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# Coordination Chemistry of 2,2′-Dipyridylamine: The Gift That Keeps on Giving

David W. Brogden and John F. Berry

Department of Chemistry, University of Wisconsin, Madison, Wisconsin, USA

The ligand 2,2'-dipyridylamine occupies a special place in modern coordination chemistry. To honor the one-hundredth anniversary of its first preparation, the chemistry of this ligand is reviewed, with a special emphasis on the structural features of the resulting metal complexes. The versatility of this ligand is manifold: it can exist in several protonation states, adopt one of nine distinct coordination modes, and stabilize complexes containing one, two, or three metal atoms, including compounds with direct metal–metal bonds. Despite its long history, new complexes of the 2,2'-dipyridylamine ligand continue to be discovered, making this ligand a gift to coordination chemists that keeps on giving.

**Keywords** coordination chemistry, metal-metal bonds, polynuclear compounds

## 1. INTRODUCTION

The ligand 2,2'-dipyridylamine (dpaH) and its deprotonated anion 2,2'-dipyrylamide (dpa) have seen widespread use in organometallic and inorganic chemistry as multidentate ligands. The synthesis of dpaH was first reported by Chichibabin and Zeide in 1914[1] and Steinhäuser and Dieplder in 1916.[2] The former group tested the route shown in Equation (1),[1] while the latter group used Equation (2) and produced a number of derivatives, including an Hg(I) complex.[2]

Address correspondence to John F. Berry, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, USA. E-mail: berry@chem.wisc.edu

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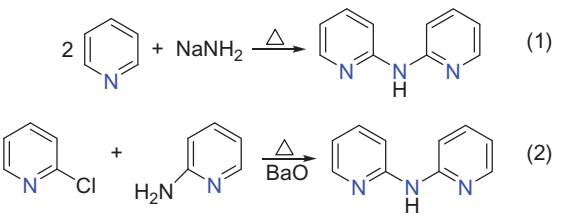


The first reports of the deliberate use of dpaH to chelate metal centers were in divalent cobalt[3] and copper[4] complexes in 1957. Since this time, the versatility of dpaH and dpa has been demonstrated by the variety of mononuclear, dinuclear, and trinuclear complexes synthesized with metals and nonmetals from across the periodic table (Figure 1). Two features of the ligands that allow for this versatility are their ability to adopt three different conformations, *cis-cis, cis-trans*, and *trans-trans* (Figure 2), and nine possible coordination modes (Figure 3).

Coordination modes **I, II**, and **III** are found in mononuclear complexes. Mode **I** features dpaH as a monodentate ligand coordinating through only one pyridine nitrogen atom. In this coordination mode, the ligand has been shown to adopt either the *cis-cis* or *cis-trans* conformations. Coordination modes **II** and **III** feature

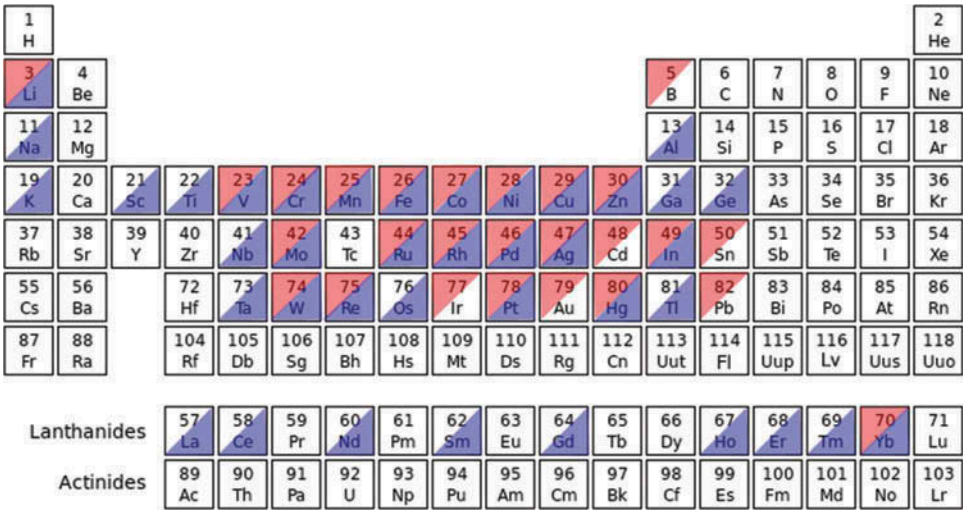


**Figure 1:** Periodic table highlighting the elements that have formed structurally characterized complexes with dpaH (red shading) and dpa (blue shading).

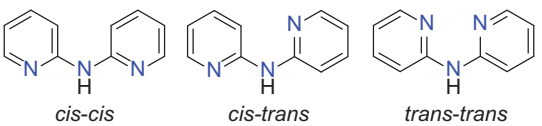


**Figure 2:** Conformations of dpaH.

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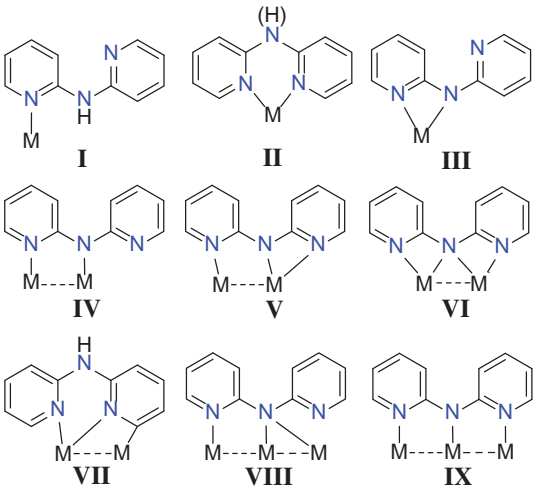


**Figure 3:** Coordination modes of dpaH and dpa.

dpaH or the dpa anion as a bidentate ligand chelating either through both pyridine nitrogen atoms in mode **II**, or through a pyridine nitrogen and the deprotonated amide nitrogen atom in mode **III**. In the case of dinuclear compounds, there are four possible coordination modes, **IV**–**VII**. Mode **IV** features dpa bound to each metal center through either a pyridine nitrogen or amide nitrogen, leaving one pyridine nitrogen unbound or dangling. In mode **V**, the dangling pyridine nitrogen now binds to the same metal center that is bound by the amide nitrogen. Mode **VI** features each pyridine nitrogen bound to a different metal center and the amide nitrogen bound to both metal centers in a $\mu_2$ bridging fashion. Coordination mode **VII** is similar to mode **II** in which both pyridine nitrogen atoms chelate to the same metal center; however, in this mode, one of the deprotonated ortho carbon atoms from the pyridine ring coordinates to a separate metal center. Two coordination modes are found in trimetallic compounds. Mode **VIII** features one pyridine nitrogen atom bound to a metal center, while the other pyridine nitrogen is unbound. The amide nitrogen atom in this mode bridges two separate metal centers. Coordination mode **IX** is found in trinuclear compounds in which each nitrogen of dpa is bound to a different metal center, forming a linear chain of metal atoms.

In this mini-review, we highlight recent compounds that have been synthesized using dpaH and dpa, and showcase the breadth of coordination chemistry in these systems. Hundreds of complexes which include a dpaH or dpa ligand have been synthesized. The goal of this work is not to describe each compound exhaustively but instead to provide an overview of the different types of complexes these ligands are able to support. The first part of this work will focus on the free ligand and its protonated form, $dpaH_2^+$. The second part will detail the mononuclear and dinuclear complexes supported by the dpaH ligand, and the third part will focus

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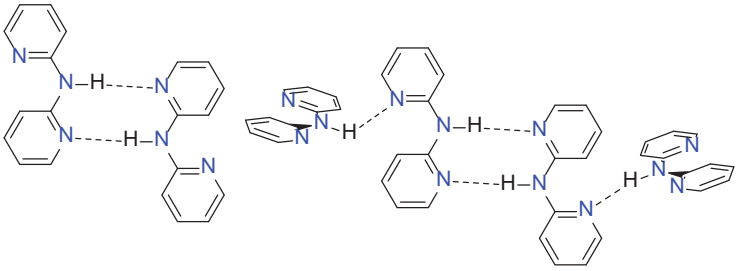

**Figure 4:** Hydrogen bonded dimer of dpaH (right) and tetrameter (left).

on the deprotonated dpa ligand and the monometallic, bimetallic, and trimetallic complexes that have been synthesized. We limit our discussion here to compounds that have been characterized by X-ray crystallography.

## 2. FREE 2,2′-DIPYRIDYLAMINE

The free dpaH ligand has been characterized to crystallize in three different polymorphs with three different space groups.[5-7] In two of the forms, orthorhombic and triclinic, the crystal structure is composed of hydrogen bonded dimers, whereas in the third form, monoclinic, dpaH crystallizes as a hydrogen bonded tetramer (Figure 4). These crystal structures show the preference for dpaH to adopt the *cis-trans* conformation, which in part is due to hydrogen bonding, plus this conformation reduces steric interactions that are found at the ortho C–H positions on the pyridine rings with dpaH in the *cis-cis* conformation.

## 3. PROTONATED 2,2′-DIPYRIDYLAMINE, $DPAH_2^+$

Protonation of dpaH can occur in two different locations and, in both instances, $dpaH_2^+$ adopts the *trans-trans* conformation. In the first case, a hydrogen atom can bond to one pyridine nitrogen atom. The pyridine rings adopt the *trans-trans* conformation in order to support an intramolecular hydrogen bond (Figure 5). The cationic $dpaH_2^+$ ion in this configuration acts as a salt in ionic compounds. For example, Cotton and coworkers reported a crystal structure containing the $dpaH_2^+$ cation as the counter ion for the dianionic

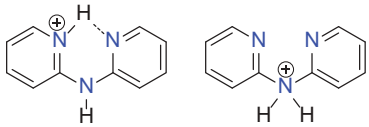

**Figure 5:** Molecular structures of the protonated $dpaH_2^+$ ion.

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$[CoCl_4]^{2-}$ complex.[8] The other possibility, which is more rarely observed, involves protonation at the amine nitrogen atom (Figure 5). In this configuration, the cationic $dpaH_2^+$ compound can either act as a counter ion[9] or can coordinate to a metal center through its pyridine nitrogen atoms, as in mode **I**, as reported by Lightfoot et al. for the complex $[Cu_2F_2(dpaH_2)_2][V_2O_7]$.[10]

## 4. 2,2′-DIPYRIDYLAMINE, DPAH

The dpaH ligand is most commonly coordinated to a metal center in coordination mode **II**, and hundreds of complexes with at least one chelating dpaH ligand are known. In this coordination mode, two inter-complex angles can be considered to investigate the flexibility of the dpaH ligand: (1) the pyridine nitrogen–metal–pyridine nitrogen ($N_{py}$–M–$N_{py}$) bite angle; and (2) the pyridine centroid–amine nitrogen–pyridine centroid angle ($Py_{cent}$–$N_a$–$Py_{cent}$). A scatter plot of these two angles for the known crystallographically characterized dpaH complexes is shown in Figure 6. These data show that there is no simple trend between the two angles, but also show that the dpaH ligand in this coordination mode is always non-planar and can accommodate many $N_{py}$–M–$N_{py}$ bite angles. However, as the bite angle widens to larger angles, the dpaH ligand does become more planar. The existence of multiple interplanar angles at acute metal bite angles suggests the possibility of dynamic behavior in the bound dpaH ligand. Despite careful variable temperature NMR studies,[11] to our knowledge dynamic flexibility of the dpaH ligand has not been quantified.

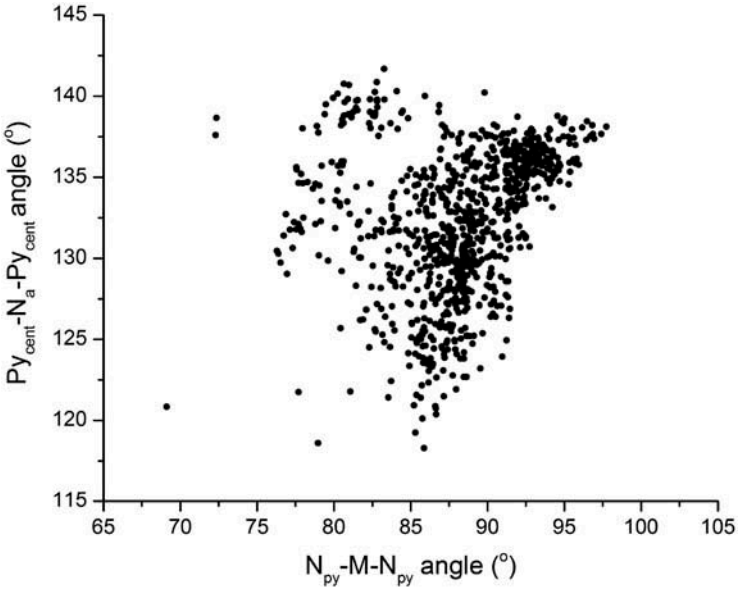


**Figure 6:** Scatter plot showing the flexibility of the dpaH ligand in coordination mode **II**.

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Many mononuclear dpaH complexes (and dpa) have been examined for their luminescence properties. Compounds containing Rh,[12] Ir,[12] Ru,[13] Hg,[14,15] Cd,[14,16,17] Zn,[17-20] Al,[21,22] and Mn[23] metal centers have shown blue luminescence in the range 300–500 nm, which is described to originate from the intraligand $\pi^* \rightarrow \pi$ transition localized on the dpaH or dpa ligand. The luminescent behavior is attributed to the ability of the ligands to chelate a metal center, which increases the rigidity of the ligand and reduces energy loss by radiationless decay.

Besides coordination mode **II**, there have been other coordination modes reported for dpaH ranging from a simple monodentate binding mode to tridentate chelating modes through an ortho-metalated carbon atom. Monodentate dpaH coordination, mode **I**, has been reported for the Group VI metals Mo and W. Reactions of $M(CO)_4$(bipy) (M = Mo or W, bipy = 2,2'-bipyridine) with dpaH results in the octahedral mixed-ligand compounds $M(CO)_3$(bipy)(dpaH), which feature a *cis-cis* monodentate dpaH ligand bound to the metal center through one $N_{py}$.[24] A similar pentacarbonyl W compound, $W(CO)_5$(dpaH), featuring the dpaH ligand in coordination mode **I**, has also been synthesized by the reaction of $W(CO)_5$(thf) with dpaH.[25] In this compound, the dpaH ligand crystallizes in the *cis-trans* orientation, which the authors attribute to steric effects (Figure 7).

In addition to mondentate and bidendate chelating modes for dpaH, there have been two examples of tridentate coordination by dpaH, modes **VII** and **VIII**. The first example was reported by Cotton et al. in 1999 in a dirhodium(II) complex, $[Rh_2(dpaH)_4][Cl_2]$, or more specifically, $[Rh_2\{\mu\text{-}(C_5H_3N)NH(C_5H_4N)\}_2\{\eta^2\text{-}(C_5H_4N)NH(C_5H_4N\}_2]Cl_2$.[26] This compound was synthesized by a melt reaction of $Rh_2(O_2CMe)_4 \cdot 2MeOH$ and dpaH (1:10 molar ratio), and its crystal structure features a metal–metal bonded $Rh_2^{4+}$ core, with each Rh center bound by a dpaH ligand in coordination mode **II**. The other two dpaH ligands each chelate and bridge both Rh centers through coordination mode **VII**, with both $N_{py}$ atoms bound to one Rh center and an ortho-carbon atom ($C_{ortho}$) on the pyridine ring bound to the other Rh center (Figure 8). Therefore, each Rh ion is five coordinate, having four Rh–$N_{py}$ bonds and one Rh–$C_{ortho}$ bond.

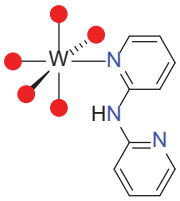


**Figure 7:** Molecular structure of $W(CO)_5$(dpaH) highlighting the *cis-trans* configuration of dpaH; red spheres represent carbonyl groups.[25]

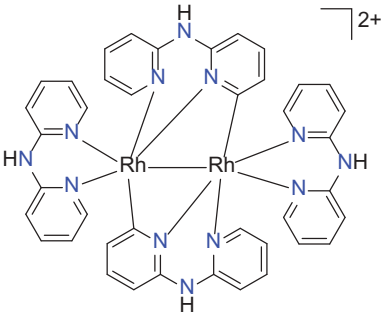


**Figure 8:** Molecular structure of $[Rh_2(dpaH)_4][Cl_2]$.[26]

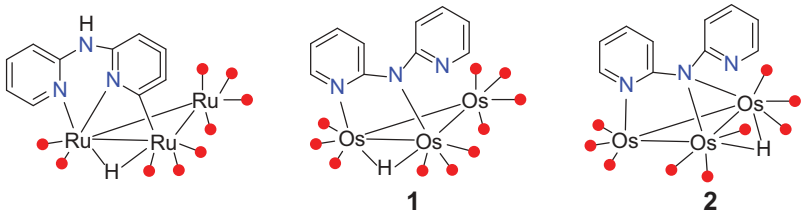


**Figure 9:** Molecular structures of $[Ru_3(\mu\text{-}H)(dpaH)(CO)_9]$ (right), $[Os_3(\mu\text{-}H)(dpa)(CO)_{10}]$ (middle), and $[Os_3(\mu\text{-}H)(dpa)(CO)_9]$ (left); red spheres represent carbonyl groups.[27]

The second example of ortho-metelation, coordination mode **VII**, was reported in 2002 by Suárez et al. in a $Ru_3$ cluster.[27] The reaction of either $[Ru_3(CO)_{12}]$ or $[Ru_3(CO)_{10}(MeCN)_2]$ with dpaH results in the formation of the triruthenium compound $[Ru_3(\mu\text{-}H)(dpaH)(CO)_9]$, or more specifically, $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^3\text{-}dpaH\text{-}C,N,N)(CO)_9]$, which features the dpaH ligand bound to two of the three Ru centers through coordination mode **VII** (Figure 9).[27] The amine nitrogen atom in this complex is bound only to a hydrogen atom and two carbon atoms, not a Ru center, as the dpaH ligand adopts a *trans-trans* conformation. Similar reactions with the analogous Os compound $[Os_3(CO)_{10}(MeCN)_2]$ and dpaH did not result in the ortho-metaled product, but instead formed the $[Os_3(\mu\text{-}H)(dpa)(CO)_{10}]$ compound more descriptively rewritten as $[Os_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}dpa\text{-}N,N)(CO)_{10}]$ (**1**), and upon further heat or light formed $[Os_3(\mu\text{-}H)(dpa)(CO)_9]$, or more specifically, $[Os_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}dpa\text{-}N,N)(CO)_9]$ (**2**). Both **1** and **2** interestingly feature the deprotonated dpa ligand and not dpaH from formal oxidative addition of the N–H bond. In **1**, dpa adopts coordination mode **IV**, with one $N_{py}$ unbound. Upon further heat or light, one of the CO ligands is lost and the amide nitrogen ($N_a$) chelates to a second Os center in an $\mu_2$ fashion, coordination mode **VIII**, but still the one $N_{py}$ remains unbound (Figure 9).[27]

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# 5. DEPROTONATED 2,2′-DIPYRIDYLAMINE, DPA

## 5.1 Monometallic

Group XIII compounds with dpaH or dpa ligands have recently garnered significant attention due to their potential application in semiconductor materials.[28] The first reported aluminum dpa compound was in 1996 by White et al.[29] They reported the Al(III) compound, $Al(dpa)_3$ (**3**), from a reaction of $[AlH_3(NMe_3)]$ and three equivalents of dpaH in diethyl ether. Compound **3** features three *cis-trans* dpa ligands in coordination mode **III**, with the central Al atom in a distorted octahedral environment in which the three dpa ligands are planar.[29] A different conformational isomer of $Al(dpa)_3$, (**4**), was reported by Stalke et al. in 2002 by dissolving $Al(dpa)_3$ in $C_6D_6$ and allowing the solvent to slowly evaporate.[28] This isomer features two *cis-trans* dpa ligands which coordinate in mode **III**, and a third dpa ligand in the *trans-trans* conformation which chelates the Al atom in mode **II**. In solution, however, the conformational isomer **4** converts to the all *cis-trans* isomer **3**, suggesting that **4** is a kinetic product.[28]

Gornitzka and Stalke were able to synthesize and characterize a complete series of Group XIII metal dpa compounds, which very nicely highlight the versatility of the dpa ligand. The compounds synthesized were [Al(dpa)$Me_2$] (**5**), [Ga(dpa)$Me_2$] (**6**), dimeric $[In(dpa)Me_2]_2$ (**7**), and polymer $[Tl(dpa)Me_2]_\infty$ (**8**).[30] The dpa ligand in **5** and **6** adopts the *trans-trans* conformation and coordinates to the metal centers through coordination mode **II**. Compound **7** features dpa in the *cis-cis* orientation and coordinated to the metal centers in mode **III**. The *cis-cis* conformation of dpa gives rise to the dimeric structure, but the five coordinate $In^{3+}$ ions do not have a metal-metal bond. The Tl structure is different from **5-7**, crystallizing as a polymer and featuring the dpa ligand in a *cis-trans* conformation. Each Tl metal center is five coordinate, chelated by a $N_{py}$ and $N_a$ from one dpa ligand, a $N_{py}$ from another dpa ligand, and two methyl groups. Each dpa ligand bridges two Tl metal centers propagating the polymer network (Figure 10). The authors suggest that the anionic dpa ligand forms covalent bonds with

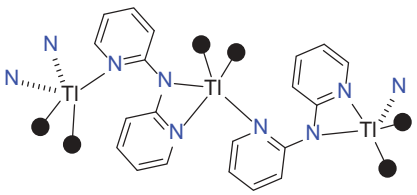


**Figure 10:** Partial molecular structure of the polymeric compound **8**, $[Tl(dpa)Me_2]_\infty$; black spheres represent methyl groups.[30]

the harder metal centers in **5** and **6**, and dpa has more of an ionic interaction with the metals in **7** and **8**. Stephan and coworkers reported the synthesis and characterization of $[(dpaH)B(C_6F_5)_3]$, which features the dpaH ligand in a *cis-trans* configuration, coordinated to the central B atom by a $N_{py}$, coordination mode **I**.[31]

## 5.2 Bimetallic

The dpa ligand has recently been shown to coordinate rare earth metals.[32-35] Müller-Buschbaum and Quitmann have synthesized a series of $Ln_2(dpa)_6$ (Ln = La, Ce, Nd, Sm, Gd, Ho, Er, Tm, Yb, and Sc) compounds by stoichiometric redox melt reactions between the lanthanide metal (activated by a mercury amalgam) and dpaH (Equation (3)).[32,34] The rare earth ions are trivalent in these structures and adopt a distorted square antiprismatic configuration. The homoleptic $Ln_2(dpa)_6$ compounds crystallize in three distinct classes based on their relative size: type (I) lanthanum ($C_c$); type (II) cerium to thulium ($P2_1/n$); and type (III) ytterbium, lutetium, and scandium ($P2_1/c$).

$$2Ln + 6dpaH \xrightarrow{\text{melt}, \Delta T} Ln_2(dpa)_6 + 3H_2 \quad (1)$$

The type II and III complexes have very similar structures. They feature eight coordinate $Ln^{3+}$ ions, with each metal atom coordinated by a *cis-cis* and a *cis-trans* dpa ligand in coordination mode **III**. In addition, the Ln ions are also coordinated by two other dpa ligands in coordination mode **VI**, with the $N_a$ bound to both $Ln^{III}$ metal ions (Figure 11). The lanthanum containing complex, $La_2(dpa)_6$, forms its own class because both lanthanum ions have a

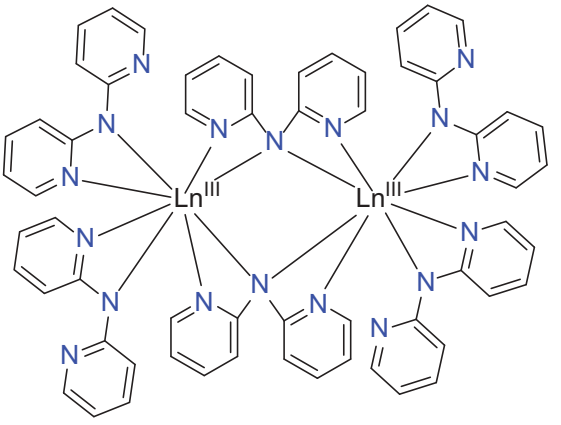


**Figure 11:** Molecular structure of type II and type III $Ln_2(dpa)_6$ complexes.[34]

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coordination number of 10, instead of eight. In this structure, there are four dpa ligands that adopt coordination mode **VI** and only two dpa ligands in the *cis-cis* conformation chelated through mode **III**.[32,34]

Leary et al. were able to synthesize and isolate the eight coordinate La isomer that falls in line with the other type II and type III structures; therefore, completing the series of eight coordinate lanthanide complexes from La to Yb.[35] Their synthetic route to the eight coordinate $La_2(dpa)_6$ compound was different than that established by M□ller-Buschbaum and Quitmann. The reaction of $LaNi_5$ and dpaH in a 1:3 molar ratio, activated by Hg, afforded the desired eight coordinate $La_2(dpa)_6$ complex, which crystallized in the $P2_1/n$ space group, as the crude reaction mixture was cooled from 170 °C. The eight coordinate structure displays the same geometric features as the type II and III complexes described previously. Interestingly, recrystallizing the isolated eight coordinate $La_2(dpa)_6$ complex in a 1:1 mixture of THF:toluene yielded the 10 coordinate isomer.[35]

Quitmann and Müller-Buschbaum have also synthesized another unique rare earth metal dpa compound, namely $[Yb_3N(dpa)_6]\cdot[Yb(dpa)_3]$ (Figure 12).[33] This compound is prepared by the reaction of Yb metal with dpaH in liquid ammonia at –50 °C. The unit cell consists of two distinct neutral Yb units. In one unit, the three $Yb^{3+}$ ions form an approximate equilateral triangle around the central nitride ion. Six dpa ligands surround the $Yb_3N$ core

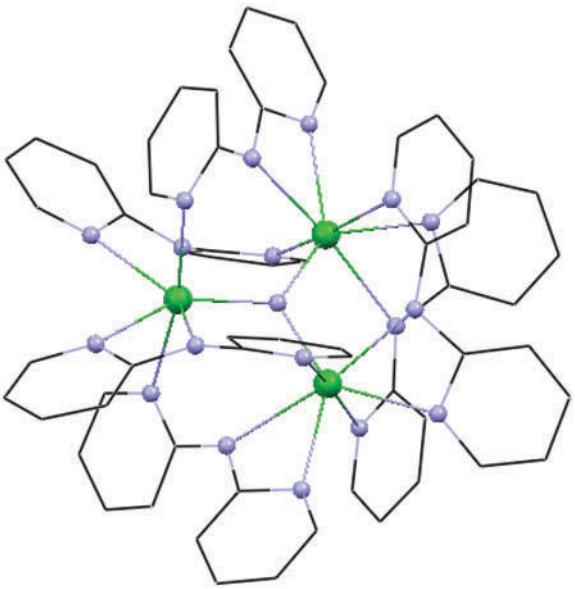

**Figure 12:** Molecular structure of $[Yb_3N(dpa)_6]$.[33] Green spheres represent Yb, blue spheres represent nitrogen, and black wireframe represents carbon. Hydrogen atoms have been omitted.

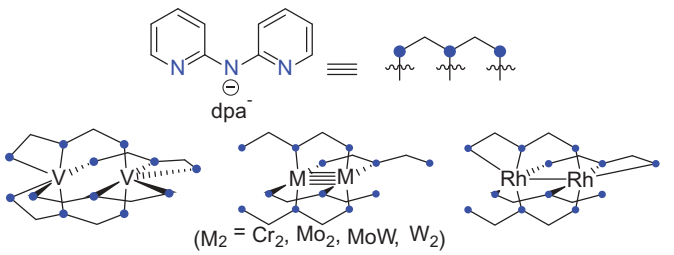


**Figure 13:** Paddlewheel type structures of $V_2(dpa)_4$ (left), $M_2(dpa)_4$ ($M_2$ = $Cr_2$, $Mo_2$, MoW, $W_2$) (right), and $Rh_2(dpa)_4$ (left), highlighting the different coordination modes of dpa.

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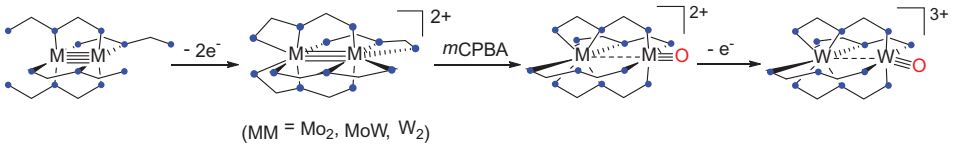
and utilize all three nitrogen atoms to coordinate in mode **V**. This chelating arrangement results in a distorted pentagonal-bipyramidal coordination sphere around each $Yb^{3+}$ ion, which has a coordination number of seven. The second molecular unit, [Yb(dpa)$_3$], features three dpa ligands surrounding the central $Yb^{3+}$ ion. The dpa ligands are all in the *cis-cis* conformation and coordinate in mode **III** with each ligand having a dangling $N_{py}$, reminiscent of Al(dpa)$_3$, leading to a Yb coordination number of six.

Substantial effort has been put forth to study homoleptic dinuclear transition metal dpa complexes of the form $M_2(dpa)_4$, $M_2$ = $V_2$,[36] $Cr_2$,[37,38] $Mo_2$,[39] MoW,[40] $W_2$,[41] and $Rh_2$.[42] These compounds feature four dpa ligands coordinated around the metal centers to form a paddlewheel type structure (Figure 13); however, the chelation mode of dpa in the $V_2$ complex is different than for the group VI metals, which is also different than observed for the $Rh_2$ complex. In the $V_2$ structure, the V atoms are at a distance of 3.04 Å from each other; therefore, there is no metal–metal bond. The lack of a V–V bond is energetically offset by the coordination of six dpa nitrogen atoms to each $V^{2+}$ ion in coordination mode **V**. The dpa ligands are aligned in a trans fashion around the $V_2$ core.

In the case of the Group VI metal complexes, $M_2(dpa)_4$ ($M_2$ = $Cr_2$ (**9**), $Mo_2$ (**10**), MoW (**11**), $W_2$ (**12**)), the metals form a strong quadruple bond, with metal–metal distances in the range 2.1–2.2 Å.[43] The dpa ligands, therefore, coordinate in a trans configuration with each ligand only bound twice, mode **IV**, through a $N_{py}$ and $N_a$ leaving the other $N_{py}$ dangling. The $Rh_2(dpa)_4$ structure features two different types of chelating dpa ligands. Two dpa ligands adopt mode **IV** and the other two dpa ligands coordinate through mode **V**, yielding five coordinate Rh centers with a Rh–Rh single bond. The dpa ligands arrange in a cis orientation around the $Rh_2$ core[42] (Figure 13).

Our group has characterized the one- and two-electron oxidized products of **10-12**[41,43,44] and the two-electron oxidized product of **9**.[43] Due to the modest oxidation potentials of **10 - 12**, Ag(OTf) or $FeCp_2$(OTf) could be the oxidizing agents. In the one-electron oxidized compounds, $[M_2(dpa)_4]^+$ ($M_2$ = $Mo_2$ (**13**), MoW (**14**), $W_2$ (**15**)), the dpa ligands adopt the same conformation and chelating




**Scheme 1:** Reaction pathway to synthesize the two-electron oxidized $[M_2(dpa)_4]^{2+}$ compounds, metal-metal-oxo $[M_2O(dpa)_4]^{2+}$ compounds, and tricationic $[W_2O(dpa)_4]^{3+}$.

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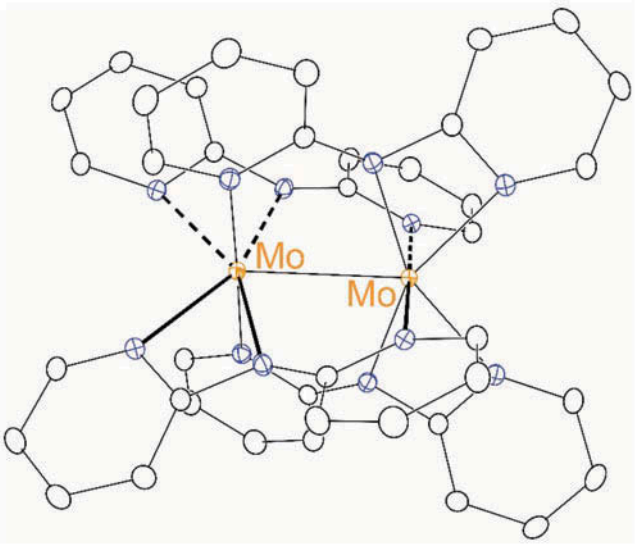


**Figure 14:** X-ray crystal structure of $[Mo_2(dpa)_4]^{2+}$.[43] Blue spheres represent nitrogen and black spheres represent carbon. Hydrogen atoms have been omitted.

mode as in the neutral compounds, mode **IV**. However, in the two-electron oxidized compounds, $[M_2(dpa)_4]^{2+}$ ($M_2$ = $Mo_2$ (**16**), MoW (**17**), $W_2$ (**18**)), the dangling $N_{py}$ chelate to the metal centers (Scheme 1 and Figure 14), resulting in six coordinate metal centers. These dicationic complexes were characterized to contain elongated metal–metal triple bonds, with metal–metal distances of 2.7–2.8 Å.[43] The two-electron oxidized product for $Cr_2(dpa)_4$ displays the same structural features as its Group VI congers, except that the Cr–Cr bond distance, 3.20 Å, and the paramagnetism of the compounds preclude the possibility of a Cr–Cr bond. The $[Cr_2(dpa)_4]^{2+}$ dication is isoelectronic and isostructural to $V_2(dpa)_4$. The longer Cr–Cr separation in the former complex is likely a result of the increased electrostatic repulsion between $Cr^{3+}$ ions vs. $V^{2+}$ ions.

Reaction of the two-electron oxidized Group VI compounds **16-18**, with *m*CPBA (*meta*-chloroperoxybenzoic acid) yields the dicationic $[M_2O(dpa)_4]^{2+}$

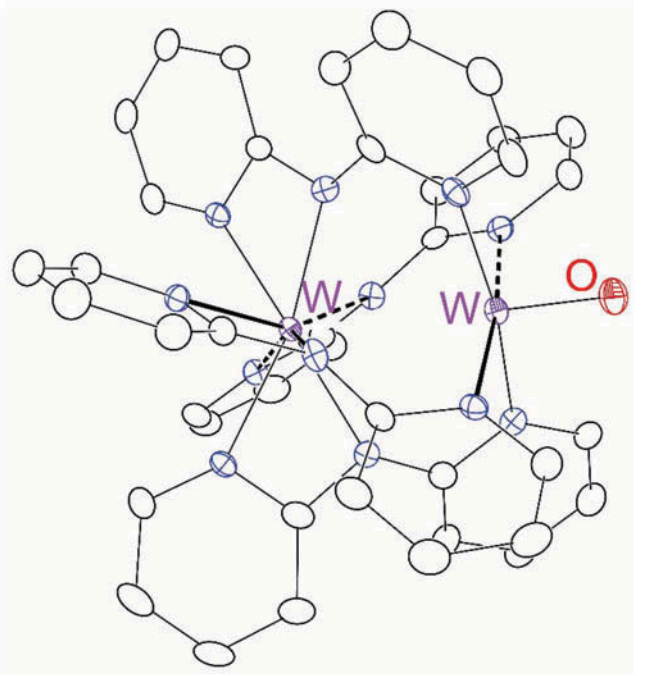


**Figure 15:** X-ray crystal structure of $[W_2O(dpa)_4]^{2+}$.[41,43] Blue spheres represent nitrogen and black spheres represent carbon. Hydrogen atoms have been omitted.

($M_2$ = $Mo_2$ (**19**), MoW (**20**), $W_2$ (**21**)) metal-metal-oxo compounds (Scheme 1 and Figure 15).[41,43] The $W_2O$ complex can be further oxidized to a $[W_2O(dpa)_4]^{3+}$ trication.[45] These structures feature two weakly interacting metal centers in very different coordination environments. The non-oxo bound metal is eight coordinate in an approximate square-antiprismatic geometry bound by four $N_{py}$ and four $N_a$ atoms. The second metal atom forms a triple bond with the oxo-moiety and four bonds with the other four $N_{py}$ atoms. The coordination by dpa, mode **V**, in these complexes is different than observed in the parent two-electron oxidized compounds **16**–**18**, and requires two of the $N_a$ atoms to rearrange and coordinate to the other metal center. It is also worth discussing the amount of flexibility the dpa ligand displays as it coordinates the oxidized and oxo compounds compared to the parent quadruply bonded, $M_2(dpa)_4$ compounds by comparing the average $N_{py}$–M–M–$N_{py}$ dihedral angles. As the charge of the dimetal core increases, the dpa ligand shows a greater degree of twisting around the $M_2$ core, going from 8° in the $M_2^{4+}$ **10**–**12**, to 29°–32° in the $M_2^{6+}$ **16**–**18**, to 55° in the $M_2^{8+}$ **19**–**21**, and 57° in $W_2^{9+}$.

Bimetallic compounds supported by only three dpa ligands have been synthesized for V,[36] W,[44] and Ru.[46] For V and Ru, the compounds have the formula $M_2(dpa)_3Cl_2$ and, in the case of W, the compound is cationic,

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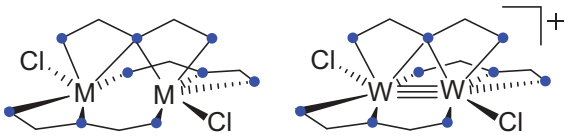


**Figure 16:** Molecular structures of $M_2(dpa)_3Cl_2$ ($M_2 = V_2$, $Ru_2$) (left) and $[W_2(dpa)_3Cl_2]^+$ (right).

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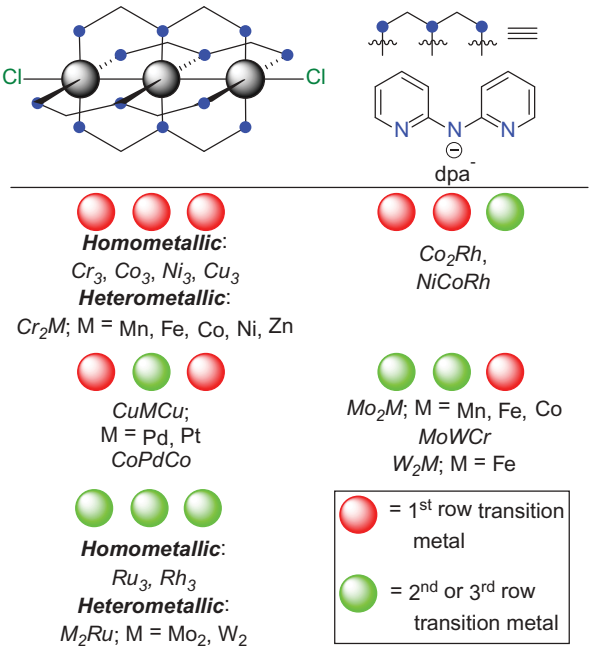
$[W_2(dpa)_3Cl_2]^+$. These compounds are nevertheless all isostructural and feature the dpa ligand in two different coordination modes. Two of the dpa ligands adopt coordination mode **V**, and the third dpa ligand coordinates through mode **VI**, where the $N_a$ atom symmetrically bridges both metal centers in an $\mu_2$-fashion (Figure 16). The other coordination sites on the metal atoms are occupied by chloride ligands, resulting in six coordinate metal centers. The V and Ru compounds feature mixed-valent $M_2^{5+}$ cores and do not possess a metal–metal bond; in fact, the metal–metal separations in the two compounds are quite similar at 3.09 Å for $V_2$,[36] and 3.02 Å for $Ru_2$.[46] The diamagnetic $[W_2(dpa)_3Cl_2]^+$ compound features two $W^{III}$ ions at a distance of 2.53 Å,[44] which could be considered to possess a long W–W triple bond based on comparison to the previously characterized $[W_2(dpa)_4]^{2+}$ structure, which features an elongated W–W triple bond at a distance of 2.72 Å.[43]

## 5.3 Trimetallic

One of the largest and most interesting classes of compounds containing the dpa ligand is the set of trinuclear compounds of the form $M_3(dpa)_4Cl_2$ (Scheme 2). These compounds feature a linear chain of metal atoms surrounded by dpa ligands, with each nitrogen atom of dpa coordinated to a separate metal atom, mode **IX**. The dpa ligands do not bind in a planar fashion, but instead show a degree of twisting around the $M_3$ core, 30–50°, as observed in the $[M_2(dpa)_4]^{2+}$ and $[M_2O(dpa)_4]^{2+}$ compounds. The first homotrimetallic compound synthesized was the Ni compound, $Ni_3(dpa)_4Cl_2$, reported by Hurley and Robinson in 1968[47] and first structurally characterized in 1991[48] and later in 1999.[49] The subsequent synthesis and characterization of the Co,[50-53] Cr,[54] Cu,[55-57] Ru,[58] and Rh[58] analogues has been reported by Peng et al.[59] and Cotton et al.[60] Three synthetic procedures are employed for the preparation of these "extended metal atom chains" (EMACs).[61] The method of Hurley and Robinson, developed in 1968 and optimized by Peng and coworkers, involves heating a mixture of the corresponding anhydrous $MCl_2$ or $M_2(OAc)_4Cl$ and dpaH in naphthalene in the presence of KO*t*Bu to deprotonate dpaH. The procedure established by Cotton and coworkers involves first deprotonating the dpaH ligand using MeLi at low temperature in tetrahydrofuran (THF), followed by the addition of the $Li^+(dpa)^-$ reaction mixture to stoichiometric amounts of the anhydrous metal dichloride,




**Scheme 2:** Trimetallic compounds of dpa.

$MCl_2$. Under refluxing THF conditions, the corresponding $M_3(dpa)_4Cl_2$ compounds are formed. A third synthetic method involves the preparation of a discrete (dpaH)•$MCl_2$ complex, and subsequent deprotonation of this complex with MeLi in THF.[62] Since their discovery, the homometallic $M_3(dpa)_4Cl_2$ compounds have been the focus of considerable experimental, crystallographic, and computational studies to understand the metal-metal bonding in the structures,[60,63-69] and considerable efforts have been made to change the axial ligands to alter their electronics.[70-73]

More recently, the synthesis, characterization, and physical properties of heterometallic EMACs has been of interest. The syntheses of the heterometallic compounds is generally more difficult than that for the homometallic compounds due to the issue of selectivity for heterometallic rather than a mix of homometallic compounds. The heterometallic compounds synthesized to date fall into three classes, as has been previously suggested[40]: (1) symmetric $M_A$–$M_B$–$M_A$,; (2) unsymmetric $M_A$–$M_A$–$M_B$; and (3) $M_A$–$M_B$–$M_C$, in which all three metal atoms are different.

Class 1: The first heterometallic EMAC, $CoPdCo(dpa)_4Cl_2$, was reported by Peng et al. in 2007.[74] This compound was synthesized by a reaction of dpaH, $CoCl_2$, $K_2PdCl_4$, and *t*-BuOK in refluxing naphthalene. Subsequent synthesis of the analogous Cu compounds has been achieved, $CuM_BCu(dpa)_4Cl_2$ ($M_B$ = Pd and Pt).[75] The use of a square planar $d^8$ Group X metal as the central metal in these

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$M_A$–$M_B$–$M_A$ compounds facilitates antiferromagnetic coupling of the outer $M_A^{2+}$ ions, and it was shown that the magnetic interaction is the strongest in the homometallic $Cu_3(dpa)_4Cl_2$ compound, J = –17 $cm^{-1}$, and decreases as the central Cu ion is replaced by Pd, J = –3.7 $cm^{-1}$, and decreases even more when replaced by Pt, J = –0.4 $cm^{-1}$, determined using the HDVV Hamiltonian $H = -2JS_1 \cdot S_2$.[75]

Class 2: Considerable work has been done by our group to synthesize compounds of the form $M_A$–$M_A$–$M_B$ where Group VI $M_A$ metals form a quadruple bond and $M_B$ is a first-row transition metal in the +2 oxidation state. The first compound of this form, $Cr_2Fe(dpa)_4Cl_2$ (**22**),[76] was prepared from the reaction of quadruply bonded $Cr_2(dpa)_4$ and divalent $FeCl_2$ in refluxing THF. Compound **22** features an elongated Cr–Cr quadruple bond compared to the precursor $Cr_2(dpa)_4$ compound, 0.08 Å longer, and a distal Fe(II) ion at a distance of 2.70 Å. Since the report of **22**, compounds containing Cr–Cr, Mo–Mo, Mo–W, and W–W quadruple bonds with appended $Cr^{II}$,[40,77] $Mn^{II}$,[78] $Fe^{II}$,[78,79] $Co^{II}$,[80] $Ni^{II}$,[81] and $Zn^{II}$[79] ions have been made. In most cases, partial σ bonding delocalization throughout the chain is achieved.[77] This series was recently expanded to include $Mo_2Ru(dpa)_4Cl_2$ and $W_2Ru(dpa)_4Cl_2$, the first heterometallic EMAC compounds not to include a first-row transition metal (Figure 17), for which heterometallic π bonding is also observed.[82]

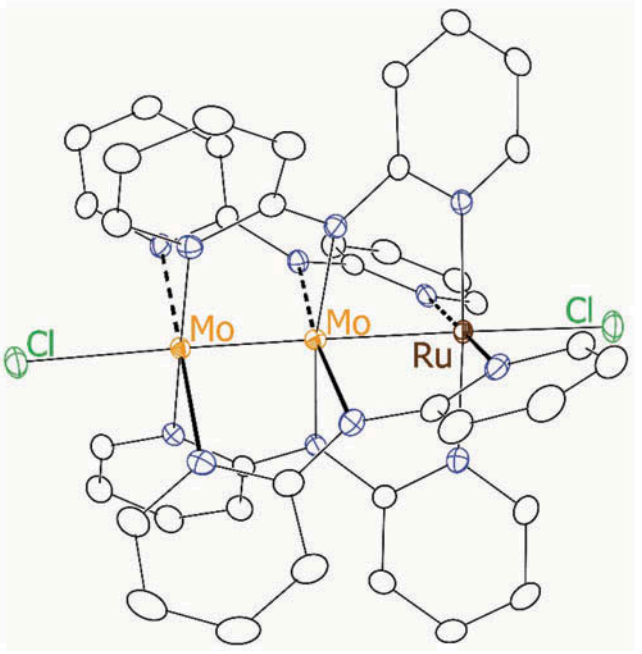
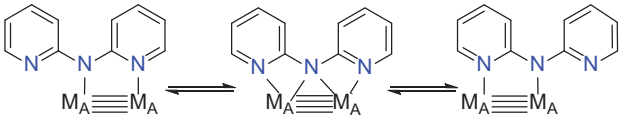



**Figure 17:** X-ray crystal structure of $Mo_2Ru(dpa)_4Cl$.[82] Blue spheres represent nitrogen and black spheres represent carbon. Hydrogen atoms have been omitted.



**Scheme 3:** Longitudinal shuffling mechanism for dpa.

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Oxidation of $Mo_2Ru(dpa)_4Cl_2$ to the corresponding cation, $[Mo_2Ru(dpa)_4Cl_2]^+$, opens up a delocalized δ bonding pathway through the compound.[83]

The mechanism by which the trimetallic chains form from their quadruply bonded precursors has been explored by our group. To form the trimetallic compounds, there must be at least two M–$N_a$ and two M–$N_{py}$ bonds broken during the rearrangement of the dpa ligand to furnish the general structural motif observed in the trimetallic compounds. A variable temperature $^1$H NMR study on the $Cr_2Zn(dpa)_4Cl_2$ compound revealed that the dpa ligand most likely undergoes a longitudinal shuffling, shifting from coordination mode **III** to mode **IV**, where the central $N_a$ bridges the quadruply bonded metal atoms, to mode **III** which allows for metalation to occur (Scheme 3).[79] For $Cr_2(dpa)_4$, refluxing THF provides enough heat to accomplish this rearrangement. For the second or third row analogs, however, the higher temperature of refluxing naphthalene is needed.

Peng et al. have also reported three compounds which fall into Class 2, namely $Co_2Rh(dpa)_4Cl_2$, $Ru_2Ni(dpa)_4Cl_2$, and $Ru_2Cu(dpa)_4Cl_2$.[84] Unlike the other class II compounds, $Ru_2Ni(dpa)_4Cl_2$ and $Ru_2Cu(dpa)_4Cl_2$ feature a unique mixed-valent $Ru^{II}$–$Ru^{III}$–$M_B{}^I$ core.

Class 3: Two compounds have been synthesized that fall into this class. Our group reported the synthesis and characterization of the pan-Group VI compound $MoWCr(dpa)_4Cl_2$ in 2009, which features a Mo–W quadruple bond with an appended $Cr^{II}$ ion.[40] This compound was synthesized similarly to the Class 2 compounds by reacting the $MoW(dpa)_4$ quadruply bonded compound with $CrCl_2$ in refluxing naphthalene. Interestingly, the incoming Cr(II) ion enters selectively on the W end of the Mo–W chain. Peng et al. reported the synthesis of $NiCoRh(dpa)_4Cl_2$, which was formed by reacting the Class 2 compound $Co_2Rh(dpa)_4Cl_2$ with $Ni(OAc)_2$ in refluxing naphthalene.[85]

## 6. CONCLUSIONS

Over the last 100 years, coordination chemists have discovered many applications for the 2,2′-dipyridylamine (dpaH) ligand, incorporating it and its deprotonated (dpa) and protonated ($dpaH_2^+$) forms in numerous monometallic,

bimetallic, and trimetallic complexes. Many of these complexes, including their synthetic preparations and chemical structures, have been reviewed in this work, and the versatility of the dpaH ligands has been highlighted in three different conformations and nine different coordination modes. Moving forward, dpaH will undoubtedly continue to be a fruitful gift for coordination chemists.

## FUNDING

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