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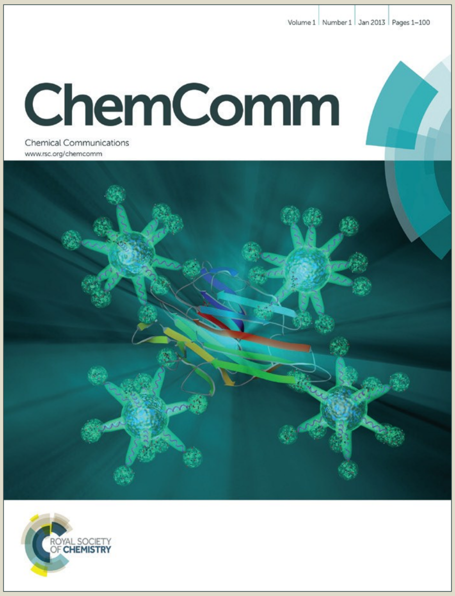

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A Sustainable Metal Alkynyl Chemistry: 3*d* Metals and Polyaza Macrocyclic Ligands

Tong Ren

Table of Contents Entry:

This article describes the recent development of sustainable metal-alkynyl chemistry based on the combination of 3*d* metals and polyaza macrocycles.

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Brief Biography:

Tong Ren received his B.S. and M.S. in chemistry in China (1981 and 1984) and his Ph.D. in inorganic chemistry from Texas A&M University under the supervision of F. Al Cotton (1990). He held postdoctoral appointments at Texas A&M University with Cotton (1991) and MIT with Stephen J. Lippard (1991–3). He was an assistant professor at Florida Institute of Technology (1993-8), an associate professor at the University of Miami (1998-2005), and has been a full professor at Purdue University since 2005. Research interests in his laboratory include organometallic molecular wires, molecular electronic devices, and catalyzed oxidation reactions.

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A Sustainable Metal Alkynyl Chemistry: 3*d* Metals and Polyaza Macrocyclic Ligands

Tong Ren[*]

Abstract: Described in this article is the chemistry of 3*d* metal alkynyls based on polyaza macrocyclic ligands - an emerging area of alkynyl chemistry that has been previously dominated by 4*d* / 5*d* metals with soft ligands. Both the abundances of 3*d* metals and inexpensive nature of 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 undergo the second alkynylation reaction to afford the dissymmetric *trans*-$[Co(cyclam)(C_2R)(C_2R')]^+$ type compounds. Similar alkynylation chemistry with complexes of cyclam derivatives TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and HMC (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has been demonstrated with the studies of $[Ni(TMC)(C_2R)]^+$ and *trans-/cis*-$[Cr(HMC)(C_2R)_2]^+$. Me_3TACN (1,4,7-*N,N',N''*-trimethyl-1,4,7-triazacyclononane) is also a proven ligand in supporting transition metal alkynyls. The *trans*-$[M(cyclam)(C_2D)(C_2A)]^+$ type compounds (D and A are donor and acceptor chromophores, respectively) are excellent candidates for probing photo-induced electron transfer and related

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photophysical/photochemical processes. 3*d* Metal ions are often of high spin ground states, which make these alkynyl compounds promising building blocks of magnetic materials.

1. Introduction and Scope

The beginning of metal alkynyl chemistry can be traced back to the work of Nast and co-workers six decades ago, in which 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 were extensively explored.[1] Homoleptic alkynyl complexes received continued interests in recent years,[2, 3] and interrogations with modern structural and computational techniques yielded in-depth understanding of molecular and electronic structures of these species. Efforts by Hagihara *et al*. demonstrated the feasibility to prepare the $[M\text{-}C{\equiv}C\text{-}Ar\text{-}C{\equiv}C\text{-}]_n$ (M = Ni, Pd and Pt) type rigid rod polymers of averaged molecular weight (M_W) as high as 10^5 in the early 80s.[4] Similar rigid rod polymers with M as Ru and Rh were developed subsequently by the laboratories of Lewis and others in the 90s.[5] Though these polymers display wire-like rigid rod structures, those based on Pd and Pt have band gaps greater than 3 eV based on their absorption edges and are generally insulators ($R \sim 10^7$ Ωcm) owing to the electronic saturation of a square planar d^8 configuration.[6] Over the years, both the synthetic chemistry of metal alkynyls and the electronic structures of these compounds have been investigated by many groups and these efforts have been reviewed elsewhere.[7-9]

Interest in metal alkynyls as molecular wires was shifted to the $M\text{-}(C{\equiv}C)_n\text{-}M$ type compounds based on the middle transition metals in the early 90s with the pioneering studies on the C_4-bridged di-iron compounds by Lapinte[10] and the C_4-bridged di-rhenium compounds by Gladysz.[11] In the ensuing decades, many examples of bimetallic compounds with an oligoyn-diyl

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bridge have emerged, including M as Fe,[10] Mn,[12] Ru,[13] W,[14] Re[11, 15] and Pt,[16] and the electronic delocalization mediated by the oligoyn-diyl bridge has been probed with voltammetric and spectroelectrochemical techniques following the classical Taube-Creutz paradigm of mixed valency.[17] Inspired by the work from the laboratories of Cotton[18] and Bear-Kadish,[19, 20] our laboratory has been investigating diruthenium alkynyls as prototypical molecular wires since the late 90s.[21-23] Diruthenium compounds with oligoyn-diyl bridges were first reported by us[24] and shortly after by the laboratory of Lehn,[25] both in this journal. With the $Ru_2(ap)_4$ capping unit (*ap* = 2-anilinopyridinate), the Ru_2-$(C{\equiv}C)_n$-Ru_2 type compounds with *n* up to 10 have been prepared, and the electronic couplings (H_{ad}) between two Ru_2 termini have been determined and rationalized on the basis of DFT studies.[26-28] The electronic couplings across the -$(C{\equiv}C)_n$-$Ru_2(DMBA)_4$-$(C{\equiv}C)_n$- bridge ($n = 1 – 4$; DMBA = *N*,*N′*-dimethylbenzamidinate) were evaluated with ferrocene as the capping unit, and Robin-Day class II-III behaviours were revealed.[29-31] Additionally, the conductivity of diruthenium alkynyls at either single or few molecules level has been examined using STM and break-junction techniques,[32, 33] yielding conductance data better than those of comparable organic systems. More recently, Ru_2-alkynyls have been used as the active materials in nano-memory devices.[34-36]

The aforementioned results are largely based on 4*d* and 5*d* metals, and only few examples based on 3*d* metal ions, namely the cases of Fe[10, 37] and Mn.[12] Furthermore, the majority of compounds use soft and polarisable ligands such as phosphines and cyclopentadienyls. With the ever increasing awareness of sustainability, we became interested in alkynyl chemistry based on 3*d* metal complexes supported by polyaza macrocycles. The latter are attractive because of the rich coordination chemistry developed for the interest of bioinorganic modelling,[38, 39] and these ligands, as *hard* bases, may render new reactivity and materials properties of the resultant metal alkynyls. In particular, many cyclam (1,4,8,11-tetraazacyclotetradecane, Chart 1) complexes of 3*d* metal ions adopt a *pseudo*-octahedral motif, in which two alkynyl ligands in a *trans*-arrangement can be easily envisioned. However, the chemistry of M(cyclam) alkynyls, both M(cyclam)(C_2R)X and *trans*-M(cyclam)($C_2R)_2$ types, was generally underdeveloped, and limited to a few Cr(III) bis-alkynyl compounds in two publications from the laboratories of Wagenknecht[40] and Nishi[41] and a dissertation chapter by Berben[42] when we initiated the study on Fe^{III}(cyclam) alkynyls around 2010.[43] Since then, we have expanded the scope to include M as Cr, Fe, and Co with C_2R as both simple alkynyls and *gem*-DEE (*geminal*-diethynyleneethene), and both the synthesis and structural characterizations form the bulk of this article.

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,[44] 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 of their Ni^{II} and $Co^{II/III}$ complexes.[45, 46] Particularly attractive are the complexes of HMC (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, Chart 1) because of the facile and inexpensive ligand synthesis. The initial proof-of-concept studies of alkynyl complexes with TMC and HMC are described herein. Also discussed are the alkynyl complexes of a triaza ligand Me_3TACN (1,4,7-*N,N',N"*-trimethyl-1,4,7-triazacyclononane, Chart 1).

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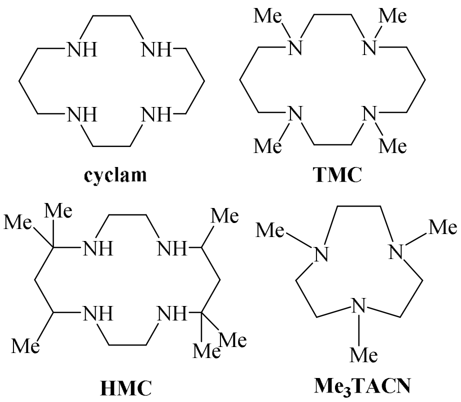
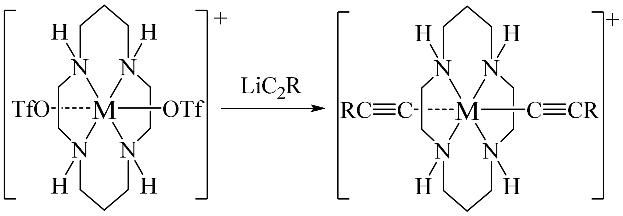
Chart 1. Polyazamacrocycle Ligands



2. Mono-nuclear M(cyclam) Alkynyl Complexes



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

The *trans*-M(cyclam)(C_2R)$_2$ type complexes are usually prepared from anion metathesis reactions between [M(cyclam)(OTf)$_2$]$^+$ and LiC_2R as shown in Scheme 1. This approach was first applied to the synthesis of [Cr(cyclam)(C_2R)$_2$]$^+$ with R as SiMe_3 and -C_6H_4-3-C_2H as described by Berben.[42] Wagenknecht *et al.* prepared Cr complexes with R as Ph, C_6H_4-4-CH_3 and C_6H_4-4-CF_3,[40] and subsequently R as C_6H_4-4-F, cyclohexyl, 1-naphthalenyl and 9-phenanthrenyl.[47] Careful examination by Wagenknecht *et al.* also revealed that LiC_2R may deprotonate the ring –*N*H to yield hydroamination side products, which can be suppressed with a reaction stoichiometry of 4 : 2 : 1 among *n*BuLi, HC_2R and [Cr(cyclam)(OTf)$_2$]$^+$, respectively.[47] Cr compounds with R as 3-thiophene[41] and 4-ethynyltetrathiafulvalene[48] were similarly prepared from [Cr(cyclam)(OTf)$_2$]$^+$ with *n*BuLi being replaced by lithium diisopropylamide.[49]

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Wagenknecht *et al.* also reported the preparation of $[Rh(cyclam)(C_2R)_2]^+$ type compounds from $[Rh(cyclam)(OTf)_2]^+$ with R as Ph, C_6H_4-4-CH_3, C_6H_4-4-F and C_6H_4-4-CF_3.[47] Similarly, the reactions between $[Fe(cyclam)(OTf)_2]^+$ and LiC_2R afforded $[Fe(cyclam)(C_2R)_2]^+$ with R as Ph, Si^iPr_3, C_2SiMe_3 (Figure 1), C_4SiMe_3 and –Fc.[43, 50] More recently, the same protocol has been extended to prepare $[Co(cyclam)(C_2R)_2]^+$ 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.[51] It should be mentioned that while the $[M(cyclam)(OTf)_2]^+$ starting materials are often a mixture of *cis*- (major) and *trans*-isomers, the products of alkynylation reaction are predominantly the *trans*-isomers (*trans*-$[M(cyclam)(C_2R)_2]^+$). Careful examination of the synthesis of $[Cr(cyclam)(C_2R)_2]^+$ by Wagenknecht *et al.* revealed that the isomer distribution is sensitive towards the nature of solvents and the use of diethyl ether to replace THF as the reaction solvent could lead to yields of *cis*-isomer as high as 66%.[52]

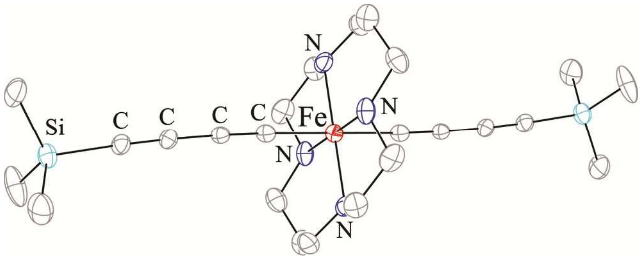

Figure 1. Structural plot of $[Fe(cyclam)(C_4SiMe_3)_2]^+$.

Because of its cross-conjugated nature, *geminal*-diethynylethene (*gem*-DEE) has received attention as a surrogate ligand for alkynyls in the compounds of Fc,[53, 54] Ru_2,[55, 56] and Ru.[57] In the context of M(cyclam) compounds, $[Cr(cyclam)(OTf)_2]^+$ reacts with Li-*gem*-DEE-X (X = Si^iPr_3 and Fc) to yield the corresponding *trans*-$[Cr(cyclam)($*gem*-DEE-X$)_2]^+$ (Scheme 2).[58] Similarly, the reactions between $[Fe(cyclam)(OTf)_2]^+$ and Li-*gem*-DEE-X (X as Ph, Si^iPr_3 and Fc) resulted in *trans*-$[Fe(cyclam)($*gem*-DEE-X$)_2]^+$,[59] and the structure of *trans*-$[Fe(cyclam)($*gem*-DEE-Ph$)_2]^+$ is shown in Figure 2. More recently, it has been shown that the *trans*-$[Co(cyclam)($*gem*-DEE-X$)_2]^+$ type compounds can be prepared in the same fashion.[60]

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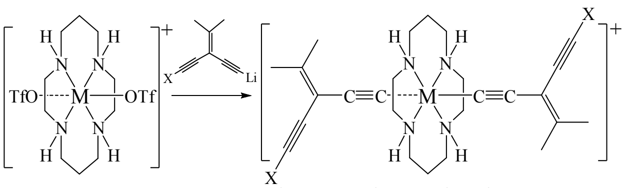

M = Cr, Fe and Co; X = $SiMe_3$ and Aryl

Scheme 2. Synthesis of the *trans*-[M(cyclam)(*gem*-DEE)$_2$]$^+$ type complexes.

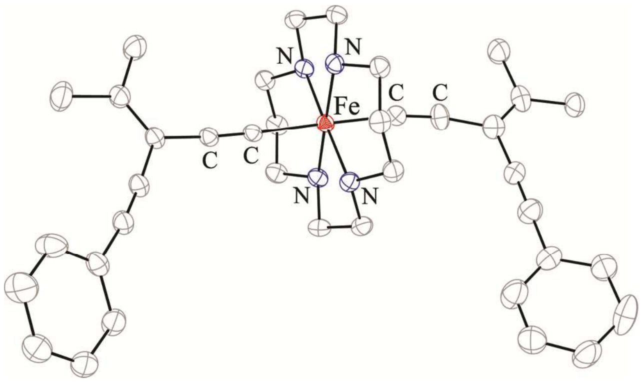

Figure 2. Molecular structure of *trans*-[Fe(cyclam)(*gem*-DEE-Ph)$_2$]$^+$.

While the reactions invoking lithiated alkynyls have provided facile access to the symmetric bis-alkynyl compounds, a reliable route to an monoalkynyl complex, i.e. *trans*-[M(cyclam)(C_2R)X]$^+$ (X is either a (pseudo)halide or coordinating solvent molecule), remains elusive for most of the 3*d* metal ions. The only exception this far is Co^{III}, for which *trans*-[Co(cyclam)(C_2Ph)Cl]$^+$ was produced from the reaction between [Co(cyclam)Cl_2]Cl and PhC_2H in the presence of Et_3N under reflux, presumably via a base-assisted dehydrohalogenation reaction.[61] Under similar conditions, the reaction between [Co(cyclam)Cl_2]Cl and $Me_3SiC_{2m}SiMe_3$ resulted in *trans*-[Co(cyclam)((C≡C)$_m$H)Cl]$^+$ (m = 1 – 3).[62] The reactions of *trans*-[Co(cyclam)(C_2Ph)Cl]$^+$ with LiC_2Ph and LiC_2SiMe_3 resulted in *trans*-[Co(cyclam)(C_2Ph)$_2$]$^+$[61] and *trans*-[Co(cyclam)(C_2Ph)(C_2SiMe_3)]$^+$,[63] respectively. The latter, being dissymmetric in the *trans*-ligands, is intriguing from the electronic point of view. More recently, several *trans*-[Co(cyclam)(C_2R)Cl]$^+$ type compounds (R = -C_6H_4-4-NO_2 in Figure 3, -

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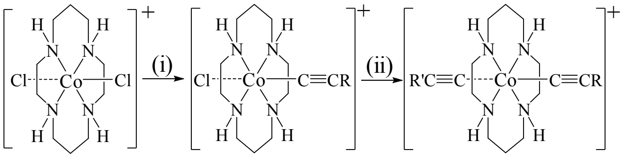
Fc and -C_6H_4-4-$SC_2H_4SiMe_3$) have been prepared, and the former reacted with LiC_2Ph to yield *trans*-[Co(cyclam)(C_2-C_6H_4-4-NO_2)(C_2Ph)]$^+$ (Scheme 3).[64]



Conditions(i) HC_2R, weak base; MeOH/THF reflux; (ii) LiC_2R', THF

Scheme 3. Stepwise synthesis of dissymmetric Co-bis-alkynyl.

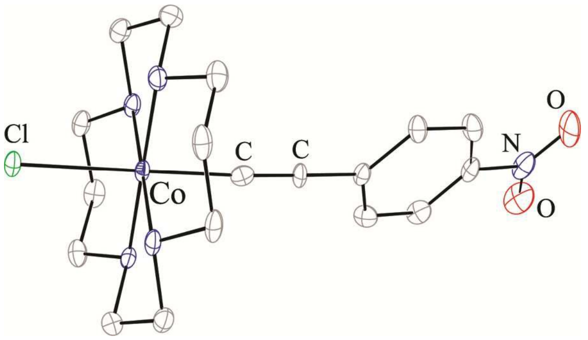


Figure 3. Molecular Structure of [Co(cyclam)($C_2C_6H_4$-4-NO_2)Cl]$^+$.

It is clear from Figures 1 – 3 that both the *trans*-[M(cyclam)(C_2R)X]$^+$ and *trans*-[M(cyclam)$(C_2R)_2$]$^+$ types compounds adopt a pseudo-octahedral coordination geometry. For the symmetric *trans*-[M(cyclam)$(C_2R)_2$]$^+$ type compounds, the M-C bond lengths are *ca.* 2.08 Å for Cr^{III}, 1.95 Å for Fe^{III} and 1.90 Å for Co^{III}, and the trend is consistent with the gradual decrease of covalent radii across the periodic table from left to right. While the majority of known structural examples are the *trans*-type, the structure of *cis*-[Cr(cyclam)$(C_2Ph)_2$]$^+$ was reported recently.[52]

3. Di- and Multi-nuclear Complexes with Bridging Alkynyl

Linear bimetallic and multimetallic assemblies linked by bridging alkynyls are key to the study of both the charge and energy transfer processes and spin couplings across carbon rich bridges.[21, 65] Assemblies of multiple M(cyclam) units using alkynyl-based linkers have been

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explored in recent years. For instance, the reaction of [Co(cyclam)Cl_2]Cl with 1,4-diethynylbenzene (DEB) or 1,3,5-triethynylbenzene (TEB) in the presence of Et_3N resulted in the bridged dimer $\{[Co(cyclam)Cl]_2(\mu\text{-DEB})\}^{2+}$ or trimer $\{[Co(cyclam)Cl]_3(\mu\text{-TEB})\}^{3+}$, respectively.[61] Refluxing [Co(cyclam)Cl_2]Cl with $Me_3Si(C{\equiv}C)_nSiMe_3$ (n = 2 and 3) led to the formation of $\{trans\text{-}[Co(cyclam)Cl]_2(\mu\text{-}(C{\equiv}C)_n)\}^{2+}$ in excellent yields, and the complex with n = 3 is shown in Figure 4.[62] Because of the thermal instability of oligoynes with $n \geq 4$, access to compounds of longer oligoyn-diyl bridges through reflux becomes limited. To circumvent the problem, the mono-oligoynyl species $trans\text{-}[Co(cyclam)((C{\equiv}C)_mH)Cl]^+$ (m = 2 and 3) was subjected to a *Glaser* type homo-coupling reaction to yield $\{trans\text{-}[Co(cyclam)Cl]_2(\mu\text{-}(C{\equiv}C)_{2m})\}^{2+}$.[62]

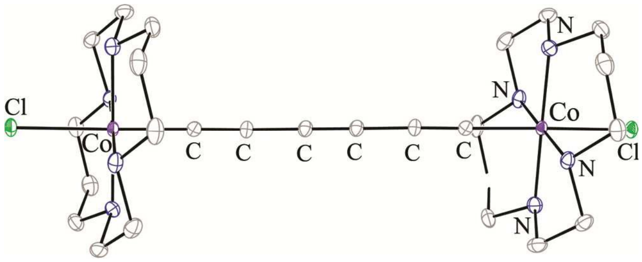

Figure 4. Molecular Structure of $[\{Co(cyclam)(Cl)\}_2(\mu\text{-}C_6)]^{2+}$.

The successful synthesis of the above-mentioned $\{trans\text{-}[Co(cyclam)Cl]_2(\mu\text{-}(C{\equiv}C)_n)\}^{2+}$ type compounds prompted us to explore the synthesis of the M-*gem*-DEE-M type compounds based on Co^{III}(cyclam) unit. Hence, the mono-*gem*-DEE compound *trans*-[Co(cyclam)(*gem*-DEE-H)Cl]Cl was prepared from the reaction between [Co(cyclam)Cl_2]Cl and Me_3Si-*gem*-DEE-$SiMe_3$ under the conditions similar to that for $trans\text{-}[Co(cyclam)((C{\equiv}C)_mH)Cl]Cl$ (Scheme 4). Further reaction between *trans*-[Co(cyclam)(*gem*-DEE-H)Cl]Cl and [Co(cyclam)Cl_2]Cl resulted in $\{trans\text{-}[Co(cyclam)Cl]_2(\mu\text{-}gem\text{-DEE})\}^{2+}$, and a *Glaser* type oxidative homocoupling of *trans*-[Co(cyclam)(*gem*-DEE-H)Cl]Cl led to $\{trans\text{-}[Co(cyclam)Cl]_2(\mu\text{-}(gem\text{-DEE})_2)\}^{2+}$.[60] Compounds

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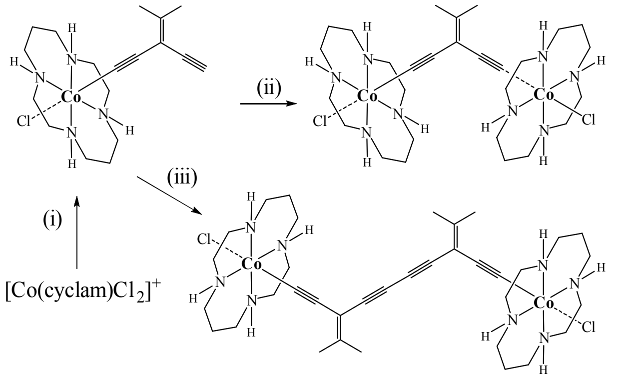
{*trans*-[Co(cyclam)Cl]$_2$(μ-*gem*-DEE)}$^{2+}$ (shown in Figure 5) and {*trans*-[Co(cyclam)Cl]$_2$(μ-(*gem*-DEE)$_2$)}$^{2+}$ are the first examples of the M-*gem*-DEE-M type compounds being structurally characterized, and they are indefinitely stable towards air and moisture.



Conditions: (i) Me_3Si-*gem*-DEE-$SiMe_3$, Et_3N, MeOH, reflux; (ii) [Co(cyclam)Cl_2]Cl, Et_3N, MeOH, reflux; (iii) CuCl/TMEDA (cat.), O_2, MeOH

Scheme 4. Synthesis of Co-μ-gem-DEE-Co type compounds.

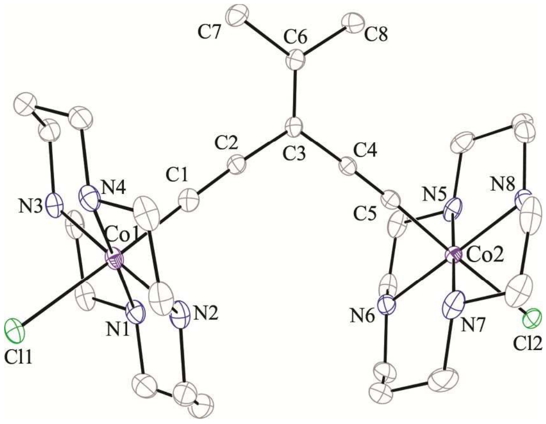


Figure 5. ORTEP plot of {*trans*-[Co(cyclam)Cl]$_2$(μ-*gem*-DEE)}$^{2+}$ at 30% probability level.

4. Other Macrocycles

Compounds based on Me_3TACN. The first example of M(Me_3TACN) alkynyls is [Ru(Me_3TACN)(PMe_3)$_2$(C_2Ph)]$^+$ reported by Che *et al*,[66] and the complex can react with another terminal acetylene to yield an η^3-butenynyl species. Cr(Me_3TACN)(C_2H)$_3$ (Figure 6) was

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prepared from the reaction between Cr(Me_3TACN)($OTf)_3$ and LiC_2SiMe_3 and structurally characterized by Berben and Long,[67] and Cr(Me_3TACN)($C_2H)_3$ was found to form interesting cation-bridged dimers [Cr(Me_3TACN)($C_2H)_3]_2$M}X and trimers [Cr(Me_3TACN)($C_2H)_3]_3$M}X (M = Na, K and Cs, X = halide and OTf). In addition, Cr(Me_3TACN)($C_4SiMe_3)_3$ and Cr(Me_3TACN)($C_4H)_3$ were also prepared, and the crystal structure of the latter was determined.[42] Likewise, Youngs *et al.* reported the reaction between Rh(Me_3TACN)Cl_3 and LiC_2Ph to afford Rh(Me_3TACN)($C_2Ph)_3$,[68] which forms an aggregate with Ag^+ salts through an η^2 coordination to Ag^+ by the acetylene bonds. Youngs *et al.* subsequently reported an analogous compound Rh(Me_3TACN)(C_2-4-Py$)_3$, which forms a trigonal bipyramidal cage upon reaction with a square planar *cis*-(P-P)Pt($NO_3)_2$.[69]

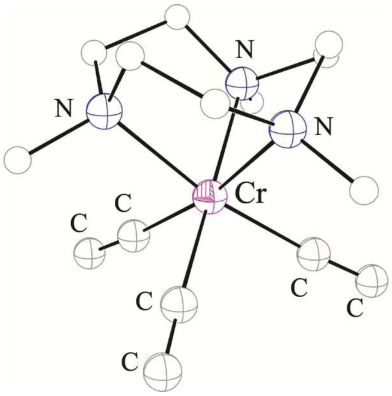

Figure 6. Molecular structure of Cr(Me_3TACN)(C≡CH$)_3$ rendered using data retrieved from Cambridge Structure Database (entry LUGDUM).

Compounds based on TMC and other cyclam derivatives. Compared with cyclam, TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) is more sterically crowded, and hence its coordination chemistry is distinguished from that of cyclam.[44] The alkynyl chemistry based on M(TMC) was unknown in literature until our recent effort with Ni^{II}(TMC), where the reaction between $[Ni(TMC)X]^+$ (X = Cl or OTf) and LiC_2R resulted in $[Ni(TMC)(C_2R)]^+$ (R = $SiMe_3$, Si^iPr_3, Ph and C_2H).[70] As exemplified by the X-ray structure of $[Ni(TMC)(C_2Ph)]^+$ (Figure 7),

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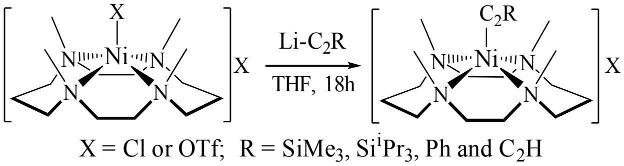
the coordination sphere of the Ni^{II} center adopts a square pyramidal arrangement with the alkynyl ligand occupying the apical position. Similar to the parent compounds [Ni(TMC)X]X (X = Cl^- and OTf^-), all four $[Ni(TMC)(C_2R)]^+$ compounds are the *RSRS* stereoisomer. Since M(TMC)X type compounds are also known for M as Cr, Fe and Co besides Ni,[44, 71] alkynylation chemistry similar to that of Ni(TMC) can be envisioned for these metals.



Scheme 5. Synthesis of Ni^{II}(TMC) alkynyls

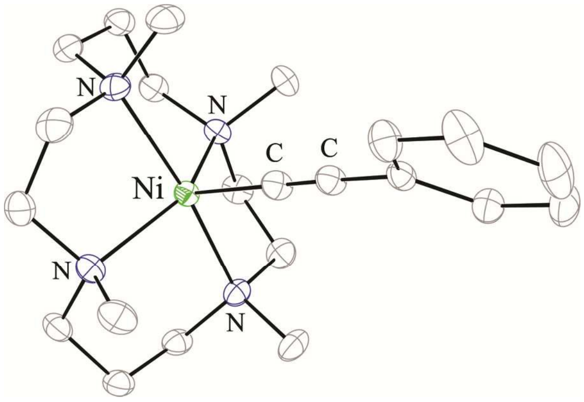


Figure 7. Molecular structure of $[Ni(TMC)(C_2Ph)]^+$.

In addition to TMC, many other 14-member tetraaza macrocycles are available owing to the efforts of both bioinorganic modelling and catalyst development based on macrocyclic ligands. Illustrative examples are the ligand 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), which have drawn considerable interest in recent decades because of the superb CO_2 reduction activity of Co^{II}(HMD) and Ni^{II}(HMC).[45, 46] A significant advantage of the HMD and HMC ligands over cyclam and TMC is the cost. HMD can be readily prepared on scale of hundreds grams via a Schiff base condensation reaction between singly

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protonated ethylene diamine and methyl vinyl ketone,[72] both of which are inexpensive materials. The reduction of HMD by $NaBH_4$ in an alcoholic solvent yields HMC.

The HMC ligand is more flexible than its parent HMD and displays diversified coordination geometry. For instance, Cr^{III} complexes of HMC ligand exist in two isomers: the more soluble *trans*-$[Cr^{III}(HMC)Cl_2]Cl$ and the less soluble *cis*-$[Cr^{III}(HMC)Cl_2]Cl$.[73] Both *trans*-$[Cr^{III}(HMC)Cl_2]Cl$ and *cis*-$[Cr^{III}(HMC)Cl_2]Cl$ react with LiC_2R to afford *trans*-$[Cr^{III}$(*meso*-HMC)$(C_2R)_2]^+$ and *cis*-$[Cr^{III}$(*rac*-HMC)$(C_2R)_2]^+$ (R = Ph and C_2H), respectively, and the structure of *cis*-$[Cr^{III}$(*rac*-HMC)$(C_2Ph)_2]^+$ is shown in Figure 8.[74] Parallel to the alkynyl chemistry of Cr(HMC), preliminary study of the reaction between $Cr^{III}(DMC)Cl_3$ (DMC = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane) and LiC_2Ph revealed facile formation of $[Cr^{III}(DMC)(C_2Ph)_2]^+$ as well.[74]

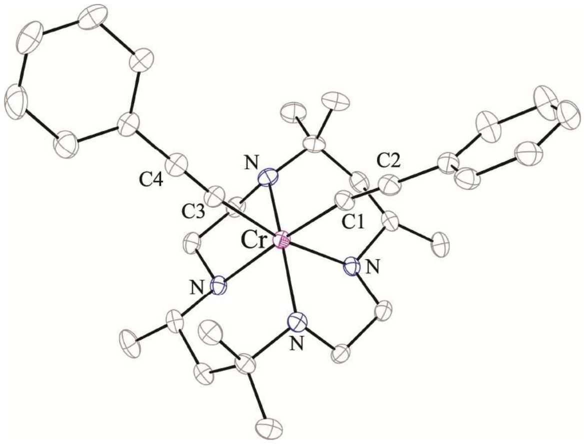

Figure 8. Molecular structure of *cis*-$[Cr^{III}$(*rac*-HMC)$(CCPh)_2]^+$.

5. Physical and Materials Properties

Voltammetric Properties. The ability to undergo multiple reversible redox processes has been a key characteristics of metal alkynyl compounds as prototypical molecular wires.[21, 65] Notable examples include $[Cp(PPh_3)_2Ru]_2(\mu\text{-}C_4)$ with four stepwise one-electron oxidations[13] and $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$ with a pair of one-electron oxidations and a pair of one-electron

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reductions.[24] The presence of multiple reversible one-electron couples enables the study of intervalence charge transfer processes associated with mixed valent ions (M^{+n}-$(C{\equiv}C)_m$-$M^{+(n+1)}$), and subsequent assessment of H_{ab} between two metal centers across the carbon bridge.[75, 76]

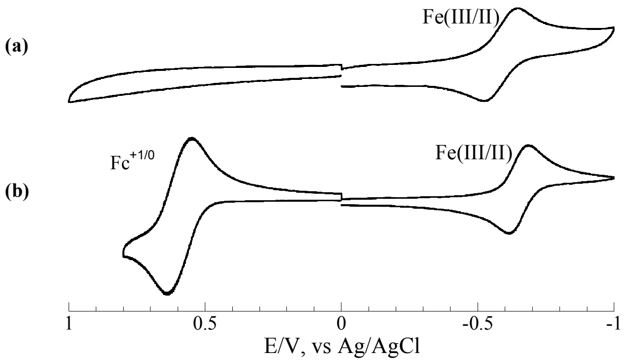

Figure 9. Cyclic voltammograms recorded for compounds $[Fe^{III}(cyclam)(C{\equiv}CSi^{i}Pr_3)_2]^+$ (**a**) $[Fe^{III}(cyclam)($*gem*-DEE-Fc$)_2]^+$ (**b**); In addition to the reduction of Fe^{III}, the latter also shows the simultaneous oxidation of both ferrocenyl substituents.

The voltammetric behaviors of the aforementioned 3*d* M-cyclam and related compounds are quite different from 4*d* and 5*d* metal compounds, or 3*d* metal compounds with soft ligands. Among cyclam compounds investigated thus far, the Fe^{III} species exhibit a quasi-reversible reduction couple (Figure 9),[43, 50, 59] Co^{III} species display multiple irreversible couples,[51, 61, 63] and Cr^{III} species are redox inactive.[40, 58] Furthermore, the *trans*-$[M^{III}(cyclam)(C_2Fc)_2]^+$ (M = Fe, Cr and Co) type compounds have been prepared, and the two ferrocenyl capping groups are only weakly coupled across the C_2-M^{III}-C_2 fragment.[50, 51] Both the absence of idealized M-centered reversible redox processes and the inability to mediate strong electronic couplings may be related to the large reorganization energy associated with the $M^{+n}/M^{+(n+1)}$ couple for 3*d* metal ions when compared with the 4*d* and 5*d* ions. This contrast is most pronounced when the coordination sphere consists of hard ligands such as N donor ligands. An illustrative example is the classical study of the electron transfer rate of the $[M(NH_3)_6]^{3+}$ / $[M(NH_3)_6]^{2+}$ self exchange reaction: the

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rate constants (*k*) are about 10^{-6} and 820 $M^{-1}s^{-1}$ for M as Co and Ru, respectively, and the contrast in *k* is clearly associated with the difference in $\Delta(d_{M\text{-}N})$ between the +2 and +3 oxidation states (0.178 Å for Co and 0.04 Å for Ru).[77]

Spectroscopic Properties. The majority of compounds described herein feature *d-d* transition bands of modest intensity in the visible region, and the LMCT bands in the UV region. The latter are likely originated from both the N centers[78] and C≡C bonds. Since the discussion of electronic absorption spectra has been based on simple ligand field model thus far, quantitative analysis based on TD-DFT calculations, as demonstrated for $M(C_2R)_6$ complexes,[3] is desired in the future study. While most of the compounds are non-emissive, the Cr^{III}-based compounds display phosphorescence originating from the ligand-field excitations. 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 around one microsecond.[47] The *trans*-[Cr(cyclam)(*gem*-DEE)$_2$]$^+$ type compounds were found to phosphoresce as well but from the ^2E_g state only.[58]

Magnetic Properties. Other than the compounds of Co^{III}, all the compounds described herein are paramagnetic. The Fe^{III} compounds are low spin with a $S = 1/2$ ground state,[43, 50, 59] Ni^{II} with a $S = 1$,[70] and Cr^{III} with a $S = 3/2$,[42, 58] on the basis of room temperature magnetic susceptibility. Temperature-dependent magnetic susceptibilities of $Cr(Me_3TACN)(C{\equiv}CH)_3$, $\{[Cr(Me_3TACN)(C{\equiv}CH)_3]_2K\}OTf$ and $\{[Cr(Me_3TACN)(C{\equiv}CH)_3]_3Cs\}Br$ were measured,[42] and weak antiferromagnetic couplings between Cr^{III} centers are mediated by the alkali ion in both $\{[Cr(Me_3TACN)(C{\equiv}CH)_3]_2K\}OTf$ ($J \sim -0.8$ cm^{-1}) and $\{[Cr(Me_3TACN)(C{\equiv}CH)_3]_3Cs\}Br$ ($J \sim -0.3$ cm^{-1}). *Trans*-$[Cr(cyclam)(C_2\text{-}3\text{-}Th)_2]^+$ forms a 1:1 salt with $[Ni(mdt)_2]^-$ (3-Th = 3-thiophene; mdt = 1,3-dithiole-4,5-dithiolate) in the form of a 1D stack with an interchain exchange of $2J = -4.2$ cm^{-1}.[41] Upon a TTF-based one-electron oxidation of $[Cr(cyclam)(C_2\text{-}4\text{-}TTF)_2]^+$ (TTF =

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tetrathiafulvalene), the resultant [Cr(cyclam)(C_2-4-TTF$)_2$]$^{2+}$ forms a 1D chain via the stacking of adjacent TTF, and a strong intrachain coupling ($2J$ = -21 cm^{-1}) between the Cr^{III} (S = 3/2) and (TTF)$_2^+$ (S = 1/2) centers.[48]

6. Challenges and Future Opportunities

Since the scope of metal alkynyls with polyaza macrocyclic supporting ligands remains limited, the synthetic approaches are largely based on the use of lithiated alkynyls and dehydrohalogenation reactions with a weak base. The primary challenge hence is the development of alternative synthetic routes with improved yields and selectivity. Organo-tin activated arylalkynyls (Me_3SnC_2Ar, Scheme 7) have been employed extensively by Lewis and coworkers to prepare many *trans*-bisalkynyl Ru(II) compounds,[7] and the synthesis of dissymmetric *trans*-[(dppe)$_2$Ru(C_2Ar)(C_2Ar′)] (dppe = 1,2-bis(diphenylphosphino)ethane) is especially noteworthy.[79] Nevertheless, the toxicity of tin reagents is concerning. As an extension of the dehydrohalogenation reaction, Hagihara coupling (CuI / organic amine, Scheme 6) has been successfully utilized in mono-alkynylation of Pt^{II} species, and Pd^{II} and Ni^{II} compounds to some degree,[80, 81] where a Cu(I) alkynyl intermediate has been suggested.[7] However, the application of Hagihara coupling to other transition metal compounds remains scarce, and it was speculated that the instability of metal starting material towards organic amines could be a limiting factor.[7] Macrocyclic compounds described herein are fairly robust towards organic amines, so it remains to be seen if Hagihara coupling would be useful. It is encouraging to note that arylalkynyls of cobalamin, a sensitive substrate, were prepared under optimized Hagihara coupling conditions recently.[82]

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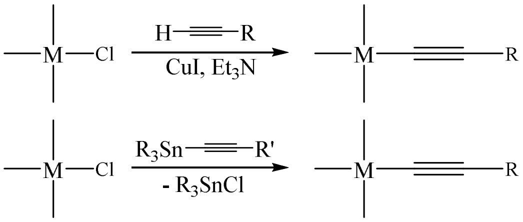

Scheme 6. Alkynylation *via* Hagihara coupling or the use of organotin alkynyls.

As a versatile synthon, alkyne undergoes a variety of organic transformations with the high reactivity owing to the unsaturation of the carbon-carbon triple bond.[83] Metal-bound alkynyls and oligoynyls may also undergo interesting reactions in addition to the *Glaser* coupling reaction mentioned earlier. For instance, ample examples of addition/insertion of TCNE and TCNQ at a less hindered C≡C bond have been provided by the laboratory of Bruce.[84, 85] Metal alkynyl may be attached to macromolecules such as DNAs or peptides containing an azido group *via* the Cu(I) catalyzed 1,3-dipolar cycloaddition reaction (*click*). These reactions remain to be explored with 3*d* metal alkynyls described here.

A key impetus in the development of macrocyclic chemistry has been bioinorganic modeling. For instance, complex $[Ni(TMC)CH_3]^+$ has been studied as a functional mimic of acetyl-CoA.[86] It is worth noting that 3*d* metal alkynyls supported by conjugated tetraaza macrocycles, namely porphyrins and corroles, have been investigated as the models of Vitamin B-12. Interesting examples include $(TPP)Co(C_2H)$ (TPP = tetraphenylporphyrin) derived from *β*-halovinyl precursor,[87] and arylalkynyls of cobalamin.[82] It is conceivable that the metal alkynyls described herein may serve as both the structural and functional mimics of acetyl-CoA and Vitamin B-12. It should be mentioned that some examples of 3*d* metal (other than cobalt) alkynyl compounds based on porphyrin ligands can be found in a review dedicated to the organometallic chemistry of porphyrins.[88]

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As discussed above, 3*d* metal macrocyclic compounds tend to be electrochemically sluggish due to large ligand reorganization energies, which make the mixed-valency approach less ideal for probing the electron / energy transfer processes in these compounds. Recently, photo-induced electron transfer within donor-bridge-acceptor (D-B-A) dyads has been used to probe the capacity of the bridge in mediating these processes. Notably, Weinstein and coworkers investigated a series of D-B-A compounds with *trans*-Pt(II)-bis-alkynyl as the bridge, phenothiazine (PTZ) as the donor, and naphthalene-monoimide (NAP) as the acceptor, and found that the excitation of the Pt-bound C≡C bonds can significantly attenuate the decay pathways.[89, 90]

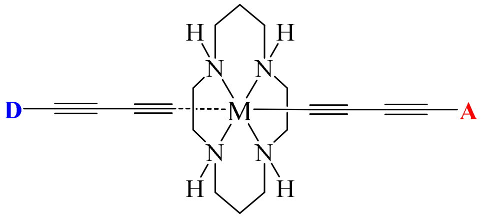

Chart 2. D-B-A type compounds based on [M(cyclam)].

The synthetic chemistry developed for dissymmetric *trans*-[M(cyclam)(C_2R)(C_2R')] clearly set the stage for probing the photo-induced electron and energy transfer processes in D-B-A dyads (Chart 2) based on earth abundant metals. The feasibility to assemble such molecules is already demonstrated for M = Co^{III},[64] and is being expanded to include Fe^{III} and Cr^{III}. Besides the cost, use of 3*d* metal ions offers an advantage over the Pt-based system in their open shell nature, and structured *d-d* bands. As shown in Figure 10, the electronic absorption spectrum of *trans*-[Cr^{III}(*meso*-HMC)(C_4H)$_2$]$^+$ displays a highly structured *d-d* band with an averaged vibronic progression of *ca*. 1950 cm^{-1}, which is likely related to the asymmetric stretching mode of C≡C bonds directly attached to the Cr^{III} center. This feature clearly illustrates that the C≡C stretches are intimately coupled to the Cr^{III} *d* orbitals, and hence may play a very pronounced role in

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attenuating photo-induced electron and energy transfer across the bridge. Recent report of the enhancement of lifetimes of the CS (charge separated) states in an applied magnetic field[91] hints at the possibility to achieve similar lifetime enhancement using a 3*d* ion as internal magnetic field.

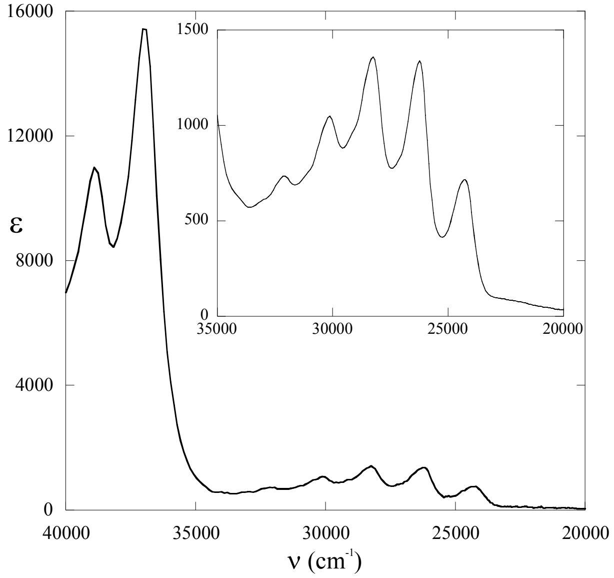

Figure 10. UV-vis spectrum of *trans*-[Cr^{III}(*meso*-HMC)(C_4H)$_2$]$^+$.

In closing, it is important to mention that all alkynyl compounds based on the M-tetraaza combination are robust towards ambient atmosphere, a feature essential for going forward with electronic and optoelectronic applications. While the price for cyclam from reagent suppliers is high (*ca.* \$1,000 / 50 g), HMC is fairly easy and inexpensive to prepare. Hence, the combination of 3*d* metal ions and tetraaza macrocycles provides a fertile ground for the development of sustainable metal alkynyl chemistry.

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