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Emissive Chromium(III) Complexes with Substituted Arylethynyl Ligands

David L. Grisenti,[†] W. Walsh Thomas,[†] Christopher R. Turlington,[†] Matthew D. Newsom,[†] Christopher J. Priedemann,[†] Donald G. VanDerveer,[‡] and Paul S. Wagenknecht*,[†]

Department of Chemistry, Furman University, Greenville, South Carolina 29613, and Department of Chemistry, Clemson University, Clemson, South Carolina 29634-0973

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Arylethynylchromium(III) complexes of the form *trans*-[Cr(cyclam)(CCC$_6$H$_4$R)$_2$]OTf (where cyclam = 1,4,8,11-tetraazacyclotetradecane, R = H, CH$_3$, or CF$_3$ in the para position, and OTf = trifluoromethanesulfonate) have been prepared and characterized by IR spectroscopy and X-ray diffraction. The complexes are emissive with excited-state lifetimes in a deoxygenated fluid solution between 200 and 300 μs.

The prospect of inventing functional photochemical molecular devices has prompted research in the area of inter- and intramolecular energy transfer between transition-metal complexes.[1,2] Recent efforts in our group have focused on determining intermolecular energy-transfer rate constants that approximate self-exchange rate constants between *trans*-[Cr(N$_4$)X$_2$]$^{n+}$ complexes (where N$_4$ = tetraazamacrocycle and X = CN$^-$, NH$_3$, F$^-$).[3] Most recently, we have become interested in the effect of subtle thermodynamic effects on energy-transfer rate constants. Thus, we have begun research on the preparation of new arylethynyl complexes of the chromium(III) cyclam moiety. Substituents on the arylethynyl ligand may provide the abilty to tune the excited-state energy and lifetime. Precedence for this type of excited-state tuning includes studies by Eisenberg's group on platinum(II) diimine complexes with substituted arylethynyl ligands, which demonstrate that replacement of a phenyl H with CH$_3$, F, or OCH$_3$ caused significant deviations in both the excited-state energies and emission lifetimes.[4] Because of the technological potential of metal alkynyl polymers, transition-metal alkynyl complexes have been intensely studied over the last several decades.[5] Herein, we present the synthesis and characterization of chromium(III) cyclam complexes with arylethynyl ligands in the trans positions (see Figure 1) and highlight their significant differences with the isoelectronic *trans*-[Cr(cyclam)(CN)$_2$]$^+$.

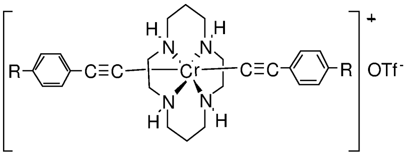

Figure 1. *trans*-[Cr(cyclam)(CCC$_6$H$_4$R)$_2$]OTf.

A series of complexes of the form of *trans*-[Cr(cyclam)(CCC$_6$H$_4$R)$_2$]OTf [where R = H (**1**), CH$_3$ (**2**), or CF$_3$ (**3**) in the para position] have been prepared by a method similar to that reported by Berben and Long[6] for the preparation of [(Me$_3$tacn)Cr(CCH)$_3$] (where Me$_3$tacn = *N*,*N′*,*N″*-trimethyl-1,4,7-triazacyclononane). For example, **1** was prepared as follows: Under an argon atmosphere, C$_6$H$_5$CCLi was prepared by the addition of *n*-BuLi (0.54 mL of a 2.5 M solution in hexanes, 1.35 mmol) to a solution of phenylacetylene (0.146 g, 1.43 mmol) in anhydrous tetrahydrofuran (THF; 8 mL) chilled to −78 °C. The mixture was allowed to warm to room temperature and was stirred for an additional 1 h. Upon the addition of [Cr(cyclam)(OTf)$_2$]OTf[7] (0.250 g, 0.357 mmol), the color of the mixture changed from pale yellow to dark brown and the contents was stirred for an additional 1 h. The reaction was then quenched with 5 drops of water, and the contents of the flask was eluted through a 3 cm plug of silica gel (in a 30 mL fritted glass funnel) using 30% (v/v) CH$_3$CN in CH$_2$Cl$_2$ (ca. 100 mL). After removal of the solvent, the oily

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* To whom correspondence should be addressed. E-mail: paul.wagenknecht@furman.edu.

[†] Furman University.

[‡] Clemson University.

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10.1021/ic801376p CCC: $40.75

residue was dissolved in a minimum volume of 10% (v/v) H_2O in THF (ca. 6 mL) and the solution was slowly added to cold diethyl ether (ca. 200 mL), resulting in a pale-yellow precipitate. Reprecipitation of this product by the same method yielded 107 mg (50%) of analytically pure **1**.[8] Derivatives **2**[9] and **3**[10] were prepared in analogous procedures starting with 4-ethynyltoluene and 4-ethynyl-α,α,α-trifluorotoluene, respectively. One interesting feature of this reaction is that arylethynyllithium preferentially reacts at the metal site in the presence of the secondary amine protons. This is presumably because of the relatively low pK_a value of phenylacetylene (20),[11] whereas secondary amines have pK_a values above 30. Apparently, ligation does not drop the pK_a value of the cyclam amines below those of the arylacetylenes.

Another feature of the synthesis is that the reaction results in only the *trans*- ethynyl complex. This is not surprising given that the isoelectronic *trans*-$[Cr(cyclam)(CN)_2]^+$ is produced stereochemically pure even though the starting material is a cis/trans mixture of $[Cr(cyclam)Cl_2]^+$.[12] Evidence for the trans geometry in the ethynyl complexes is provided using IR spectroscopy for complexes **1**−**3** and X-ray diffraction data for **1**. The patterns of vibrational bands in the cyclam N−H bending region (~900 cm^{-1}) have been shown by Poon to be indicative of either cis or trans geometry for transition-metal cyclam complexes. Specifically, the trans complexes display a doublet near 900 cm^{-1}, whereas for the less symmetric cis complexes, the peak is split into at least three peaks.[13] Compounds **1**−**3** all show a vibrational doublet in this region. In addition, the X-ray structure of a yellow monoclinic crystal obtained by diffusion of a 9:1 Et_2O/hexanes solution into a concentrated solution of $[Cr(cyclam)(CCPh)_2]OTf$ in acetonitrile demonstrates the trans geometry (Figure 2).[14] To establish that there had not simply been a selective crystallization of the trans isomer from a cis/trans mixture, powder X-ray diffraction analysis was performed on a bulk sample, resulting in a pattern that closely matches the pattern predicted from the observed crystal structure.[15]

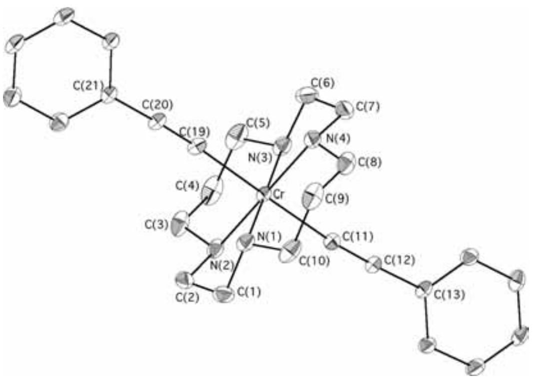

Figure 2. Thermal ellipsoid plot (50% probability level) of the complex cation of $[Cr(cyclam)(CCC_6H_5)_2]OTf$. Hydrogen atoms are omitted for the sake of clarity. This is one of two crystallographically distinct complexes in the unit cell (the other is on an inversion center). Selected interatomic distances (Å) and angles (deg): Cr−C(11) 2.079(4), Cr−C(19) 2.067(4), C(11)−C(12) 1.214(5), C(19)−C(20) 1.218(5); C(11)−Cr−C(19) 179.19(15).

The Cr−N bond lengths and the N−Cr−N bond angles are comparable to related cyclam complexes.[16] The average Cr−C and C≡C bond lengths for the arylethynylchromium(III) complexes reported herein are each ~0.02 Å longer than the values for $[(Me_3tacn)Cr(CCH)_3]$ reported by Berben and Long.[6] Although C≡C bond lengths have been used to suggest the extent of π interactions in metal alkynyl complexes, Manna et al. have demonstrated that there is a low sensitivity of the C≡C bond length to differences in metal alkynyl bonding.[5b] Because the C≡C bond lengths for *trans*-$[Cr(cyclam)(CCPh)_2]OTf$ fall within the normal range[5b] for metal alkynyl complexes, no significant conclusions about the type of bonding can be drawn from the structural data.

Vibrational data have also been used to determine the extent of π interactions in metal complexes. Raman spectroscopy on complexes **1**−**3** reveal ν(C≡C) values of 2077, 2079, and 2086 cm^{-1}, respectively. For comparison, we have measured ν(C≡C) by Raman spectroscopy on neat samples of the respective parent acetylenes: ethynylbenzene, 2110 cm^{-1}; 4-ethynyltoluene, 2108 cm^{-1}; 4-ethynyl-α,α,α-trifluorotoluene, 2115 cm^{-1}. Thus, there is a common shift of 31 ± 2 cm^{-1} to lower energy for ν(C≡C) of the chromium(III) complex versus the free parent acetylene. These data suggest that there is no significant M → CCR π back-bonding. If there were significant back-bonding, one would have expected the significantly more electron-withdrawing $C{\equiv}CC_6H_4CF_3$ ligand[17] to have a noticeably larger shift of ν(C≡C) (relative to the parent acetylene) to lower energy than the $C{\equiv}CC_6H_4CH_3$ ligand. Thus, the ~31 cm^{-1} shift to

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(8) Characterization of **1**. UV−vis (MeCN): λ_{max} (ϵ_M) 352 (528), 360 (554), 373 (550), 387 (560), 400 (597), 414 (380), 432 (343). Anal. Calcd (found) for $C_{27}H_{34}CrF_3N_4O_3S$: C, 53.72 (53.61); H, 5.68 (5.75); N, 9.28 (9.13).

(9) Characterization of **2**. UV−vis (MeCN): λ_{max} (ϵ_M) 355 (620), 365 (635), 376 (629), 380 (631), 392 (673), 404 (703), 421 (443), 436 (400). Anal. Calcd (found) for $C_{29}H_{38}CrF_3N_4O_3S$: C, 55.14 (55.34); H, 6.06 (6.09); N, 8.87 (8.87).

(10) (a) Characterization of **3**. UV−vis (MeCN): λ_{max} (ϵ_M) 348 (452), 382 (358), 394 (363), 406 (369), 424 (258), 438 (224). Anal. Calcd (found) for $C_{29}H_{32}CrF_9N_4O_3S$: C, 47.09 (47.12); H, 4.36 (4.36); N, 7.57 (7.45). (b) For this synthesis, a 2:1 ratio of $LiCCC_6H_4CF_3$ to $[Cr(cyclam)(OTf)_2]OTf$ was used.

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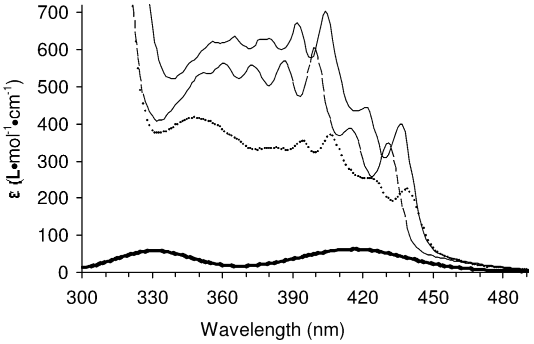

Figure 3. Absorption spectra taken in CH_3CN for **1** (- - -), **2** (—), **3** (•••), and *trans*[Cr(cyclam)$(CN)_2$]$^+$ (thick —) in an aqueous solution.

Table 1. Photophysical Data for *trans*-[Cr(cyclam)$(CCC_6H_4R)_2$]$^+$

	emission λ_{max} (nm)[a, b]		τ (μs)[d]	
	CH_3CN	H_2O[e]	CH_3CN	H_2O[e]
1	748	745	6 (225)[b]	37 (293)[b]
2	749	746	5 (259)[c]	30 (285)[c]
3	748	746	6 (203)[b]	32 (313)[b]

[a] The excitation spectrum for each complex closely resembles its UV−vis spectrum, confirming that emission is not due to an impurity. [b] λ_{ex} = 380 nm. [c] λ_{ex} = 440 nm. [d] Air (degassed). [e] An ion-exchange resin, Dowex 2-X8 Chloride Form 20−50 mesh, was used to assist the solubility of the complexes in H_2O.

lower energy relative to the free acetylenes is unlikely to be due to π back-bonding and can likely be attributed to the $M^{\delta+}-C^{\delta-}$ bond polarization, as suggested by Manna et al.[5b]

The UV−vis absorption spectra of the ethynyl complexes between 320 and 500 nm [typical region for transitions from the $^4A_{2g}$ ground state to the $^4T_{1g}$ and $^4T_{2\,g}$ (O_h) excited states] demonstrate extinction coefficients ranging from 200 to 700 M^{-1} cm^{-1} (Figure 3 and refs 8−10). The molar extinction coefficients are much larger than typical d−d transitions for centrosymmetric species. The spectrum of the isoelectronic *trans*-[Cr(cyclam)$(CN)_2$]$^+$ is shown for comparison and has extinction coefficients of approximately 60 M^{-1} cm^{-1}.[11] Such large extinction coefficients along with the fine structure apparent in the absorption spectrum suggest possible intensity stealing from a proximal charge-transfer band,[18] as has been observed for other alkynyl complexes of chromium(III).[19] The observed fine structure and large extinction coefficients are absent in the analogous *alkyl*ethynyl complexes (the spectra of which look very similar to that of *trans*-[Cr(cyclam)$(CN)_2$]$^+$),[20] suggesting that these features are associated with the aromaticity of the arylethynyl ligands. Low-temperature absorption spectroscopy will be necessary to correlate the fine structure with vibrational data.

Photophysical data for complexes **1**−**3** are summarized in Table 1. Given the comparisons between CN^- and the isoelectronic ethynyl ligands, we expected these arylethynyl complexes to demonstrate emission from their ^2E_g (O_h) excited state like *trans*-[Cr(cyclam)$(CN)_2$]$^+$. However, the steady-state room temperature emission spectra for these ethynyl complexes are broad and structureless, with emission maxima red-shifted relative to the 650−710 nm region observed for most ^2E_g emitters.[21] Such spectra are characteristic of $^2T_{1g} \rightarrow {}^4A_{2g}$ (O_h) transitions.[22] Typical $^2T_{1g}$ emitters of similar structure (e.g., *trans*-[Cr(cyclam)$(OH)_2$]$^+$ and *trans*-[Cr(tet a)F_2]$^+$, where tet a is *C*-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) can be characterized as having axial ligands that are both σ and π donors.[23] Assignment of the emission as originating from the $^2T_{1g}$ excited state only reflects an asymmetry of π effects (π-donating or π-withdrawing) between the axial and equatorial ligands.[24] However, the Raman data and literature precedence[5,19] would suggest that these arylethynyl ligands are acting as π donors toward the electron-poor chromium(III). The excited-state lifetimes of these complexes are solvent-dependent and also sensitive to the presence of oxygen (Table 1). The oxygen sensitivity stands in contrast to *trans*-[Cr(cyclam)$(CN)_2$]$^+$[11] but is consistent with observations for *trans*-[Cr(cyclam)$(NCS)_2$]$^+$.[25] Such oxygen sensitivity for the lifetimes of chromium(III) complexes has been attributed to the presence of π electron density on the coordinated ligand.[26]

In conclusion, we have demonstrated a simple and general method for preparing arylethynyl complexes of the Cr^{III}(cyclam) moiety. Significant differences between these complexes and *trans*-[Cr(cyclam)$(CN)_2$]$^+$ are likely due to differences in the ligand π characteristics. Current investigations include expansion of the range of complexes to the related alkylethynyl complexes, along with full photophysical characterization of the complexes.

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Supporting Information Available: X-ray data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org and from the Cambridge Crystallographic Data Centre (CCDC 694282), obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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