to overlap of solvent oxidation/reduction. $^b$Voltages reported versus Fc/Fc$^+$.  

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stability of CH₂Cl₂ and reductive stability of THF allow us to scan an electrochemical window from −2.4 V to +1.8 V (vs Fc/Fc⁺). When scanning to positive voltages, two electrochemically reversible waves are observed. These are assigned to ligand-based redox events.

Based on related nickel o-phenylenediamine complexes, these are assigned to the o-diaminodiquinone and benzodiaminoquinone forms, respectively (Scheme 2). For 4b–c, a third oxidative wave is detected in CH₂Cl₂ at high positive voltages (+1.3–1.6 V). Based on literature reports, this wave is assigned to the Ni(II)/Ni(III) redox couple. The Ni(II)/Ni(III) wave was absent for 4a since at these voltages, significant degradation occurred at the working electrode.

A different picture arises when scanning to negative voltages. For the archetypical [Ni(H₂PhenTAA)] (4a) complex, an electrochemically irreversible event is detected at −1.9 V, with a large peak separation of 770 mV at a 200 mV s⁻¹ scan rate. Increasing the scan rate led to more narrow peak separation, indicative of an EC mechanism, i.e., reversible electron transfer followed by a reversible chemical step. As shown computationally (vide supra), this is most likely a ligand-centered reduction of the α-iminocarbon. The electrochemically irreversible nature is presumably due to reversible chemical dimerization of the two ligand radical species (Figure 9), as this is also observed for [Ni(Salphen)] complexes.

Moreover, a metal-centered Ni(II)/Ni(I) redox couple is excluded on the basis of literature reports, as these tend to occur at even more negative voltages. The ketimine based complexes (R = Me/Ph) 4b–c exhibit contrasting electrochemical properties, featuring a fully electrochemically reversible reduction. This behavior is consistent with the hypothesis of dimerization occurring at the α-imino carbon, as the electrogenerated radical experiences enhanced steric and electronic stability at this carbon (Figure 9). Cyclic voltammetry on 4b–c in THF was possible down to −2.4 V vs Fc/Fc⁺, revealing another reduction at −2.16 V (4b) and −2.25 V (4c). This additional wave is not electrochemically reversible and gives rise to an additional, smaller wave at −0.33 V (4b) and −0.47 V (4c). At higher scan rates, the cathodic current of this second reduction increases relatively to the anodic current, and an EC mechanism is assigned to this redox event. Based on computational data, this is assigned to a second ligand-based reduction of the remaining imine position to yield a tetraanionic R₂PhenTAA ligand (Scheme 2).

**Spectroelectrochemistry.** UV/vis-spectroelectrochemical measurements (UV/vis–SEC) were performed to gather more information on the redox chemistry of nickel complexes 4a–c and to assign the ligand/metal oxidation states. The spectral changes are listed in Table S6 and visualized in Figure 10. At 0 V (vs Ag wire), all species revealed the same spectrum as with the cell turned off in both THF and CH₂Cl₂. This confirms that the CV assignments with respect to reduction or oxidation are correct. Overall, the UV/vis–SEC measurements corroborate the results observed with CV with four different detectable species for 4a (one reduced and two oxidized species) and five for 4b–c (two reduced and two oxidized species). The most discernible spectral changes occur upon the first oxidation or reduction for all three complexes, with the second oxidation or reduction resulting in only minor spectral perturbations. This suggests that departure from the diatomic form of the R₂PhenTAA macrocycle induces the strongest change in the overall excitations, which applies to both reduction and oxidation of the ligand. This observation is in line with the results of the TD–DFT calculations, which indicate that the electronic excitations are dominated by donation from the diaryl-o-phenylenediamine moiety to the...
acceptor diimino moiety. The first oxidation of the donor moiety (or reduction of the acceptor) is expected to strongly perturb the intramolecular donor → acceptor process, manifested by dramatic changes in the UV/vis spectrum. Additional oxidation or reduction leads to a further departure from the already disturbed donor → acceptor relationship, giving rise to a minor change to the overall spectrum. Reduction of the Ni complexes produces a clear difference for 4a vs 4b−c, in line with CV measurements. Going from 4a to (4a)−2 (see Figure 10), two main features for 4a (III and IV) broaden into several large features at 519, 579, and 733 nm with III. For 4b−c, features III and IV only slightly shift to longer wavelengths but do not broaden as much. Therefore, these two features are likely strongly affected by changes on the α-iminocarbon.

In line with with TD–DFT calculations, these features III and IV match excitations from the donor diaryl-o-phenyl-enediamine moiety to the acceptor diimino moiety and reduction of the diimino moiety is expected to strongly affect such excitations. Upon oxidation, the three complexes all gain a new broad feature at around 360 nm (feature V) that is present for both the singly and doubly oxidized complexes. For the defining features III and IV, a distinct difference between 4a and 4b−c is again present. For the first oxidation, feature III sharpens and is red-shifted for 4a, whereas for 4b−c, it decreases in intensity but does not shift. Feature IV collapses into the baseline for 4a but is broadened and blue-shifted for 4b−c. For the second oxidation to the benzoiminoquinone state, both features III and IV collapse almost entirely into the baseline for all three complexes. This spectral difference between 4a and 4b−c is attributed to the geometric difference of the complexes as per XRD of the neutral complexes and DFT studies of the reduced and oxidized complexes (vide supra). The collapse of features III and IV for all three complexes in their doubly oxidized form can be attributed to the absence of electrons in the HOMO of the neutral parent complexes.

**TD–DFT Calculations of the Oxidized and Reduced Ni Complexes.** To acquire more insight into these spectral changes and correlate them to the proposed computed states, TD–DFT calculations were performed for all five oxidation states and varying spin states using the same parameters as for the neutral complexes (vide supra). For integer spin states, the closed-shell singlet (CSS), triplet, and quintet states were calculated. For noninteger spin states, the doublet, quartet, and sextet spin states were calculated. In all cases, the best match was obtained for the low-spin states, in line with the ground state DFT calculations. For clarity, the 4b redox series and the orbital transitions are visualized here (Figure 11). The 4a and 4c series can be found in the Supporting Information (pages 90−132). Feature I cannot be assigned to a single, dominant transition and is composed of several excitations for all three
complexes in all oxidation states. These often involve excitation from either a very low-lying orbital to the LUMO/LUMO+1 or from the HOMO/HOMO−1 to a high energy vacant orbital.

The other features are highly dependent on the overall ligand oxidation state but are quite similar for all three Ni complexes with the same oxidation state. In both the singly reduced and neutral form, this changes to a transition of the diaryl-o-phenylenediamine site to a global quinoidal structure. In the oxidized forms, feature II primarily consists of a π → π* transition of the diimino moiety. Features III and IV, as with the neutral complexes, correspond largely to excitations within the four frontier orbitals described in Figure 6. Exceptions are the doubly reduced complexes (4b−2−4c−2), because these show excitation from the quinoidal HOMO to higher lying global π* antibonding states. Likewise, the doubly oxidized complexes do not have a defined feature IV, and the still present feature III now reveals a reversed donor → acceptor relationship, with excitations occurring mainly from the diimino moiety to the benzoiminosemiquinone moiety.

Feature V, a feature not present for the neutral complexes, but visible for both the reduced and oxidized forms, corresponds mainly to excitations from the acceptor diimino moiety to higher lying π* antibonding states. Changing the oxidation state from −2 to +2 only shifts the starting donor orbital, still centered on the diimino moiety, to a lower energy.

X-Band EPR Spectroscopy. Seeking additional experimental evidence for the ligand-based nature of the redox events for R₆PhenTAA complexes 4a−c, we turned to X-band EPR spectroscopy. Anisotropic spectra recorded in frozen solutions (40−80K) are shown in Figure 12, and the obtained simulated data are reported in Table 2. Isotropic spectra recorded at RT are shown in the Supporting Information (Figures S35−S40). Chemical reductions were performed using 1 eq. of freshly produced sodium anthracenide solution in 2-MeTHF. Chemical oxidation was achieved using 1 eq. of a solution of freshly prepared thianthrenium tetrafluoroborate (ThiBF₄) in CH₂Cl₂. Reduction of 4a gave a faint and rapidly diminishing signal at RT in 2-MeTHF with a signal at giso = 2.0026, in line with a transient ligand radical. A follow-up ¹H NMR measurement of this sample revealed the formation of a new diamagnetic species that does not correspond to the neutral complex 4a. This conforms to the hypothesis that upon reduction, the radical 4a−1 dimerizes into a diamagnetic species. Freeze quenching of 4a−1 gave an axial anisotropic spectrum at 80 K void of any hyperfine interactions (HFIs) (g₁₁ = g₂₂ = 2.0043; g₃₃ = 2.1047) (Figure 12). These values correspond to a metastable ligand radical. The g-value at 2.10 suggests spin−orbit coupling involving the SOMO interacting with an empty orbital close in energy.

Reduction of 4b and 4c at RT gave a broad and stable signal at giso = 2.0223 and giso = 2.0380, respectively, in line with ligand radical species. Interestingly, the isotropic spectrum of

![Figure 12. Anisotropic X-band EPR spectra obtained after reduction of Ni complexes 4a−c with sodium anthracenide in 2-MeTHF (top) or oxidation with thianthrenium tetrafluoroborate in CH₂Cl₂:MeCN (1:1 v/v) (bottom). For experimental details, see Supporting Information, page 36.](image-url)

| Table 2. Simulated g-Values of Singly Reduced/Oxidized Complexes 4a−c Derived from X-Band EPR Spectroscopy Measurements at 40−80 K |
|-----------------|-----------------|-----------------|-----------------|
|                 | 4a              | 4b              | 4c              |
|                 | g₁₁  | g₂₂  | g₃₃  | g₁₁  | g₂₂  | g₃₃  | g₁₁  | g₂₂  | g₃₃  |
| Reduction       |      |      |      |      |      |      |      |      |      |
| Species 1       | 2.0013 | 2.0064 | 2.1043 | 2.0010 | 2.0061 | 2.1040 | 2.0149 | 2.0050 | 2.0868 |
| Species 2       | 2.0074 | 1.9963 | 2.0844 | 1.9947 | 2.0071 | 2.0853 |
| Species 3       | 1.9864 | 2.0061 | 2.0625 |          |      |      |
| Oxidation       |      |      |      |      |      |      |      |      |      |
| Species 1       | 2.0104 | 2.0140 | 1.9789 | 1.9580 | 2.0044 | 2.0148 | 1.9855 | 2.0133 | 2.0146 |
| Species 2       | 1.9867 | 2.0153 | 2.0243 | 1.9766 | 2.0034 | 2.0036 |
4b1− features an apparent large hyperfine interaction with a single (apparently I = 3/2) nucleus. Due to all hydrogen atoms occurring at least twice (due to symmetry) and because naturally occurring nickel isotopes do not have a nuclear spin, this could only be simulated by including hyperfine coupling with a single 23Na atom. Apparently, sodium ions introduced together with the reducing agent bind to 4b1−. Anisotropic spectra were obtained after freeze quenching, and measurement at 80 K revealed a mostly axial spectrum, similar to that of 4a1−. However, for 4b1−, the feature at high g-values corresponds to three different species. As with the isotropic room temperature spectrum, this is attributed to various coordination modes of the sodium counterion. Interestingly, this is not observed for 4c1−, which shows a rhombic spectrum at higher g-value (g11 = 2.0149; g22 = 2.0050; g33 = 2.0868), void of HFIs. For both 4b and 4c, this is in accordance with a ligand radical.

Oxidation of 4a−c with ThiBF4 afforded clean, stable isotropic spectra for all three complexes (4a: giso = 1.9994; 4b: giso = 1.9991 and 4c: giso = 2.0004). Their g-values are again in line with ligand radical species. Addition of a CH3Cl solution of ThiBF4 to an equimolar solution of 4a−c in MeCN, followed by freeze quenching and subsequent measurement with X-band EPR, revealed a slightly rhombic EPR spectrum for 4a1+ (g11 = 2.0104; g22 = 2.0140; g33 = 1.9789) measured at 40 K. As with reduced 4b, oxidation of 4b to 4b1+ gave a rhombic spectrum that featured several additional small hyperfine interactions. In line with CV measurements in THF (another coordinating solvent), this is attributed to coordination of the now cationic 4b+1 with acetonitrile, resulting in several different solvent adducts (Species 1: g11 = 1.9580; g22 = 2.0044; g33 = 2.0148 (weight = 0.50). Species 2: g11 = 1.9867; g22 = 2.0153; g33 = 2.0243 (weight = 0.50) (A14N1)1=11 = 32.1603 MHz; A14N12 = 0 MHz; A14N13 = 0 MHz (A14N2)1 = 25 MHz; A14N22 = 0 MHz; A14N23 = 0 MHz). A similar coordination effect may be present for 4c1+, although a rhombic spectrum void of HFIs was obtained (Species 1: g11 = 1.9855; g22 = 2.0131; g33 = 2.0146 (weight = 0.63). Species 2: g11 = 1.9666; g22 = 2.0034; g33 = 2.0036 (weight = 0.37)). These g-values correspond to ligand-centered radicals, analogous to the room-temperature spectra. All the EPR spectra gave signals that correspond to a doublet spin state (S = 1/2). These findings are in line with the UV/vis−SEC measurements and the computational results from DFT and TD−DFT analysis.

**EXPERIMENTAL SECTION**

**General Considerations.** All reactions were carried out under argon using standard Schlenk techniques or under an inert atmosphere in a N2-filled glovebox, unless noted otherwise. All chemicals were of commercial grade and used without further purification, unless noted otherwise. All solvents used were predried using either a Solvent Purification System (SPS) from MBraun (MB SPS-800, with standard MBraun drying columns) or were dried and distilled from sodium (PhMe/pentane), sodium/benzophenone (THF/EtOH) or CaH2 (CH3Cl, MeOH). All solvents were further dried/stored on activated 3 Å molecular sieves and degassed by sparging with argon unless mentioned otherwise. Additional information regarding NMR, EPR, HRMS, UV/vis, CV, XRD, and spectroelectrochemical measurements can be found in the Supporting Information.

**Synthesis and Characterization of Ligands. Synthesis of 2-Amino benzaldehyde (1a).** Compound 1a was prepared according to a modified literature procedure. To a 1 L round-bottom flask was added Fe (55.85 g, 1 mol), 2-nitrobenzaldehyde (15.11 g, 0.1 mol), 300 mL of absolute EtOH, and 75 mL of H2O. This mixture was bubbled through with Ar for 10 min after which HCl (0.75 mL; 37%) was added. The mixture was brought to reflux under Ar for 14 h. After cooling down, the mixture was filtered via Celite and washed with EtOH. The filtrate was concentrated in vacuo, subsequently extracted with CH3Cl/H2O, washed with brine, dried with Na2SO4, filtered over cotton, and evaporated in vacuo until a yellow oil remained. Next, the crude product was purified via column chromatography (CH2Cl2). The pure fractions were identified via TLC (1a Rf = 0.2) and evaporated in vacuo. Yield: 10 g (83%). 1H NMR (400 MHz, DMSO-d6): δ 9.81 (s, 1H, CHO), 7.51 (d, 1H, o-ArH), 7.50 (t, 1H, o-ArH), 7.10 (s, 2H, o-NH2), 6.76 (d, 1H, o-ArH), 6.63 (t, 1H, o-ArH) (Figure S59).

**General Procedure A for Dicarbonyl Building Blocks 2a−2c. n-BuO (200 mL) was filtered over activated basic alumina. To this was added o-diiodobenzene (1 equiv) and aniline (2.2 equiv). To a separate 1 L Schlenk flask was added 500 mesh Cu powder (20 mol %), CuI (2 mol %), and K2CO3 (4 equiv). To this Schlenk flask the n-BuO solution was added, and this mixture was brought to reflux for 6 days. After cooling, the salts were filtered off over a short silica plug and washed with CH3Cl until the effluent was colorless, and the solvent was removed in vacuo. The crude mixture was then recrystallized from CH2Cl2/pentane or purified via column chromatography (CH2Cl2/petroleum ether (40−60) gradient).

**Synthesis of N,N′-1,2-Phenyldiaminomino-bis(2-amino benzaldehyde) (2a).** The reaction was performed according to general procedure A (see above) on a 37.5 mmol scale. The product was isolated after column chromatography (CH3Cl/petroleum ether (40−60) gradient). Gradient: 50% CH3Cl/PE (fractions 1−30); 75% CH3Cl/PE (fractions 31−50); 100% CH3Cl/PE (fractions 51−80); 25% EtOAc/75% CH3Cl (fractions 81−all color eluted). The first fraction is the monocoordinated product (Rf = 0.9), the second fraction is compound 2a (Rf = 0.6), and the final fraction is the 2-amino benzaldehyde starting material (Rf = 0.2). The pure fractions were identified via TLC and evaporated in vacuo. Yield: 6.64 g (56%).
the mixture was stirred at reflux for 10 days, during which the color gradually changed to dark brown. The salts and molecular sieves were filtered off aerobically over Celite and washed with dichloromethane, and the solvents were removed in vacuo. The residue was recrystallized from CH₂Cl₂/pentane at −20 °C for 3 h. The tan-yellow crystalline needles were filtered off and washed with pentane (∼300 ml). Yields: 892 mg (42%). ¹H NMR (400 MHz, CDCl₃): δ 12.07 (s, broad, 2H, NH), 7.69 (dd, ³JHH = 6.5 Hz, ³JHH = 1.5 Hz, 2H, NH-CH₃), 7.67 (dd, ³JHH = 7.0 Hz, ³JHH = 3.6 Hz, 2H, o-CH), 7.39 (dd, ³JHH = 8.5 Hz, ³JHH = 0.9 Hz, 2H, o-CH), 7.22 (dd, ³JHH = 6.9 Hz, ³JHH = 1.3 Hz, 2H, m-CH), 7.18 (dd, ³JHH = 6.0 Hz, ³JHH = 3.3 Hz, 2H, o-CH), 7.15 (dd, ³JHH = 6.0 Hz, ³JHH = 3.5 Hz, 2H, m-CH), 6.96 (dt, ³JHH = 9.2 Hz, ³JHH = 3.3 Hz, 2H, m-CH), 6.73 (dd, ³JHH = 7.6 Hz, ³JHH = 1.2 Hz, 2H, m-CH), 2.41 (s, 6H, CH₃) (Figure S8a). ¹C NMR (101 MHz, CDCl₃): δ 168.66 (2C, N-C), 147.39 (2c, ipso-C), 141.01 (2c, ipso-C), 135.07 (2c, ipso-C), 131.99 (2c, m-C), 131.47 (2c, m-C), 126.01 (2c, o-C), 124.91 (2c, o-C), 124.08 (2c, m-C), 121.62 (2c, m-C), 119.40 (2c, ipso-C), 116.70 (2c, m-C), 112.31 (2c, o-C), 19.10 (2c, CH₃) (Figure S8b). UV/vis (nm (ε)): 233 (50666), 265 (38000), 306 (24666), 365 (13333). HRMS: m/z = 309.1492, m/z = 415.1927. ³b* (z = 1) calc. 415.1923.

**Synthesis and Characterization of Complexes. General Procedure B for the Metatation of Free Bases 3a and 3b.** Free base ligand (1 equiv) and Ni(OAc)₂·H₂O (2 equiv) were added to a Schlenk flask. To this mixture was added DMF (40–45 ml). The reaction was brought to reflux under Ar for 16 h, after which the reaction was cooled, and the solvent was removed in vacuo. The residue was redissolved in CH₂Cl₂, filtered over cotton, and washed three times with water. The organic layer was then washed with brine and subsequently dried with Na₂SO₄. The Na₂SO₄ was filtered off, and the solution was concentrated in vacuo. The product was obtained after recrystallization from CH₂Cl₂/pentane.

**Synthesis of Ni₃(H₄Ph₃PentAA) (4a).** The reaction was performed according to general procedure A (see above) on a 0.649 mmol scale. Yield: 255.5 mg (88%). ¹H NMR (500 MHz, CDCl₃): δ 8.01 (s, 2H, N = CH), 7.80 (d, ³JHH = 8.9 Hz, 2H, o-CH), 7.58 (dd, ³JHH = 6.0 Hz, ³JHH = 3.3 Hz, 2H, m-CH), 7.40 (dd, ³JHH = 6.1 Hz, ³JHH = 3.3 Hz, 2H, o-CH), 7.32 (d, ³JHH = 7.9 Hz, 2H, o-CH), 7.16 (dt, ³JHH = 9.2 Hz, ³JHH = 1.2 Hz, 2H, m-CH), 7.05 (dd, ³JHH = 6.2 Hz, ³JHH = 3.3 Hz, 2H, o-CH), 6.57 (dd, ³JHH = 3.4 Hz, 3.4 Hz, 2H, m-CH), 6.55 (t, ³JHH = 6.7 Hz, 2H, m-CH) (Figure S8c). ¹C NMR (126 CDCl₃) δ 150.31 (2c, N = CH), 149.83 (2c, ipso-C), 147.82 (2c, ipso-C), 145.17 (2c, ipso-C), 135.39 (2c, o-C), 133.19 (2c, m-C), 127.80 (2c, m-C), 127.75 (2c, m-C), 120.07 (2c, o-C), 119.38 (2c, o-C), 117.33 (2c, m-C), 116.39 (2c, m-C), 115.26 (2c, o-C) (Figure S7f). ¹N NMR (51 CDCl₃): 189 (2N, N=CH) (Figure S91). HRMS: m/z = 448.0895. 4a* (z = 1) calc. 448.0885.

**Synthesis of Ni₃(Me₃PentAA) (4b).** The reaction was performed according to general procedure A (see above) on a 0.484 mmol scale. Yield: 204 mg (90%). ¹H NMR (400 MHz, CDCl₃): δ 7.57–7.55 (2H, o-CH), 7.55–7.51 (2H, o-CH), 7.27 (dt, ³JHH = 9.4 Hz, ³JHH = 3.4 Hz, 2H, m-CH), 6.97 (dd, ³JHH = 9.2 Hz, ³JHH = 6.6 Hz, 2H, o-CH), 6.82 (m, 2H, m-CH), 6.92–6.86 (m, 2H, m-CH), 6.86–6.80 (m, 2H, m-CH), 6.60 (t, ³JHH = 6.1 Hz, ³JHH = 3.4 Hz, 2H, m-CH), 6.35 (t, ³JHH = 7.5 Hz, 2H, m-CH), 2.52 (s, 6H, CH₃) (Figure S92). ¹C NMR (101 CDCl₃): δ 162.72 (2C, N = CH), 148.76 (2C, ipso-C), 148.20 (2C, ipso-C), 147.75 (2c, ipso-C), 132.05 (2c, o-C), 132.02 (2c, m-C), 126.07 (2c, m-C), 125.83 (2c, ipso-C), 127.75 (2c, m-C), 116.93 (2c, m-C), 118.36 (2c, o-C), 118.02 (2c, o-C), 117.45 (2c, m-C), 20.16 (2C, CH₃) (Figure S93). ¹N NMR (41 CDCl₃, CDCl₃): 187 (2N, N=CH) (Figure S97). HRMS: m/z = 472.1201. 4b* (z = 1) calc. 472.1198.

**Synthesis of Ni₃(Ph₃PentAA) (4c).** Compound 2c (1000 mg, 2.13 mmol), o-phenylenediamine (230.5 mg, 2.13 mmol), and Ni(OAc)₂·H₂O (531 mg, 2.13 mmol) were added to a Schlenk flask. To this was added xylene (30 ml), which was connected with a Dean–Stark trap. The trap was filled with 11.5 ml of xylene to the top, and the
apparatus was connected to the reaction flask under Ar. The mixture was refluxed vigorously for 7 days, after which it was cooled down, and the solvent removed in vacuo. The dark black-purple residue was redissolved in CH₂Cl₂/petroleum ether (40:60) (1:1 v/v) and passed over a short silica plug. The first fraction is the product (Rₛ = 0.8 (CH₂Cl₂)), the second fraction is compound 2c (Rₛ = 0.3 (CH₂Cl₂)), and an unidentified greyish spot remains on the baseline. The first fraction was evaporated in vacuo and recrystallized from CH₂Cl₂/MeOH. Yield: 403.5 mg (32%).

Accession Codes

CCDC 2277307–2277310 and 2300376 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c03708.

Experimental details; synthetic procedures; EPR, NMR, UV–Vis, in-situ ATR–FT–IR and ESI–MS spectroscopic data as well as DFT calculations. Crystallographic details for CCDC 2277309 (2a), 2277308 (2c), 2277307 (3a), 2300376 (4a), and 2277310 (4c) (PDF)

Notes

The authors declare no competing financial interest.

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