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Syntheses, Structures and Bonding of 3*d* Metal Alkynyl Complexes of Cyclam and Its Derivatives

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Abstract: Described in this review is the chemistry of 3*d* metal alkynyls based on tetraaza macrocyclic ligands. Both the abundance of 3*d* metals and easy access to the tetraazacyclotetradecane type ligands make these compounds more affordable and sustainable alternatives to metal alkynyls based on precious metals. Taking advantage of a rich variety of starting materials available in literature, the *trans*-$[M(cyclam)(C_2R)_2]X$ type (cyclam = 1,4,8,11-tetraazacyclotetradecane) compounds have been prepared from the reactions between $[M(cyclam)X_2]X$ (M = Cr, Fe and Co; X = Cl or OTf) and LiC_2R. With $[Co(cyclam)Cl_2]^+$, both the $\{$*trans*-$[Co(cyclam)Cl]_2(\mu\text{-}(C\equiv C)_n)\}^{2+}$ and *trans*-$[Co(cyclam)(C_2R)Cl]^+$ type compounds can be prepared through a dehydrohalogenation reaction. The latter type compounds can undergo a second alkynylation reaction with LiC_2R' to afford the dissymmetric *trans*-$[Co(cyclam)(C_2R)(C_2R')]^+$ type compounds, including the *trans*-$[Co(cyclam)(C_2A)(C_2D)]^+$ dyads with *A* and *D* as acceptor and donor chromophores respectively. These compounds are being studied to probe photo-induced electron transfer and related photophysical/photochemical processes. The *trans*-$[Co(cyclam)(C_2R)(NCMe)]^{2+}$ type complexes react with unactivated HC_2R'

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Dedicated to Professor Armando Pombeiro, an early pioneer of metal-acetylide electrochemistry, on the occasion of his 70th birthday.

Keywords: cyclam; 3d-metal; acetylide; synthesis; structure

in the presence of a weak base to provide *trans*-[Co(cyclam)(C_2R)(C_2R')]$^+$ in high yields. Similar alkynylation chemistry with complexes of cyclam derivatives, like TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), HMC (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and DMC (5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), has been demonstrated with the studies of [Ni(TMC)(C_2R)]$^+$, *trans-/cis*-[Cr(HMC/DMC)$(C_2R)_2$]$^+$ and *trans*-[Co(DMC)$(C_2R)_2$]$^+$.

1. Introduction

Early examples of metal alkynyl chemistry can be traced back to homoleptic $[M(C\equiv CR)_6]^{n-}$ (M = Cr, Mn, Fe and Co), $[M(C\equiv CR)_4]^{n-}$ (M = Mn, Ni, Pd, Pt, Zn, Cd and Hg), and $[M(C\equiv CR)_2]^{n-}$ (M = Cu, Ag and Au) complexes developed by Nast and co-workers [1]. Similar species based on complexes of d^0 metal ions, such as Ta, Hf, Zr [2], as well as M^{III} complexes (M= Cr, Co, and Fe) [3] were studied to further understand the structure-property relationship using modern structural and computational techniques. Formation of rigid-rod polymers $[M\text{-}C\equiv C\text{-}Ar\text{-}C\equiv C]_n$ (M = Ni, Pd and Pt) can be traced back to work by Hagihara *et al.* in the late 70s and early 80s [4]. Lewis and co-workers developed similar motifs with metals of groups 8 - 10 in the 90s by utilizing a trimethyl tin reagent and CuI to induce polymerization [5,6]. While these polymers display wire-like rigid rod structures, they are poor conductors. Square planar d^8 configuration Pd and Pt poly-ynes exhibited band gaps greater than 3 eV, based on their absorption edges, thereby acting as insulators ($R \sim 10^7 \Omega\text{cm}$) [7]. The synthetic chemistry of metal alkynyls, their electronic structures as well as their applications in opto-electronics have been investigated by many groups and these efforts have been reviewed elsewhere [8-12].

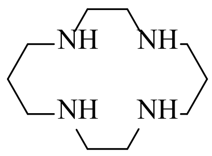
Since the pioneering studies of the C_4-bridged dirhenium compounds by Gladysz [13] and C_4-bridged diiron compounds by Lapinte [14], the focus of wire like $M\text{-}(C\equiv C)_n\text{-}M$ type compounds has been based on *middle* transition metals. There have been many examples of bimetallic compounds with an oligoyn-diyl bridge, including M as Mn [15], Ru [16], W [17], and Pt [18]. Examples of oligoen-diyl bridged species are scarce and limited largely to those capped with Ru(II) by the laboratories of Jia [19-21] and Liu [22-24]. Electron movement across the oligoyn-diyl bridge has been studied via voltammetric techniques and analysed using the framework of the classic Taube-Creutz mixed valency [25]. Drawing motivation from the work of Cotton [26] and Bear-Kadish [27,28], we reported the first diruthenium compounds with oligoyn-diyl bridges [29]. The Lehn laboratory published on similar compounds shortly thereafter [30]. Since the late 90s, our laboratory has continued to probe diruthenium alkynyls as prototypical molecular wires [31-33]. Electrochemical and spectroelectrochemical analysis of the electronic couplings (H_{ad}) between two Ru_2 termini in Ru_2-$(C{\equiv}C)_n$-Ru_2 type compounds (n = 2-10), where $Ru_2(ap)_4$ is the capping unit (ap = 2-anilinopyridinate), showed good electronic coupling with a Robin-Day class II behaviour [34-36]. Similar studies were conducted for -$(C{\equiv}C)_n$-$Ru_2(DMBA)_4$-$(C{\equiv}C)_n$- bridge ($n = 1 - 4$; DMBA = *N*,*N*′-dimethylbenzamidinate) end-capped with ferrocenyls, and Robin-Day class II-III behaviours were observed for the $[Fc\text{-bridge-}Fc]^+$ moieties [37-39]. STM and break-junction techniques have been utilized to study how conductivity in Ru_2 alkynyl species compare to similar organic systems, and revealed that the Ru_2 systems perform better overall [40,41]. Since then, Ru_2-alkynyls have been incorporated and studied in flash-memory devices [42-44]. Facile electronic delocalization facilitated by metal-alkynyl linkage has also been demonstrated with high nuclearity clusters, such as linear Ru_3 array [45] and Os-carbonyl clusters [46-49].

In an effort to advance metal alkynyl chemistry towards more sustainable materials, we have transitioned towards earth abundant 3*d* metal complexes supported by tetraaza macrocycles. The previously discussed alkynyl chemistry is primarily based on 4*d* and 5*d* metals, with only a few examples of 3*d* metals, more specifically based on Fe [14,50] and Mn [15]. First row transition metals originally gained popularity for their rich coordination chemistry developed to study bioinorganic modelling [51,52]. Use of a *hard* base as the supporting ligand in place of the soft polarizable ligands, previously mentioned, could result in different reactivity and applications for metal alkynyl species. When our laboratory began looking into Fe^{III}(cyclam) alkynyls in 2010 [53], examples of M(cyclam) alkynyl chemistry were restricted to a few Cr(III) bis-alkynyl compounds in two publications from the laboratories of Wagenknecht [54] and Nishi [55] and a dissertation chapter by Berben [3]. In less than 10 years, this family of compounds has been expanded to include metals such as Cr, Fe, Co, and Ni coordinated to simple alkynyls, cross-conjugated alkynyls, like *gem*-DEE (*geminal*-diethynyleneethene), and simple alkynyl chromophores. The majority of this review will discuss both the synthesis and structural characterizations of these compounds. It is worth noting that the scope of cyclam-based organometallic chemistry remains very limited. Besides the metal alkynyl chemistry described herein, Martins and co-workers have investigated extensively the $Zr^{IV}(R_2cyclam)X_2$ type compounds, where R is *N* benzyl / allyl susbstitutent at 1- and 8- positions, 4- and 11-nitrogen are amido (deprotonated), and X can be halide or alkyl [56-59]. Among many Zr^{IV} species isolated are mono- and bis-phenylacetylide complexes based on $Zr^{IV}(Bn_2cyclam)$ [59], though the X-ray structures of these compounds were not established.

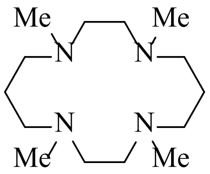
There are many derivatives of cyclam, both *N*- and *C*-substituted, available in literature. It is well established that the coordination chemistry of TMC (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, Chart 1) is significantly different from that of cyclam [60], and alkynyl compounds based on M(TMC) should be unique as well. The *C*-substituted cyclams have been subject to intense scrutiny in recent years because of the CO_2 reduction activity for their Ni^{II} and $Co^{II/III}$ complexes [61,62]. Particularly attractive are the M(HMC) complexes (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, Chart 1) due to the facile and inexpensive ligand synthesis. A number of Co(III) and Cr(III) alkynyl complexes of DMC (5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), HMC and MPC (4,14-Dimethyl-7,12-di-p-tolyl-1,4,8,11-tetraazacyclo-tetradecane) are described herein. The capacity of the 1,4,8,11-

tetraazacyclotetradeca-4,11-diene macrocycle to support metal alkynyl complexes has also been recently demonstrated [63].

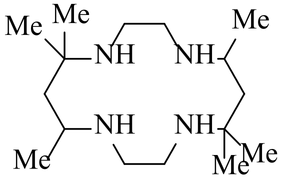
Chart 1. Tetraazamacrocycle Ligands



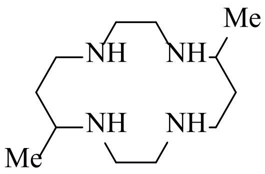
Cyclam
(1,4,8,11-tetraazacyclotetradecane)



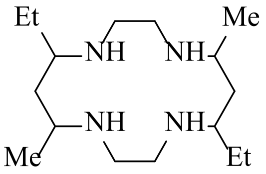
TMC
(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)



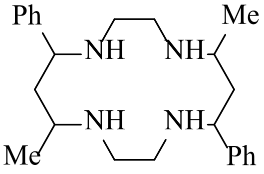
HMC
(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)



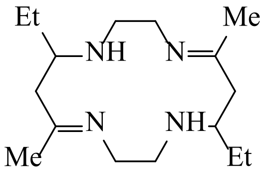
DMC
(5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)



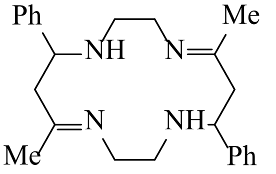
MEC
(5,12-diethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane)



MPC
(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane)



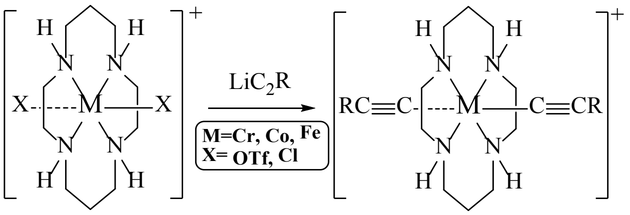
MED
(5,12-diethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)



MPD
(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)

2. Alkynyl Complexes of M(cyclam)

2.1. Symmetric bis-alkynyl compounds



Scheme 1. Synthesis of bis-alkynyl M(III) cyclam complexes

Traditionally, *trans*-M(cyclam)(C_2R)$_2$ type complexes are prepared through the reaction between [M(cyclam)(OTf)$_2$]$^+$ and LiC$_2$R (Scheme 1). Berben first applied this technique to prepare several [Cr(cyclam)(C_2R)$_2$]$^+$ species (R= -SiMe$_3$ and -C$_6$H$_4$-3-C$_2$H) [3]. Wagenknecht *et al.* further expanded on this class of symmetric alkynyl compounds with R as -Ph, -C$_6$H$_4$-4-CH$_3$

and -C_6H_4-4-CF_3 [54], R as -C_6H_4-4-F, cyclohexyl, 1-naphthalenyl and 9-phenanthrenyl [64] and -C_6F_5 [65]. Further experiments carried out by Wagenknecht *et al.* revealed ways to i) suppress hydroamination byproducts formed from deprotonation of the –NH groups on the cyclam ring by replacing *n*-BuLi with lithium diisopropylamide [66], and ii) enhance the yields of *cis*-isomer with the use of diethyl ether in place of THF [64]. Analogous Cr^{III}(cyclam) complexes bearing cross-conjugated *geminal*-diethynylethene (*gem*-DEE) type ligands were prepared from the reactions between $[Cr(cyclam)(OTf)_2]^+$ and Li(*gem*-DEE) through a collaboration between our lab and Wagenknecht [67]. Contemporary to the work of Wagenknecht, Nishijo and coworkers prepared a series of $[Cr(cyclam)(C_2Ar)_2]^+$ (Ar = thiophene, 6-methoxynaphthalene and tetrathiafulvalene (TTF)) and investigated the weak ferromagnetism therein [55,68-72]. Similar reactivity is observed for $[Fe(cyclam)(OTf)_2]^+$ and $[Co(cyclam)(OTf)_2]^+$, which upon treatment with LiC_2R afforded $[Fe(cyclam)(C_2R)_2]^+$ with R as -Ph, -Si^iPr_3 (structure shown in Figure 1), -C_2SiMe_3, -C_4SiMe_3 and -Fc [53,73], and, $[Co(cyclam)(C_2R)_2]^+$ with R as -CF_3, -Fc, -Ph, -C_6H_4-4-CH_3, -C_6H_4-4-CN and -C_6H_4-4-CF_3, respectively [74]. The products of the above mentioned reactions are predominantly observed in the *trans*-isomer form, despite the fact that the $[M(cyclam)(OTf)_2]^+$ starting materials are generally a mixture of *trans*-(minor) and *cis*-(major) isomers. These reactions utilize alkynyl lithium reagents and are an effective route to form symmetric $[M(cyclam)(C_2R)_2]^+$.

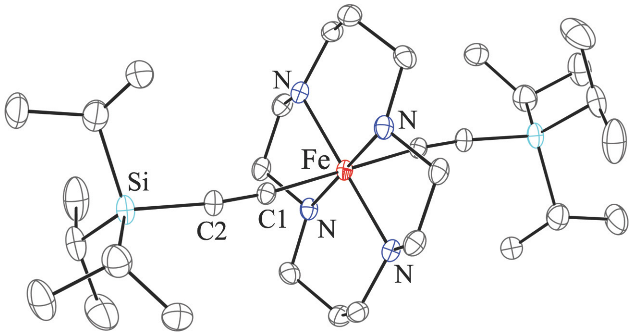
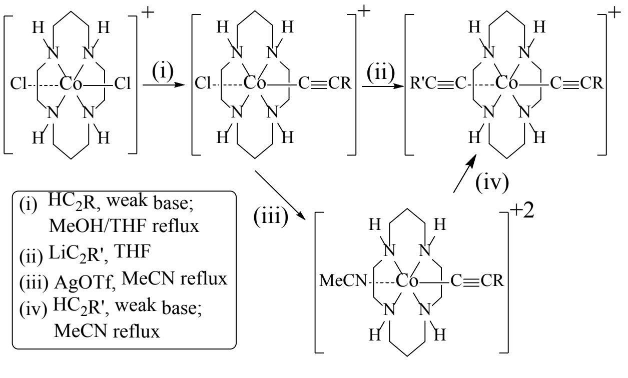


Figure 1. Molecular structure of $[\mathrm{Fe(cyclam)(C_2Si^{\mathit{i}}Pr_3)_2}]^+$ (generated from CCDC 844147, originally reported in Ref. [53]).

On the other hand, selective formation of mono-alkynyl species, for example $[\mathrm{M(cyclam)(C_2R)X}]^+$, has remained elusive for the majority of 3*d* metals. The exceptions are currently limited to $\mathrm{Co^{III}}$(cyclam). Synthesis of *trans*-$[\mathrm{Co(cyclam)(C_2Ph)Cl}]\mathrm{Cl}$ was achieved through reaction of $\mathrm{HC_2Ph}$ and $[\mathrm{Co(cyclam)Cl_2}]\mathrm{Cl}$ in a weakly basic solution by Shores and coworkers (Scheme 2) [75]. Similar conditions were employed to produce *trans*-$[\mathrm{Co(cyclam)((C{\equiv}C)_{\mathit{m}}H)Cl}]^+$ ($m = 1 - 3$) through the reaction of $\mathrm{MeSiC_{2m}SiMe_3}$ with $[\mathrm{Co(cyclam)Cl_2}]\mathrm{Cl}$ [76], several *trans*-$[\mathrm{Co(cyclam)(C_2R)Cl}]^+$ type compounds (R = $\mathrm{-C_6H_4\text{-}4\text{-}NO_2}$ (structure shown in Figure 2), -Fc and $\mathrm{-C_6H_4\text{-}4\text{-}SC_2H_4SiMe_3}$) [77], as well as *trans*-$[\mathrm{Co(cyclam)(C_2C_6F_5)Cl}]^+$ and *trans*-$[\mathrm{Co(cyclam)(C_2C_6H_4\text{-}4\text{-}NMe_2)Cl}]^+$ [78,79]. The mild conditions required to alkynylate $\mathrm{Co^{III}}$(cyclam) has allowed for simple chromophores to be coupled to the metal center. These species include *trans*-$[\mathrm{Co(cyclam)(C_2Np)Cl}]^+$ (Np = naphthalene) [80], *trans*-$[\mathrm{Co(cyclam)(C_2ANT)Cl}]^+$ (ANT = anthracene) [80], and *trans*-$[\mathrm{Co(cyclam)(C_2NAP^{iPr})Cl}]^+$ ($\mathrm{NAP^{iPr}}$ = N-isopropyl-1,8-naphthalimide) [81].



Scheme 2. Stepwise synthesis of dissymmetric $\mathrm{Co^{III}}$(cyclam)-bis-alkynyl.

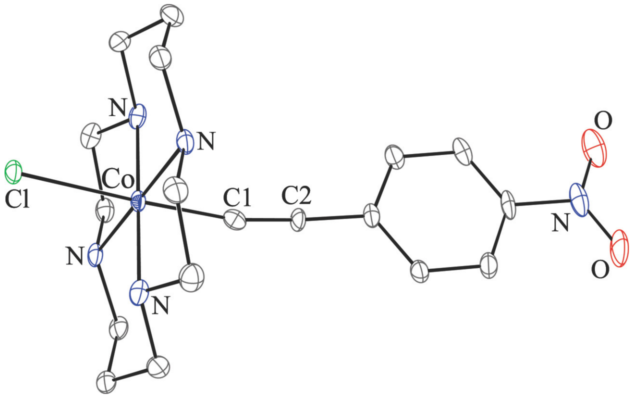


Figure 2. Molecular structure of *trans*-[Co(cyclam)(C_2-C_6H_4-4-NO_2)Cl]$^+$ (generated from CCDC 1411094, originally reported in Ref. [77]).

More recently, it was demonstrated that, with a Co^{III} species, stepwise formation of a bis-alkynyl species could be achieved under ambient conditions through a [Co(cyclam)(C_2R)(NCMe)]$^{2+}$ intermediate (Scheme 2). This reaction can also be employed to selectively form both symmetric and dissymmetric *trans*-alkynyl complexes; the dissymmetric species will be discussed later on [78,79]. Refluxing a MeCN solution containing [Co(cylam)($C_2C_6F_5$)Cl]Cl with AgOTf led to the formation of [Co(cyclam)($C_2C_6F_5$)(NCMe)](OTf)$_2$ and AgCl. Formation of [Co(cyclam)($C_2C_6F_5$)$_2$]OTf was accomplished through the reaction of [Co(cyclam)($C_2C_6F_5$)(NCMe)](OTf)$_2$ with excess $HC_2C_6F_5$ in the presence of Et_3N under reflux [79]. Similar conditions afforded [Co(cyclam)($C_2C_6H_4$-4-NMe_2)$_2$]OTf [79], and [Co(cyclam)(C_2Np)$_2$]OTf (structure shown in Figure 3) [80]. Unless specified otherwise, the compounds mentioned above adopt a *trans*-[M(cyclam)(C_2R)X]$^+$ and *trans*-[M(cyclam)(C_2R)$_2$]$^+$ pseudo-octahedral coordination geometry. Isomerically pure *cis*-[Cr(cyclam)(C_2Ph)$_2$]$^+$ was isolated from a solution containing the *trans*-counterpart through careful precipitation using THF and ether [64]. The M-C bond lengths observed in the symmetric *trans*-[M(cyclam)(C_2R)$_2$]$^+$ type compounds, 2.08 Å for Cr^{III}, 1.95Å for Fe^{III} and 1.90 Å for Co^{III}, are consistent with gradual decrease of covalent radii across the periodic table from left to right.

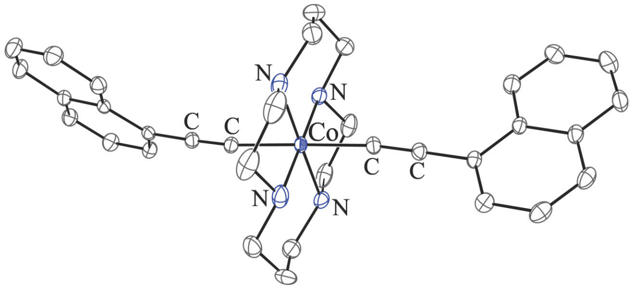


Figure 3. Molecular structure of *trans*-[Co(cyclam)($C_2Np)_2$]$^+$ (generated from CCDC 1590057, originally reported in Ref. [80]).

2.2. Dissymetric D-B-A alkynyl compounds

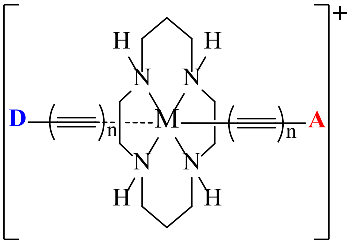


Chart 2. D-B-A type compounds based on M(III) cyclam.

Stepwise alkynylation unlocked the potential to form dissymmetric bis-alkynyl metal complexes. Reaction of *trans*-[Co(cyclam)(C_2Ph)Cl]$^+$ with LiC_2Ph and LiC_2SiMe_3 resulted in *trans*-[Co(cyclam)($C_2Ph)_2$]$^+$ [75] and *trans*-[Co(cyclam)(C_2Ph)(C_2SiMe_3)]$^+$ [82], respectively. The dissymmetric species, *trans*-[Co(cyclam)(C_2Ph)(C_2SiMe_3)]$^+$, is intriguing from the electronic point of view and provided a synthetic platform that was further expanded on to form a pseudo Donor-Bridge-Acceptor (D-B-A) species, *trans*-[Co(cyclam)(C_2-C_6H_4-4-NO_2)(C_2Ph)]$^+$ (structure shown in Figure 4). Formation of this complex was achieved through reaction of LiC_2Ph with *trans*-[Co(cyclam)(C_2-C_6H_4-4-NO_2)Cl]$^+$ [77]. However, these reactions suffered from low reaction yields and often resulted in scrambling to form both symmetric and dissymmetric products that were impractical to separate. Since then, two routes have been established to promote selective alkynylation i) the previously mentioned method, in which an intermediate species with a more labile leaving group is generated [78,79] and ii) cooling the lithiation to -78°C thereby kinetically promoting the formation of the dissymmetric *trans*-$[Co(cyclam)(C_2R)(C_2R')]Cl$ species [81]. Under the former conditions, formation of *trans*-$[Co(cyclam)(C_2C_6H_4\text{-}4\text{-}NMe_2)(C_2C_6F_5)]OTf$ and *trans*-$[Co(cyclam)(C_2C_6F_5)(C_2Ph)]OTf$ have been observed [78,79]. Utilizing the latter conditions, formation of the first true Co^{III} D-B-A species was realized. The addition of 1.1 equivalents of $LiC_2C_6H_4\text{-}4\text{-}NMe_2$ to 1 equivalent of *trans*-$[Co(cyclam)(C_2NAP^{iPr})Cl]^+$, at -78°C, results in selective formation of the dissymmetric *trans*-$[Co(cyclam)(C_2NAP^{iPr})(C_2C_6H_4\text{-}4\text{-}NMe_2)]^+$ species in 50% yield. This method was also utilized to synthesize *trans*-$[Co(cyclam)(C_2NAP^{iPr})(C_2TPA)]^+$, a panchromic D-B-A species (TPA = 4-*N,N*-bis(4-methoxyphenyl)aniline), and *trans*-$[Co(cyclam)(C_2NAP^{iPr})(C_2Ph)]^+$ [81]. These compounds are actively being probed to understand the dynamics of photo-induced electron-transfer in comparison to their Pt^{II} counterparts, *trans*-(4-ethynyl-N-octyl-1,8-naphthalimide)(N-(4-ethynyl-benzyl)-phenothiazine)$Pt(PBu_3)_2$ and *trans*-(4-ethynyl-N-octyl-1,8-naphthalimide)$(C_2Ph)Pt(PBu_3)_2$ [83-85].

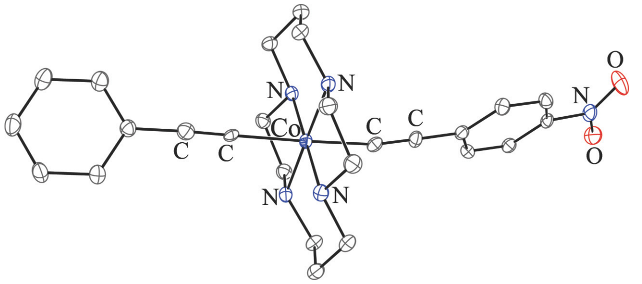


Figure 4. Molecular structure of *trans*-$[Co(cyclam)(C_2\text{-}C_6H_4\text{-}4\text{-}NO_2)(C_2Ph)Cl]^+$ (generated from CCDC 1411097, originally reported in Ref. [77]).

3. Alkynyl Complexes of M(cyclam′)

3.1 M(cyclam′)

While M(cyclam) alkynyl complexes are still being investigated, the more sterically crowded derivatives such as TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), DMD (5,12-dimethyl-1,4,8,11-tetraazacyclotetradiene), its reduced form DMC (5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), MPD (4,14-Dimethyl-7,12-di-p-tolyl-1,4,8,11-tetraazacyclo-tetradiene), its reduced form MPC (4,14-Dimethyl-7,12-di-p-tolyl-1,4,8,11-tetraazacyclo-tetradecane), HMD (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and its reduced form HMC (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) have also drawn interest for their differing structural and electrochemical properties when compared to M(cyclam) species. Alkynyl chemistry based on TMC was championed by our group: reaction between $[Ni(TMC)X]^+$ (X = Cl or OTf) and LiC_2R yielded a variety of $[Ni(TMC)(C_2R)]^+$ type complexes with R = $-SiMe_3$, $-Si^iPr_3$, -Ph (structure shown in Figure 5) and $-C_2H$ [86]. The facile synthesis coupled with the low cost of starting materials to synthesize the aforementioned alkyl substituted macrocycles give them a significant advantage over cyclam and TMC. Both MPD and HMD can readily be synthesized via a Schiff base condensation reaction between singly protonated ethylene diamine and the corresponding vinyl ketone [87], both of which are inexpensive reagents. Reduction of MPD or HMD by $NaBH_4$ in an alcoholic solvent resulted in MPC and HMC respectively, both in high yields. DMC is prepared similarly, albeit in lower yields [88].

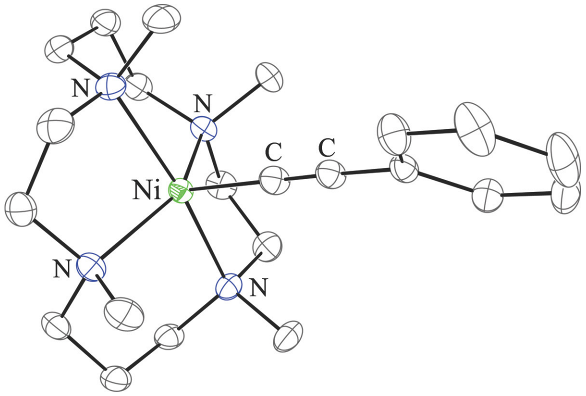
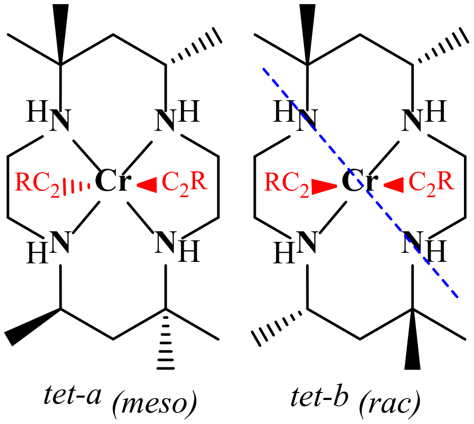


Figure 5. Molecular structure of $[Ni(TMC)(C_2Ph)]^+$ (generated from CCDC 1889854, originally reported in Ref. [86])

3.2 Mono/Bis-alkynyl Cr(cyclam′)

As mentioned previously, Cr(cyclam) alkynyl chemistry has been a fertile ground with a variety of interesting outcomes. Recent work has focused on elucidating how the configuration, *cis* vs *trans,* affects its spectral properties such as absorption and emission [80,89,90]. In contrast to cyclam, the steric crowding caused by the *C*-substitution in HMC ligand and DMC ligand results in intriguing coordination geometry. For example, the reaction of Cr^{III} with HMC results in the formation of two easily separated isomers: the more soluble *trans*-$[Cr^{III}(HMC)Cl_2]Cl$ and the less soluble *cis*-$[Cr^{III}(HMC)Cl_2]Cl$ [91]. The *trans* and *cis* configurations are primarily dictated by the stereochemistry of the ligand with *meso*-HMC forming *trans* product and *rac*-HMC *cis* product [89]. Furthermore, it has been demonstrated that the respective *cis/trans* configuration of the starting material is retained upon alkynylation [80,89,92]. The two stereoisomers can readily be differentiated, where the *rac*-HMC is commonly folded across the nitrogen plane and the *meso*-HMC is planar (Scheme 3). While under certain reaction conditions the *rac*-HMC ligand can rearrange from folded to planar, it cannot rearrange to form the *meso*-HMC [93-95]. Similarly, *trans*-$[Cr^{III}(DMC)Cl_2]Cl$ and *cis*-$[Cr^{III}(DMC)Cl_2]Cl$ can also be prepared and readily separated [96], however the stereochemistry observed in the starting materials is not necessarily retained upon alkynylation [90].



Scheme 3. Stereoisomers of HMC; the folding axis for *cis*–[Cr(*rac*–HMC)$(C_2R)_2$]Cl complexes is shown as the blue dashed line.

When reacted with LiC_2R *trans*-[Cr^{III}(*meso*-HMC)Cl_2]Cl and *cis*-[Cr^{III}(*rac*-HMC)Cl_2]Cl result in the formation of *trans*-[Cr^{III}(*meso*-HMC)$(C_2R)_2]^+$ and *cis*-[Cr^{III}(*rac*-HMC)$(C_2R')_2]^+$ (R = -Ph and -C_2H; R' = -Ph and -C_2TMS), respectively [89]. The crystal structure of *cis*-[Cr(HMC)$(C_4TMS)_2$]Cl is shown in Figure 6. Analogous to the alkynyl chemistry of Cr(HMC), the product stereochemistry of the reaction between Cr^{III}(DMC)Cl_3 and LiC_4TMS/H is dependent on the starting material, with *cis*-[Cr^{III}(DMC)Cl_2]Cl forming *cis*-[Cr^{III}(DMC)$(C_4TMS)_2$]Cl and *trans*-[Cr^{III}(DMC)Cl_2]Cl forming *trans*-[Cr^{III}(DMC)$(C_4H)_2$]Cl. However, unlike with Cr^{III}(HMC), isomerization of *cis*-[Cr^{III}(DMC)$(C_4TMS)_2$]Cl to the thermodynamically favored *trans*-[Cr^{III}(DMC)$(C_4H)_2$]Cl could be observed in polar solvents via UV-Vis and ESI-MS [90]. In the presence of bulkier alkynes, the reaction of LiC_2R with *cis*-[Cr^{III}(DMC)Cl_2]Cl and *trans*-[Cr^{III}(DMC)Cl_2]Cl both resulted in the formation of *trans*-[Cr^{III}(DMC)$(C_2R)_2$]Cl (R = -Ph and -Fc (structure shown in Figure 7)), producing lower yields when starting from the *cis* species [90].

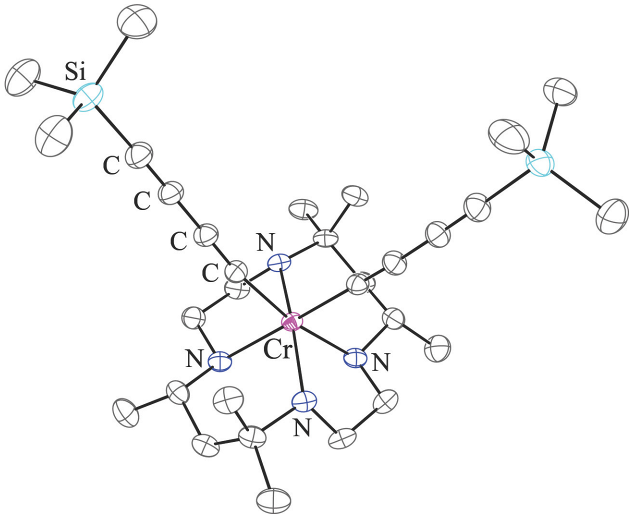


Figure 6. Molecular structure of *cis*-[Cr^{III}(HMC)(C$_4$TMS)$_2$]$^+$ (generated from CCDC 1507917, originally reported in Ref. [89])

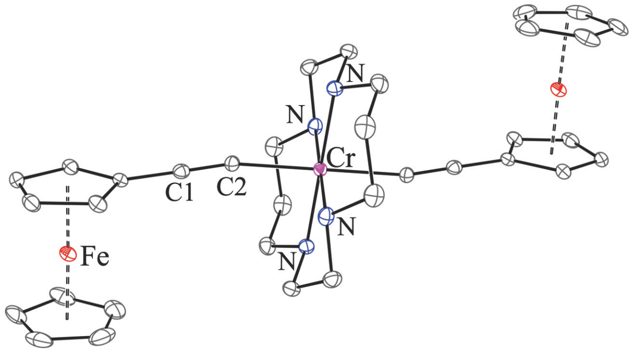


Figure 7. Molecular structure of *trans*-[Cr^{III}(DMC)(C$_2$Fc)$_2$]$^+$ (generated from CCDC 1531350, originally reported in Ref. [90])

Recent efforts have shifted focus towards the isolation of mono-alkynyl species [Cr(HMC)(C$_2$R)Cl]Cl, which would be the obvious precursor for the dissymmetric [Cr(HMC)(C$_2$R)(C$_2$R')]$^+$ type complexes. Early experimental work has shown that formation of both *cis*-[Cr(HMC)(C$_2$Ph)Cl]$^+$ and *trans*-[Cr(HMC)(C$_2$Ph)Cl]$^+$ can be achieved through controlled acid degradation of *cis*-[Cr(HMC)(C$_2$Ph)$_2$]$^+$ and *trans*-[Cr(HMC)(C$_2$Ph)$_2$]$^+$, respectively [92]. While formation of dissymmetric *cis*-[M(cyclam′)(C$_2$R)(C$_2$R′)]$^+$ has yet to be achieved, this early work represents a considerable stepping stone towards making these types of compounds.

3.3 Mono/Bis-alkynyl Co(cyclam′)

The success in isolating *cis*-Cr(cyclam′) alkynyl species [80,89,90] raised the possibility of preparing *cis*-Co(cyclam′) alkynyl species in a stepwise fashion. Use of an electrochemically active metal center, like Co, in place of electrochemically silent Cr would allow for the study of how altering the stereochemistry could affect the cyclic voltammetry, which will be discussed later. Recently, it was demonstrated that Co alkynyl species supported by MPD, its reduced form MPC, and the less sterically bulky DMC could be used to form both mono and bis-alkynyl species. Synthesis of mono-alkynyl complexes *trans*-[Co(MPD)(C_2Ph)Cl]Cl, *trans*-[Co(MPC)(C_2Ph)Cl]Cl, and *trans*-[Co(DMC)(C_2Ph)Cl]Cl were achieved under weak base conditions [63,97]. Formation of *trans*-[Co(MPD)(C_2Ph)$_2$]Cl and *trans*-[Co(MPC)(C_2Ph)$_2$]Cl was achieved in the presence of excess LiC_2Ph [63]. The stepwise weak-base reaction pathway, discussed previously [79], was utilized to form *trans*-[Co(DMC)(C_2Ph)$_2$]OTf via the *in situ* reaction of *trans*-[Co(DMC)(C_2Ph)Cl]Cl with AgOTf, followed by the addition of HC_2Ph and Et_3N [97]. While *cis*-Co(cyclam′) alkynyl species remain elusive, the ability for *C*-substituted macrocycles to support Co proves promising. Additionally, formation of *trans*-[Co(MPD)(C_2Ph)Cl]Cl (structure shown in Figure 8) and *trans*-[Co(MPD)(C_2Ph)$_2$]Cl is noteworthy as they are the first examples of metal acetylide complexes based on a 1,4,7,11-tetra-azacyclotetradeca-4,11-diene type ligand [63]. When comparing *trans*-[Co(MPC)(C_2Ph)$_2$]Cl, *trans*-[Co(DMC)(C_2Ph)$_2$]OTf, and *trans*-[Co(cyclam)(C_2Ph)$_2$]Cl, there is a noticeable trend tied to increased *C*-substitution of the macrocycle and relative length of the both the Co-N bond lengths and the Co-C bonds lengths. The most substituted macrocycle, *trans*-[Co(MPC)(C_2Ph)$_2$]Cl has the longest Co-N bond, 2.004(2)Å, and the shortest Co-C bond, 1.924(3)Å [63]. By comparison, *trans*-[Co(cyclam)(C_2Ph)$_2$]Cl has the shortest Co-N bond length of 1.983(2) and the longest Co-C bond length of 2.001(3) [75]. *trans*-[Co(DMC)(C_2Ph)$_2$]OTf falls in the middle with an average Co-N bond length of 1.992(2) Å and a Co-C bond length of 1.927(2) Å [97]. While these metric parameters differ slightly from the unsubstituted cyclam variant, they are within the range of previously reported Co-N and Co-C bond lengths [77-80,98].

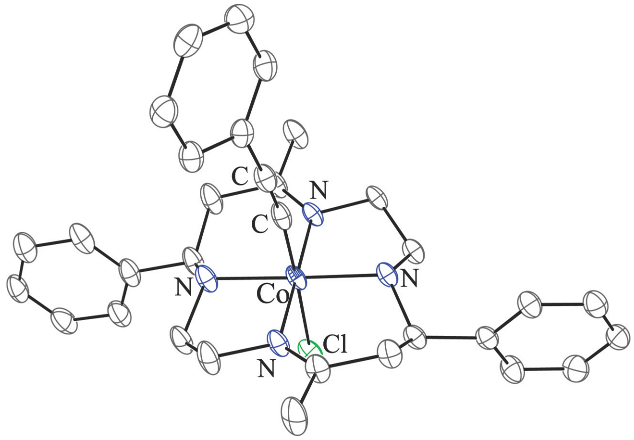


Figure 8. Molecular structure of *trans*-[Co(MPD)(C_2Ph)Cl]$^+$ (generated from CCDC 1872102, originally reported in Ref. [63])

4. Physical and Material Properties

4.1 Spectroscopic-Emission

The characteristic absorption spectra of the compounds discussed herein feature LMCT bands in the UV region and *d-d* transition bands of weak to modest intensity in the visible region, with the weakest *d-d* transitions occurring in M(cyclam′) complexes with aryl substituted macrocycles [63,99]. The LMCT bands are attributed to both the N centers and C≡C bonds [100]. Highly structured *d-d* bands were observed for *cis/trans*-$[Cr(HMC)(C_2Ph)_2]^+$ and for *cis/trans*-$[Cr(HMC)(C_4R)_2]^+$ (R= H or TMS), which were attributed to vibronic coupling. The vibronic progressions for the former ranged from 800-900 cm^{-1} and likely arose from aromatic C-H bending, N-H bending, and CH_2 rocking; the vibronic progressions of the latter ranged from 2023-1971 cm^{-1} and correlated well with the experimentally observed C≡C stretches [89]. Until recently, the only cyclam species that displayed emission were Cr^{III} based, which possess phosphorescence originating from the ligand-field excitations [66,67,80,89,90]. The *trans*-$[Cr(cyclam)(C_2R)_2]^+$ type compounds were found to emit from both the ^2E_g and $^2T_{1g}$ states with a lifetime of about 1 μs [66]. A similar trend was also observed for several $[Cr(HMC)(C_2R)_2]^+$ and $[Cr(DMC)(C_2R)_2]^+$ type compounds [80,89,90]. The *trans*-$[Cr(cyclam)($*gem*-DEE$)_2]^+$ type compounds were found to phosphoresce as well but only from the ^2E_g state [67]. As shown in Table 1, the *cis*-Cr^{III} species tend to have a shorter lifetime that is difficult to measure at room temperature. This is attributed to additional geometric strain caused by the *cis* configuration, which favours nonradiative decay in comparison to its *trans* counterpart [101]. Comparison of the λ_{em} of the *cis* and *trans* pairings, for example *cis*-$[Cr(HMC)(C_2Ph)_2]^+$ vs. *trans*-$[Cr(HMC)(C_2Ph)_2]^+$ or *cis*-$[Cr(HMC)(C_2Np)_2]^+$ vs. *trans*-$[Cr(HMC)(C_2Np)_2]^+$, reveals that the λ_{em} of the *cis* species is shifted to lower energy, which is likely a consequence of differing stereochemistry between the *cis* and *trans* species (Table 1).

Table 1. Photophysical Data for Cr(cyclam′) Complexes

	Room Temperature[a]			**Frozen Glass**[b/b*]		
	λ_{ex} (nm)	λ_{em} (nm)	τ (μs)	λ_{ex} (nm)	λ_{em} (nm)	τ (μs)
cis-$[Cr(HMC)(C_2Ph)_2]^{+}$ [c]	424	764	-	425	763	212
trans-$[Cr(HMC)(C_2Ph)_2]^{+}$ [c]	425	746	-	425	744	469
cis-$[Cr(HMC)(C_4TMS)_2]^{+}$ [c]	402	771	-	443	777	129
trans-$[Cr(HMC)(C_4H)_2]^{+}$ [c]	402	746	-	405	771	455

cis-[Cr(HMC)(C$_2$Np)$_2$]$^+$ [d]	430	777	-	430	777	97
trans-[Cr(HMC)(C$_2$Np)$_2$]$^+$ [d]	445	747	218	445	747	447
				445	727	362
cis-[Cr(DMC)(C$_4$TMS)$_2$]$^+$ [e]	427	777	68	427	780	160
trans-[Cr(DMC)(C$_4$H)$_2$]$^+$ [e]	403	755	113	403	777	358
trans-[Cr(DMC)(C$_2$Ph)$_2$]$^+$ [e]	420	750	95	424	745	380
				424	728	222
trans-[Cr(cyclam)(C$_2$Ph)$_2$]$^+$ [f]	380	748	225	430*	745*	343*
trans-[Cr(cyclam)(C$_2$Np)$_2$]$^+$ [f]	440	749	250	360*	748*	343*

[a] In degassed acetonitrile. [b] Dissolved in 4:1 EtOH:MeOH glass, taken at 77K. [b*] Indicates dissolved in H$_2$O/DMSO glass, taken at 77K.. [c] From ref [89]. [d] From ref [80]. [e] From ref [90]. [f] From ref [66]. Cyclam′ refers to *C*-substituted derivatives of cyclam.

Use of a fluorophore ligand in conjunction with Cr^{III} was theorized to alter the emission properties. However, it was found for *cis*-[Cr(HMC)(C$_2$Np)$_2$]Cl [80], *trans*-[Cr(HMC)(C$_2$Np)$_2$]Cl [80], and *trans*-[Cr(cyclam)(C$_2$Np)$_2$]Cl [66] that the emission was dominated by the excited states at the Cr^{III} metal center. Figure 9 provides a direct visual comparison between the emission of free Me$_3$SiC$_2$Np, *trans*-[Cr(HMC)(C$_2$Np)$_2$]Cl, and *trans*-[Co(cyclam)(C$_2$Np)$_2$]Cl, where the organic chromophore emission dominates when coordinated to Co(cyclam) [80].

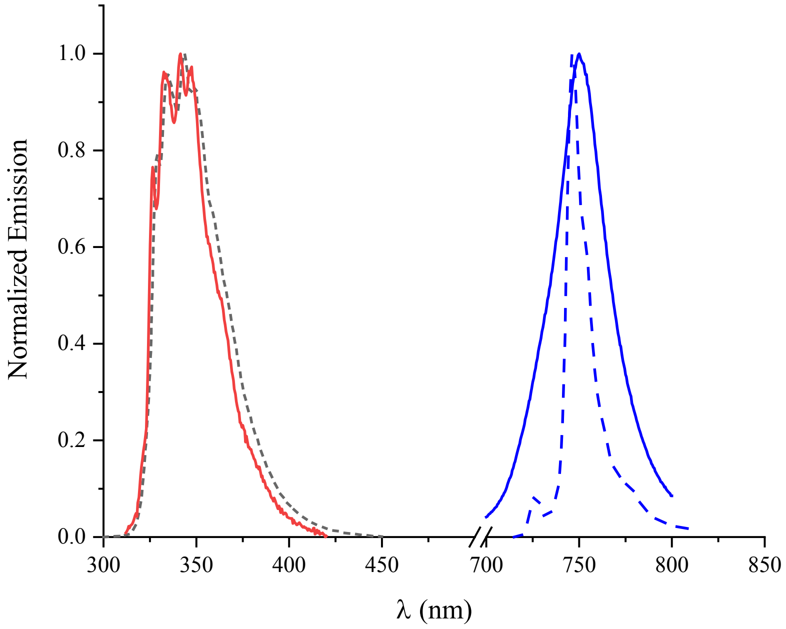


Figure 9. Normalized emission spectra for [Co(cyclam)(C_2Np)$_2$]OTf (red) in DCM at RT, free ligand Me_3SiC_2Np (black) in DCM at RT and *trans*-[Cr(HMC)(C_2Np)$_2$]Cl emission (blue) in 4:1 EtOH:MeOH at RT (solid) and 77K (dash), plotted using data from Ref. [80].

In parallel to Cr^{III} overshadowing the chromophore emission, quenching effects were observed for Ru_2(DMBA)$_4$(C_2Ar)$_2$ (Ar = 1-naphthalene (Np), 9-anthracene (ANT), *N*-isopropyl-1, 8-naphthalimide (NAP^{iPr}), *N*-methyl-1, 8-naphthalimide (NAP^{Me})) where the fluorescence of the free ligands (listed in Table 2) were completely quenched [102]. This led our laboratory to perturb the emission properties of alkynyl chromophores when coordinated to a non-emissive metal center like Co^{III}(cyclam). While florescence quenching by the metal center is still apparent (Table 2) for Co-bound Me_3SiC_2ANT [80], Me_3SiC_2Np [80], and HC_2NAP^{iPr} [81], it is notable that emission is observed for this previously non-emissive Co species. Furthermore, the distinct shift in emission, hypsochromic for [Co(cyclam)(C_2ANT)Cl]Cl [80] and bathochromic for [Co(cyclam)(C_2NAP^{iPr})(C_2R)]Cl [81], suggests that coordination to Co^{III} alters the electronic ground state of the chromophore ligand (Table 2). Emission, based on Φ, tended to be significantly stronger for the panchromic Co^{III}(cyclam) complexes such as [Co(cyclam)(C_2NAP^{iPr})$_2$]Cl and [Co(cyclam)(C_2NAP^{iPr})(C_2TPA)]Cl than the singly chromophore containing species like [Co(cyclam)(C_2NAP^{iPr})Cl]Cl and [Co(cyclam)(C_2NAP^{iPr})(C_2Ph)]Cl [81]. The Φ for [Co(cyclam)(C_2Np)Cl]Cl and [Co(cyclam)(C_2Np)$_2$]OTf could not be determined due to instrument limitations [80].

Table 2. Photophysical Data for Co(cyclam) Complexes & Respective Chromophore Ligands

	λ_{ex} (nm)	λ_{em} (nm)	Φ
trans-[Co(cyclam)(C_2ANT)Cl]$^{+}$ [a]	263	408	0.022
Me_3SiC_2ANT [a]	263	414	0.633
trans-[Co(cyclam)(C_2Np)Cl]$^{+}$ [a]	298	342	-

trans-[Co(cyclam)(C_2Np)$_2$]$^{+}$ [a]	234	341.5	-
Me_3SiC_2Np [a]	290	343.5	-
trans-[Co(cyclam)(C_2NAP^{iPr})Cl]$^{+}$ [b]	400	438	0.0066
trans-Co(cyclam)(C_2NAP^{iPr})(C_2Ph)]$^{+}$ [b]	400	437	0.0043
trans-[Co(cyclam)(C_2NAP^{iPr})$_2$]$^{+}$ [b]	400	439	0.0143
trans-[Co(cyclam)(C_2NAP^{iPr})($C_2C_6H_4$-4-NMe_2)]$^{+}$ [b]	400	439	0.0068
trans-[Co(cyclam)(C_2NAP^{iPr})(C_2TPA)]$^{+}$ [b]	400	461	0.0104
HC_2NAP^{iPr} [b]	340	401	0.423

All photophysical data collected in CH_2Cl_2 at room temperature. [a]From ref [80]. [b]From ref [81].

4.2 Voltammetry

An important criterion for metal alkynyl species functioning as molecular wires is the ability to undergo multiple reversible redox processes [31,103,104]. Some of the most notable examples include $[Cp(PPh_3)_2Ru]_2(\mu\text{-}C_4)$, which exhibits four stepwise one-electron oxidations [16], $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$, which has a pair of one-electron oxidations and a pair of one-electron reductions [29], and $Ru_2(ap)_4(C_2C_6H_4P(O)(OH)_2)$ which functions as the active species in a highly robust flash memory device [44]. Furthermore, compounds containing multiple reversible one-electron couples are of interest because they allow for the study of intervalence charge transfer processes between two metal centers across a polyyn-diyl bridge resulting in mixed valence compounds such as $(M^{+n}\text{-}(C{\equiv}C)_m\text{-}M^{+(n+1)}$ [105,106]. Specifically, using voltammetric and spectroelectrochemical studies, our group demonstrated significant electronic coupling between capping Ru_2 units in $[Ru_2(Xap)_4]_2(\mu\text{-}C_{2m})$ with *m* ranging from 2-10 [36]. However, the electrochemical behaviors of 3*d* M-cyclam compounds are vastly different from 4*d* and 5*d* metal compounds. Generally, Co^{III} species display multiple irreversible couples [74,75,77,82] and Cr^{III} species are redox inactive [54,67].

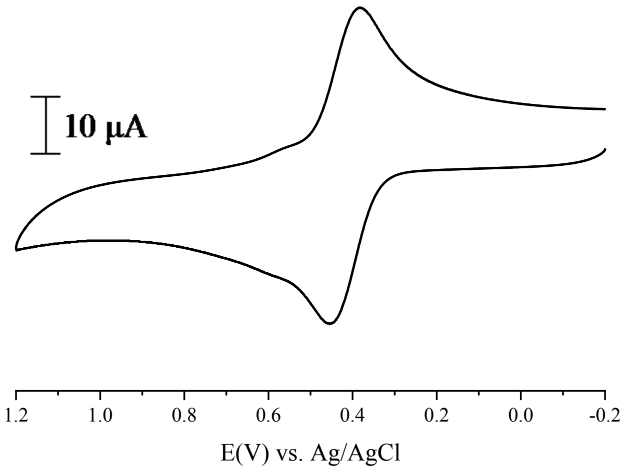


Figure 10. Cyclic voltammogram of a 1.0 mM solution of *trans*-[Cr^{III}(DMC)($C_2Fc)_2$]ClO_4 in a 0.2 M solution of Bu_4NPF_6 in acetonitrile at scan rate of 100 mV/s), plotted using data from Ref. [90].

To study the Fc-Fc coupling across a 3*d* metal center, *trans*-[M^{III}(cyclam)($C_2Fc)_2$]$^+$ (M = Fe, Cr, and Co) type compounds have been prepared and their voltammetric responses analyzed using the Richardson and Taube method [107]; the two ferrocenyl capping groups are only weakly coupled across the C_2-M^{III}-C_2 bridge [67] [73,74]. To determine the effect of the supporting macrocycle on coupling, *trans*-[Cr^{III}(DMC)($C_2Fc)_2$]ClO_4 was synthesized and studied electrochemically. Figure 10 shows the observed quasi-reversible 2e^- oxidation for *trans*-[Cr^{III}(DMC)($C_2Fc)_2$]ClO_4 with an estimated ΔE value of 50 mV based on Richardson-Taube method, suggesting a weak coupling between the two ferrocenyl groups [90].

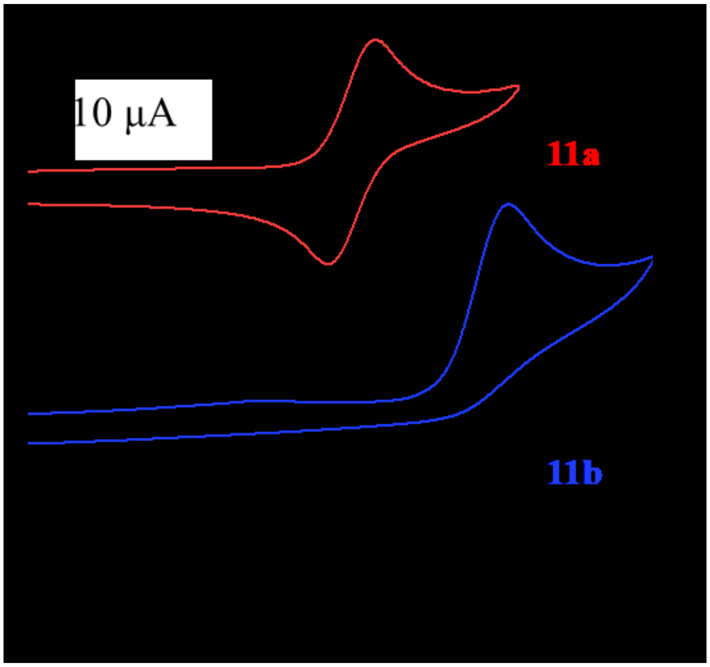


Figure 11. Cyclic voltammograms of a 1.0 mM solution of [Co^{III}(cyclam)($C_2C_6F_5$)$_2$]OTf (**11a**) and [Co^{III}(cyclam)($C_2C_6H_4$-4-NMe$_2$)$_2$]OTf (**11b**) in a 0.2 M solution of Bu_4NPF_6 in DCM at scan rate of 100 mV/s, plotted using data from Ref. [79].

The only cyclam complexes that consistently display reversible metal-center redox couples are Fe^{III} species [53,73,108], all of which undergo a one electron reduction. It was noted recently that Co^{III}(cyclam) species bearing electron withdrawing ligands, such as pentafluorophenylacetylide [65,79], and trifluoropropynyl [65,109], underwent reversible one electron reductions and was attributed to the π-accepting nature of the acetylide ligand. Figure 11 shows a direct comparison of the Co(+3/+2) couple for [Co^{III}(cyclam)($C_2C_6F_5$)$_2$]OTf (**11a**) versus [Co^{III}(cyclam)($C_2C_6H_4$-4-NMe$_2$)$_2$]OTf (**11b**). Coordination of the electron withdrawing pentafluorophenylacetylide ligand to Co(cyclam) resulted in a reversible Co(+3/+2) couple that occurs at a more positive potential than that of the irreversible Co(+3/+2) couple observed for the Co(cyclam) complex bearing the electron donating 4-ethynyl-*N,N*-dimethylaniline ligand. A quasi-reversible reduction attributed to Co was also observed for [Co(MPC)(C_2Ph)$_2$]Cl, but in this case was thought to be a result of increased electron density on the metal center from MPC [63]. These observations suggest that reversible electrochemical couples can be achieved in 3*d*-M cyclam species with careful attenuation of both the axial alkynyl and supporting macrocyle ligands.

4.3 Magnetism

Bis-alkynyl complexes of Co(III) are always diamagnetic, while those of Fe(III) are of an S = 1/2 ground state. Bis-alkynyl complexes of Cr(cyclam) and Cr(cyclam') are consistently paramagnetic with an S = 3/2 ground state. Temperature dependence of magnetic susceptibility between 5 – 300 K were examined for several $[Cr^{III}(HMC)(C_2R)_2]^+$ complexes, which is consistent with a zero-field splitting (ZFS) of an S = 3/2 species, and a D of *ca.* -0.5 cm^{-1} [89]. Using 3-Th (3-thiophene) and TTF (tetrathiafulvalene) containing acetylides, Nishijo and coworkers demonstrated the formation of 1-D and 2-D coordination polymers based on $[Cr^{III}(cyclam)(C_2R)_2]^+$, which exhibit interesting ferri- and ferro-magnetic ordering through the π-π stacking of TTF rings [55,68-72]. Room temperature magnetic susceptibility measurements of $[Ni(TMC)(C_2R)]^+$ type compounds yielded effective magnetic moments consistent with an S = 1 ground state, which was further corroborated by both CASSCF and density functional theory calculations [86].

5. Conclusions and Outlook

The strategies applied here to synthesize metal alkynyl species supported by tetraaza macrocyclic ligands mainly employ lithiation or weak base dehydrohalogenation techniques. Therefore, the main obstacle for 3*d* metal alkynyl complexes is the development of alternative synthetic routes with both improved yields and selectivity. Recently, our lab was able to selectively synthesize dissymmetric $[Co(cyclam)(C_2R)(C_2R')]^+$ type compounds utilizing a triflate intermediate [79]. However, this method only works for a limited scope of alkynyl compounds and has not been proven as a successful method with more complex ligands. This led us to revaluate lithiation techniques as a means to form $[Co(cyclam)(C_2R)(C_2R')]^+$ compounds. Early attempts were plagued by low reaction yields as a result of poor selectivity, as products could include the symmetric $[Co(cyclam)(C_2R)_2]^+$ and $[Co(cyclam)(C_2R')_2]^+$ in addition to the target compound [77]. This issue has since been circumvented by cooling the lithiation reaction down to -78°C [81]. These approaches are restricted to complexes based on Co^{III}(cyclam) and Co^{III} (DMC) and are unsuccessful thus far for other 3*d* metals.

Other synthetic strategies that are being investigated include i) organo-tin activated arylalkynyls, ii) Hagihara coupling (CuI / organic amine) as a variation of the dehydrohalogenation reactions, and iii) controlled acid degradation of symmetric M acetylides. Lewis and coworkers employed organo-tin activated arylalkynyls to numerous *trans*-bisalkynyl Ru(II) compounds [8], including dissymmetric *trans*-$[(dppe)_2Ru(C_2Ar)(C_2Ar')]$ (dppe = 1,2-bis(diphenylphosphino)ethane) [6]. The Hagihara dehydrohalogenation reaction, has been effectively utilized to form Pt^{II} , Pd^{II} and Ni^{II} alkynyl compounds [85,110,111]. We speculate that the Hagihara reaction could be a good fit for M(cyclam') alkynyl compounds due to their robust nature towards organic amines [112]. This is further substantiated by the work done on arylalkynyls of cobalamin that were prepared using Hagihara coupling conditions [113]. Finally, the prospect of using controlled acid degradation to isolate new mono-alkynyl Cr(HMC) species shows promise. While only simple alkynyl species were studied, namely $[Cr(HMC)(C_2Ph)Cl]^+$, this method is relatively new and work is actively being done to isolate more complex species [92].

In looking towards the future, the synthetic strategies mentioned above will be instrumental in developing new 3*d* metal alkynyl species for studying electron transfer processes. Synthesis of the first true D-B-A species, with a Co^{III}(cyclam) bridge, has been achieved and is actively being probed to understand the role of the bridging metal center [81]. It is important to acknowledge that all the M(cyclam) and M(cyclam′) discussed herein (M = Cr, Fe, and Co) are stable under an ambient atmosphere, an essential quality for optoelectronic devices. Additionally, use of earth abundant 3*d* metals paired with the inexpensive and facile synthesis of cyclam′ derivatives continues to make these complexes a valuable target for further development.

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Graphic Abstract