An unsymmetric ligand framework for non-coupled homo- and heterobimetallic complexes.

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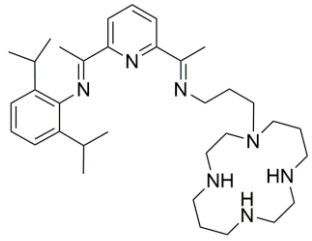
Supporting Information Placeholder

ABSTRACT: We herein introduce a new unsymmetric ligand, PDIpCY, that offers two distinct, non-coupled coordination sites. A series of homo- and hetero-bimetallic complexes, $[Zn_2(PDIpCy)(THF)(OTf)_4]$ (**1**), $[Ni_2(PDIpCy)(THF)(OTf)_2](OTf)_2$ (**2**), and $[NiZn(PDIpCy)(THF)(OTf)_4]$ (**3**), are described. The compounds were structurally characterised and their redox properties were examined. The PDI unit of the ligand supports a number of ligand-centered redox processes. The one-electron reduced bimetallic compounds, $[Zn_2(PDIpCy)(OTF)_3]$ (**4**), $[Ni_2(PDIpCy)(OTf)](OTf)_2$ (**5**), and $[NiZn(PDIpCy)(OTf)_3]$ (**6**), were successfully isolated, and their electronic structures verified by absorption and EPR spectroscopy. The reduced compounds are charge-separated species, with electron storage at either the PDI ligand (**4**) or at the PDI-bound metal ion (**5**, **6**).

An impressive assortment of multi-nuclear complexes has been reported over the years, the synthesis of which frequently was motivated by multi-electron reaction targets (e.g. O_2, N_2 activation). Multi-metallic compounds may be ideally suited for chemistry involving manifold redox processes, as such systems offer a wider range of redox states and a more varied coordination environment than a single metal ion. Cooperative interactions between the metal centers also can be beneficial for reactivity. Indeed, the enzymes that catalyze small molecule reactions commonly employ multiple metal cofactors, and both of the aforementioned effects are key to the reactivity of the biological active sites.[1] Consequently, numerous biomimetic homo- and hetero-nuclear complexes have been synthesized in particular.[1b, 2]

A number of contemporary molecular design strategies have focused specifically on the assembly of varying combinations of metal ions that each adopt distinct coordination environments and functions. Notable examples include the growing series of M-M bonded complexes, which feature modular combinations of early to late transition metal ions and main group elements, encapsulated within a single ligand scaffold.[3] A number of unique unsymmetric ligands also have been synthesized, that support a neighbouring arrangement of two different transition metal ions via coupled M-Y-M motifs.[4] Multinuclear complexes that pair transition metal centers with alkali metal, alkaline earth elements or lanthanide binding sites – again, mainly via M-Y-M bridging motifs – also have become more abundant.[5] Such platforms with distinct metal binding sites offer advantages for reactivity.[5b, 5d, 6]

As part of our own efforts to generate complexes for multi-electron reactions, we now have synthesized a new ligand scaffold, PDIpCy (Scheme 1), that provides a platform for unsymmetric bimetallic compounds. The molecule contains two discrete coordination sites furnished by pyridyldiimine (PDI) and tetraazadecane (cyclam; Cy) groups, separated by a flexible propyl linker. A related PDI-based ligand tethered to a crown ether unit for coordination of alkali metals was previously reported by Delgado et al.[5c] PDIpCy, however, was generated with the aim of binding transition metal ions at both coordination sites, and the potential to support redox reactivity at both centers; coordination complexes of each ligand type are well known.[7] and have demonstrated promise for reactions that include CO_2 reduction, H_2 evolution and olefin epoxidation.[8] PDIpCy offers a framework for *non-coupled* binuclear centers, in contrast to the aforementioned M–M and M-Y-M motifs. We envisioned that the motif would allow each metal center to individually be tuned both with respect to electronic properties and function. An additional feature of the PDIpCy ligand is the redox-active PDI group. The non-innocent unit can supply up to four electrons, independent of the coordinated metal. The combination of redox-active and -innocent ligands may permit charge-localization, enabling the formation of formal mixed valent compounds via ligand-centered reduction. We herein describe the first homo- and hetero-bimetallic Zn- and Ni-PDIpCy complexes, which provide initial insight into the coordination chemistry and redox properties of our new multidentate ligand.



PDIpCy

Scheme 1. The unsymmetric ligand PDIpCy

PDIpCy was synthesized *via* two consecutive condensation reactions of 2,6-diacetylpyridine with 2,6-di*iso*propylaniline[9] and 3-(1,4,8,11-tetraazacyclotetradecan-1-yl)propan-1-amine, respectively (Scheme S1). The latter N_4-macrocyclic precursor was obtained by a Michael addition of acrylonitrile to cyclam, followed by reduction of the nitrile group using Raney nickel. Only 70% conversion to product was achieved in the final reaction step,

however, the target ligand was cleanly isolated upon recrystallization from acetonitrile at low temperatures (−30°C). The ^{1}H NMR spectrum of PDIpCy (Figure S11) was assigned using additional data from ^{13}C, COSY, HSQC and HMBC NMR measurements (Figures S12 – S15). Nearly all of the individual proton signals could be assigned, with the exception of the methylene protons of the cyclam group, most of which are encompassed by a broad multiplet at 2.50 – 2.78 ppm.

The bimetallic complexes were subsequently synthesized upon addition of $M(OTf)_2$ salts to PDIpCy (Scheme S2). The synthesis of the dizinc compound, $[Zn_2(PDIpCy)(THF)(OTf)_4]$ (**1**), proceeded at room temperature, whereas the coordination of nickel to generate $[Ni_2(PDIpCy)(THF)(OTf)_2](OTf)_2$ (**2**) required heating of the reaction mixture (80 °C). The heterobimetallic complex $[NiZn(PDIpCy)(THF)(OTf)_4]$ (**3**) was obtained by simultaneous addition of one equiv. of each $M(OTf)_2$ salt to the ligand in EtOH. The formation of the heterobimetallic complex was confirmed by mass spectrometry (MS, Figure S29 and S30). We also examined mixtures of **1** and **2**, to see whether exchange of the metal ions, and formation of **3**, can occur under various conditions (Figures S31 and S32). Metal ion exchange was not observed for mixtures of the homobimetallic complexes in MeCN at room temperature, as verified by MS. However, formation of the heterobimetallic species does occur upon heating of an MeCN solution (60 °C), as well as in MeOH (rt and 60 °C).

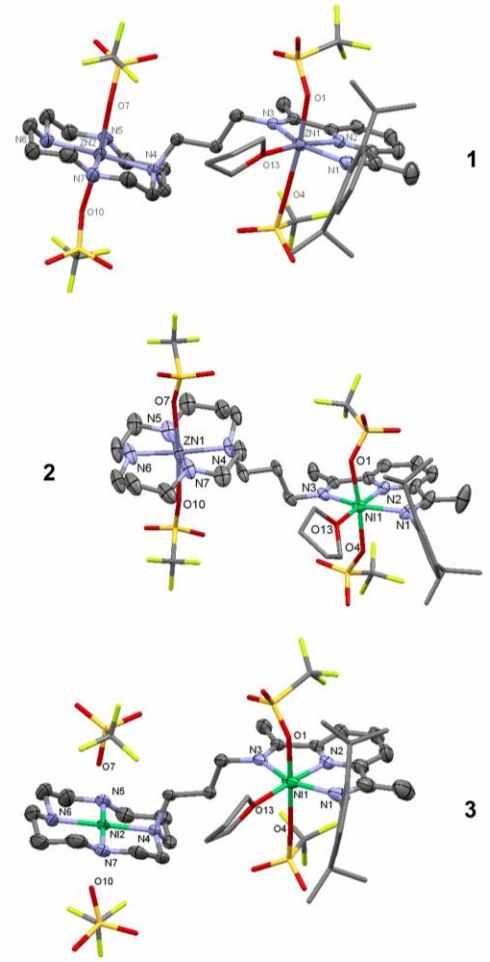


Figure 1. Molecular structures of **1** – **3** (50% probability ellipsoids). Hydrogen and solvent molecules are omitted for clarity.

Figure 1 depicts the molecular structures of all three binuclear compounds (see Table S1 – S2 for crystallographic information). The metal centers of **1** – **3** are separated by ca. 8 Å. Both Zn ions of **1** adopt a six-coordinate tetragonal geometry. The N-atoms of the cyclam and PDI units form the equatorial plane of each site, with an additional THF molecule coordinated to Zn_{PDI}. Two triflate anions also are coordinated to each metal ion ($Zn_{PDI}\cdots O_{avg}$ ~ 2.16 Å; $Zn_{Cy}\cdots O_{avg}$ ~ 2.32 Å) in a *trans*-arrangement. The dinickel compound is structurally similar to **1**. However, the triflate ions localized near the cyclam unit are only weakly associated with the Ni^{II} ion ($Ni_{Cy}\cdots O_{avg}$ ~ 2.7 Å), such that the geometry of Ni_{Cy} is effectively square planar. The bond lengths of all Ni–N bonds of **2** are shorter than the analogous Zn–N distances, as expected given the smaller ionic radius of the Zn^{II} ion. The bond distances are in agreement with literature values for related mononuclear PDI and cyclam compounds.[10] The molecular structure of **3** highlights preferred coordination of the Ni^{II} ion to the PDI site, whereas the N_4-macrocycle is occupied by the zinc atom. As in **1** and **2**, the chiral cyclam adopts the R,S,S,R configuration. The macrocyclic unit is situated 'above' the plane of the M-PDI moiety, in contrast to its orientation in the homobimetallic structures.

The solution ^{1}H NMR spectrum of the diamagnetic **1** (Figure S16) shows a slight upfield shift of all proton resonances, vs. the corresponding signals of the PDIpCy spectrum, due to the presence of the dicationic metal centers. Two distinct signals are observed for H_9 and H_{18}, and several other resonances exhibit more complex splitting patterns, indicating an overall loss of symmetry upon coordination of the zinc ions. A signal for the coordinated THF molecule, as seen in the solid state structure, is not observed in the NMR spectrum. The solvent molecule appears to be highly labile. Compounds **2** and **3** are paramagnetic. Evans magnetic susceptibility measurements yielded a magnetic moment of 3.2 μ_B for both compounds. The value is consistent with an S = 1 Ni^{II} ion in the PDI site, alongside a diamagnetic M^{II}_{Cy} center (M = Ni^{II} (**2**); Zn^{II} (**3**)). The resonances of the ^{1}H NMR spectra (Figure S21) appear in a broad range from −7 – 210 ppm. The largest shifts and significant broadening are observed for the PDI protons, while the protons closest to the diamagnetic M-cyclam unit are less affected.

The electronic spectrum of **1** exhibits a characteristic trio of intense transitions centered at 300 nm, along with a lower energy feature at 352 nm, which all can be assigned as π-π* transitions associated with the Zn-PDI unit.[11] The Ni-containing **2** and **3** likewise exhibit PDI-based π-π* bands in this region.[12] The spectrum of **2** features additional absorptions at longer wavelengths (λ_{max} = 369, 461 nm), as observed among Ni-cyclam complexes.[13] The spectrum of **3**, in contrast, lacks these distinctive visible absorption bands, whereas the higher energy spectral region (< 350 nm) is nearly superimposable with that of **2**, providing further evidence that the Ni^{II} ion of the heterobimetallic complex resides in the PDI site. The Ni-containing compounds additionally exhibit broad bands in the NIR region, with λ_{max} = 948 (**2**) and 960 (**3**) nm (Figure S23).

The incorporation of the redox-active PDI unit in the bimetallic framework offers access to a series of ligand-centered redox processes. In principal, the ligand can accept up to four electrons via its diimine π* orbitals, associated with the electron transfer series, $[PDI]^0 \rightarrow [PDI]^{4-}$. Metal complexes coordinated by the mono- through tri-anionic forms have been identified.[14] The PDI unit acts as the sole electron storage site in the dizinc-containing **1**. Thus, the first one-electron reduction at −1.3 V in the CV of **1** (CVs shown in Figure 2) corresponds to the formation of the monoanionic $PDI^{\bullet-}$, while the ensuing quasi-reversible couple at −1.7 V can be assigned to the $PDI^{\bullet-}/PDI^{2-}$ couple. Compound **2**, on the other hand, contains two Ni^{II} ions that can compete with the ligand for electrons. The CV of **2** depicts multiple redox events including a reversible metal-centered oxidation at +0.8 V, as well as three reversible reductions at −0.9, −1.4, and −1.6 V.

The CV of **3** further helps to elucidate the nature of the redox processes. An oxidative event is absent in both the CVs of **1** and **3**, such that the one-electron oxidation of **2** ensues at the cyclam bound nickel center ($Ni_{Cy}^{III/II}$). The absence of the oxidative couple in the CV of 3 is further evidence that the heterobimetallic complex is stable in solution – scrambling of the metal centers does not occur. The redox couples at −0.9 V in the CV of both **2** and **3** seemingly can be attributed to the $Ni_{PDI}^{II/I}$ couple, followed in each case by one-electron reduction of the PDI ligand ($PDI/PDI^{\bullet-}$) at −1.4 V. However, both ligand- and metal-centered one-electron reduced Ni-PDI complexes are described in the literature.[12, 15] The addition of the third electron to **2** occurs at −1.6 V, and can be attributed to either the $PDI^{\bullet-}/PDI^{2-}$ or $Ni_{Cy}^{II/I}$ couples. The potential for one-electron reduction of related mononuclear cyclam compounds is highly dependent on the nature of additional ligands, but similar values were reported.[16] Since a third reductive event is not observed in the CV of **3**, reduction of the cyclam bound Ni^{II} ion likely accounts for the final redox process in the CV of **2**.

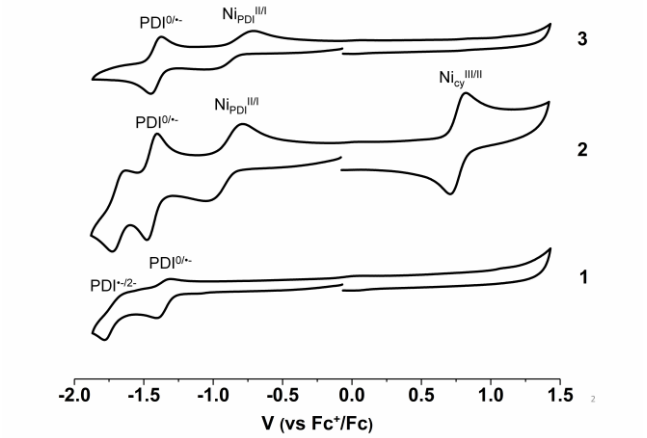


Figure 2. Cyclic voltammograms of **1** – **3** (MeCN, 0.5 mM complex 0.1 V s^{-1}, 0.1 M $[N(n\text{-}Bu)_4]PF_6$.

We have thus far successfully isolated the one-electron forms of all three bimetallic compounds. The reduction of **1** was carried out using decamethylcobaltocene and yielded the bright orange complex $[Zn_2(PDIpCy)(OTF)_3]$ (**4**). Compounds **2** and **3**, which possess more positive one-electron reduction potentials, were reduced using cobaltocene to produce the dark blue $[Ni_2(PDIpCy)(OTf)](OTf)_2$ (**5**) and $([NiZn(PDIpCy)(OTf)_3]$ (**6**) (Scheme S3). CHN analytical and mass spectrometry data (see SI) verify the composition of the reduced compounds.

The solution electronic spectra of **4** – **6** (Figure S24) differ markedly from those of **1** – **3**. In contrast to the divalent **1**, the reduced **4** exhibits visible bands at λ_{max} = 492 and 566 nm. The spectra of **5** and **6** display multi-structured features that encompass the full visible region, as well as NIR transitions up to ca. 1200 nm. The spectra of **4** – **6** further indicate that reduction of the divalent PDIpCy complexes occurs at the M(PDI) site in all three complexes.[12, 15, 17] However, with the exception of **4**, the question of ligand- vs. metal-centered reduction cannot be settled on the basis of the absorption spectra alone.

EPR spectroscopy resolves the electronic structures of **4** – **6**. A near anisotropic spectrum for **4** with g = (2.0105, 2.0060, 2.0005) is synonymous with a ligand-centered radical confined to the PDI portion of the ligand that is attached to a Zn^{II} ion (Figure S27). The room temperature spectra of **5** and **6** exhibit isotropic signals with g-values of 2.1512 and 2.1510, respectively, consistent with a d^9 paramagnetic center (Figure 3, left). This electronic structure is confirmed by the frozen solution spectra recorded in an MeCN/toluene glass at 140 K (Figure 3, right). These spectra are identical, and essentially axial with g = (2.2363, 2.1310, 2.0858) for **5**, and g = (2.2336, 2.1412, 2.0901) for **6**. The $g_{\|} > g_{\perp} > g_e$ pattern is the hallmark of a Ni^{I} species with an unpaired electron in the σ* MO of the Ni-PDI unit (d_{z2} in C_{2v} symmetry). Therefore, **5** and **6** are mixed valent $[Ni^{I}Ni^{II}(PDIpCy)]^{3+}$ and $[Ni^{I}Zn^{II}(PDIpCy)]^{3+}$, with a four-coordinate Ni^{I} ion at the PDI site, with the inclusion of a solvent molecule (MeCN) in the coordinaton sphere.[15, 18]

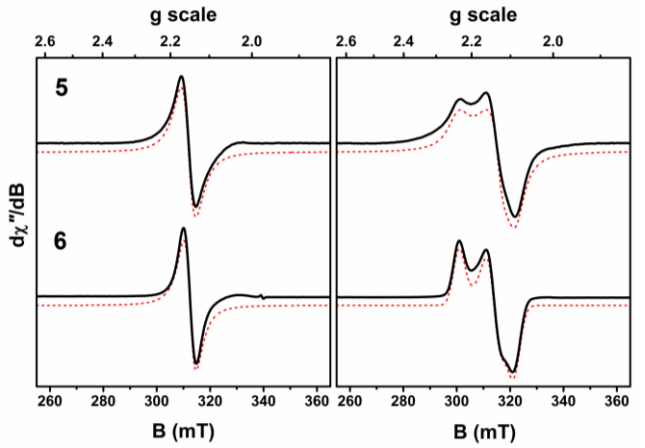


Figure 3. X-band EPR spectra of **5** and **6**. Left panel: MeCN solution at 293 K; right panel: MeCN/toluene frozen glass at 140 K. Experimental data are shown by the solid line; simulation depicted by the dashed trace (experimental conditions: frequency, 9.410 GHz; modulation, 0.5 mT; power, 0.63 mW).

The results of studies with the series of M-PDIpCy compounds already highlight several unique features of our new ligand system. The metal ions in **1** – **3** are physically connected via the propyl linker, but electronically uncoupled. The compounds afford disparate coordination environments, including variations in the number and orientation of labile coordination sites. It should-indeed be feasible to individually tune the properties of each site for discrete functions. Nevertheless, we speculate that the flexible propyl bridge separating the two coordination sites might permit cooperative interactions under appropriate conditions, e.g. in the presence of suitable substrates or added ligands that could bind in a bridging fashion. Compounds **5** and **6** represent conventional metal-centered, one-electron, mixed valence ($Ni_{PDI}^{I}Ni_{Cy}^{II}$, $Ni_{PDI}^{I}Zn_{Cy}^{II}$) complexes. In contrast, charge localization also ensues in **4**, but via electron storage at the PDI ligand ($[Zn^{II}((PDI^{\bullet-})pCy)Zn^{II}]^{+}$). All three complexes are thus primed for redox reactions at the M_{PDI} site; the M_{Cy} center could potentially act in a lewis acid capacity. The electrochemistry data imply that two-electron charge localized species also are accessible, since at least the first two electrons are consistently taken up by the M-PDI unit of **1** – **3**. The generation of such *formally* two-electron mixed-valent $M^{0}_{PDI}\cdots M^{II}_{Cy}$ species could offer significant advantages for multi-electron reactions.[19] Aspects concerning reactivity, as well as the formation of additional heterobimetallic compounds, will subsequently be explored.

ASSOCIATED CONTENT

Supporting Information

The supporting material is available free of charge via the Internet at http://pubs.acs.org.
Detailed experimental procedures, analytical data, spectra and X-ray crystallographic data.

Accession Codes

CCDC 1572803 – 1572805 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 CB21EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interests.

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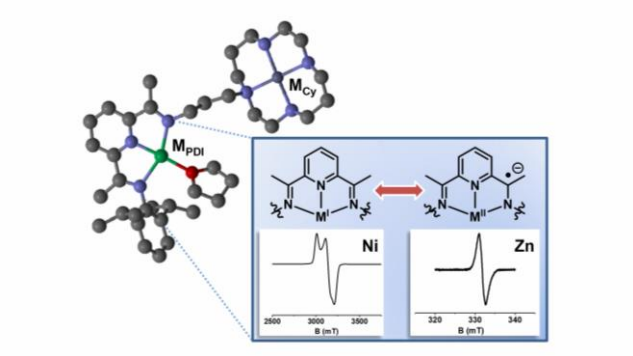

The new ligand, PDIpCy, offers two distinct, non-coupled coordination sites: a redox-active pyridyldiimine (PDI) group and a cyclam (Cy) unit. The series of homo- and heterobimetallic Ni- and Zn-PDIpCy complexes described herein, includes charge-separated forms.