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Trifluoropropynyl as a Surrogate for the Cyano Ligand and Intense, Room-Temperature, Metal-Centered Emission from Its Rh(III) Complex

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Supporting Information

ABSTRACT: The trifluoropropynyl ligand $-C{\equiv}CCF_3$ was studied as a possible surrogate for the cyano ligand. Complexes of the type *trans*-[M(cyclam)$(C{\equiv}CCF_3)_2$]OTf (where M = Cr^{3+}, Co^{3+}, and Rh^{3+}; OTf = trifluoromethanesulfonate) were prepared and then characterized by electronic spectroscopy and by cyclic voltammetry for the Co^{3+} complex. The UV−vis spectra for all three bear a remarkable similarity to that of the *trans*-M(cyclam)$(CN)_2^+$ cations. The trifluoropropynyl complex of Co^{3+} shows electrochemical behavior nearly identical with that of its dicyano analogue. Metal-centered phosphorescence from the Rh(III) complex in room-temperature aqueous solution has a quantum yield of 0.12 and a lifetime of 73 μs, nearly 10 times higher than those of its dicyano analogue.

Since the original discovery of Prussian Blue, cyano transition-metal complexes and clusters have captured the attention of chemists, with the magnetic properties of polynuclear cyano-bridged clusters being of particular recent interest.[1] Alkynyl ligands, because they are isoelectronic with the cyano ligand, have also garnered a great deal of interest, and their transition-metal complexes are being investigated for materials applications ranging from molecular magnetism[2,3] to molecular wires.[4,5] These applications involve communication between the metal centers through an alkynyl bridge, and thus a detailed understanding of the metal−ligand bonding interactions in these complexes is important.[6] Our recent interest in transition-metal alkynyl complexes was sparked by the unique photochemistry/photophysics of the *trans*-Cr(cyclam)$(CN)_2^+$ and *trans*-Rh(cyclam)$(CN)_2^+$ cations,[7,8] which exhibit unusually long-lived excited states in room temperature fluid solution. Thus, we began efforts to prepare and characterize the analogous M(cyclam)$(CCR)_2^+$ complexes.[9] Although emissive, these complexes demonstrated differences in their photophysical behavior that indicated that the isoelectronic analogy between the alkynyl and cyano ligands has significant limitations, as has been clearly demonstrated in several other examples.[6] A key question revolves around whether the alkynyl ligand is acting as a net π donor or π acceptor, with the answer likely being specific to the metal−ligand combination. Our own studies with Cr(III) complexes are consistent with aryl- and alkylethynyl ligands being more electron-rich than CN^- and more prone to behaving as π donors.[9] The question addressed here involves whether or not the addition of a strong electron-withdrawing substituent to the alkynyl ligand can result in an appropriate electronic surrogate for the cyano ligand. Herein we suggest that, indeed, the trifluoropropynyl ligand serves as a suitable replacement for the cyano ligand in the *trans*-[M(cyclam)$(C{\equiv}CCF_3)_2$]OTf complexes (**1a**, M = Rh^{3+}; **2a**, M = Cr^{3+}; **3a**, M = Co^{3+}). In addition, **1a** and **2a** have phosphorescence lifetimes that exceed those of their cyano analogues, with **1a** exhibiting intense room-temperature phosphorescence visible to the naked eye.

The syntheses of the trifluoropropynyl complexes followed the general method reported earlier by our group, wherein alkynyllithium is generated in situ in tetrahydrofuran (THF) in the presence of the [M(cyclam)$(OTf)_2$]OTf precursor (Figure 1).[9] The preparation of η^1-trifluoropropynyl complexes of transition metals is limited to a few examples.[10,11]

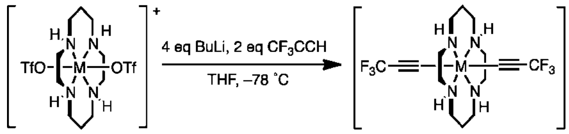

Figure 1. General synthesis of the trifluoropropynyl complexes.

Although it has been reported that trifluoropropynyllithium has a lifetime of just a few minutes in a THF solution at −78 °C,[11] we reasoned that if it were prepared in situ with [M(cyclam)$(OTf)_2$]OTf, the trifluoropropynyl anion might react to form the desired complex prior to decomposition. This appears to have been realized because analytically pure samples of [M(cyclam)$(C{\equiv}CCF_3)_2$]OTf were prepared in 50−80% yield. The trans isomers predominated and were separated by recrystallization. The isomeric purity was confirmed by IR spectroscopy (see the Supporting Information). For the purpose of comparison, the corresponding dicyano complexes **1b**−**3b** were prepared according to literature procedures.[12] In contrast with the analogous phenylethynyl complexes, M(cyclam)$(C{\equiv}CPh)_2^+$, the M(cyclam)$(C{\equiv}CCF_3)_2^+$ complexes bear a striking electronic similarity to their corresponding dicyano complexes, as demonstrated by electronic absorption and emission spectra and cyclic voltammetry.

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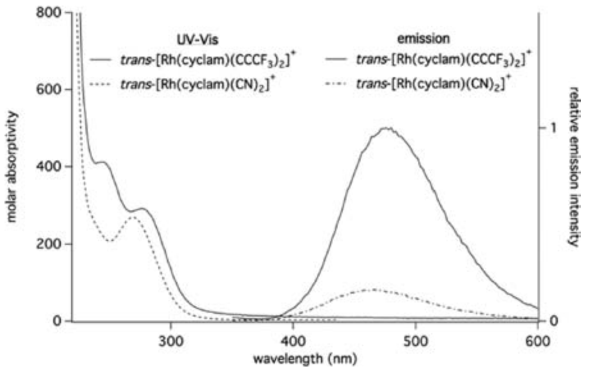

Figure 2. Absorption and emission spectra of **1a** and **1b** in water. The emission spectra are for samples that were absorbance-matched at the excitation wavelength (λ = 269 nm).

Table 1. Photophysical Data for *trans*-$[Rh(cyclam)X_2]^+$ in a Room-Temperature Aqueous Solution[a]

	λ_{max}, nm	$\tau(H_2O)$,[b] μs	ϕ_p[c]
$[Rh(cyclam)(CCCF_3)_2]OTf$[d]	476	73	0.12
$[Rh(cyclam\text{-}d_4)(CCCF_3)_2]OTf$[d]		180	0.26
$[Rh(cyclam)(CN)_2]ClO_4$[e]	470	8.0	0.015[d]

[a] In 1×10^{-4} M HCl to prevent base quenching. [b] λ_{ex} = 337 nm. [c] ±15%. [d] This work. [e] Reference 8.

Rhodium Complexes. The UV−vis and emission spectra of **1a** in aqueous solution bear a close resemblance to that of **1b** (Figure 2). The lowest-energy d−d absorption band of **1a** is red-shifted by 6 nm relative to **1b**. The red shift allows observation of a second higher-energy band before the steep rise in absorbance at 220 nm. Likewise, the emission spectrum is red-shifted to 476 nm versus the reported value of 470 nm for **1b**.[8] The *small* phosphorescence red shift is in stark contrast with that of the arylethynyl complexes, $Rh(cyclam)(C{\equiv}CAr)_2^+$, whose phosphorescence occurs between 520 and 546 nm.[9] The similarity of the electronic transition band shape and energy between the cyano and trifluoropropynyl complexes suggests that these ligands occupy similar positions in the spectrochemical series.

Most remarkable is that the blue-green emission from **1a** is readily visible with the naked eye both in the solid state and in solution at room temperature. By analogy with **1b**, this emission is likely due to metal-centered $^3A_{2g} \rightarrow {}^1A_{1g}$ (D_{4h}) phosphorescence.[8] The phosphorescence quantum yields, ϕ_p, for both complexes have been measured in a room-temperature aqueous solution (Table 1) using literature methods.[13] The value of 0.12 for **1a** is 8 times higher than that of **1b**. Deuteration of the cyclam amine protons of **1a** increases ϕ_p to 0.26. This response to N-deuteration indicates a significant weak-coupling mechanism for nonradiative decay from the excited state.[14] The relationship between quantum yields and lifetimes can be explained using eq 1, where k_p is the rate constant for phosphorescence, k_{nr} is the sum of the rate constants for nonradiative excited-state decay, and τ is the excited-state lifetime.[15,16]

$$\varphi_p = \frac{k_p}{k_p + k_{nr}} = k_p\tau \tag{1}$$

Assuming that k_p is the same for **1b** as it is for both *N*-deuterio and protio **1a**, ϕ_p should track with the excited-state lifetime. This is indeed observed (Table 1) and indicates that the greater ϕ_p for the trifluoropropynyl complex is due to a decreased value of k_{nr}. It is also noteworthy that, like its dicyano analogue, **1a** phosphorescence is not quenched by dissolved oxygen. This is in contrast with the corresponding arylethynyl complexes, which do show phosphorescence quenching by dissolved oxygen.[9] Finally, to rule out emission due to impurity, the excitation spectrum was recorded and is an extremely good match with the UV−vis spectrum (see the Supporting Information). The coincidence in the emission wavelengths and structures of **1a** with **1b** and the deuterium isotope effect for **1a** also support emission from the target complex.

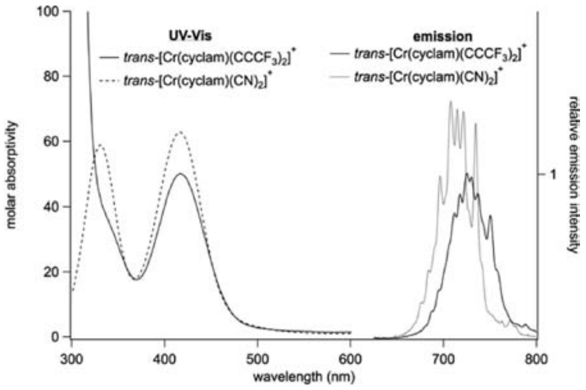

Figure 3. Absorption and emission spectra of **2a** and **2b** in water. The emission spectra are for samples that were absorbance-matched at the excitation wavelength (λ = 417 nm).

Chromium Complexes. The d−d absorption bands of **2a** are very similar in energy and intensity to those of **2b** (Figure 3), with the higher-energy band being obscured by a charge-transfer band for **2a**. This is again consistent with the trifluoropropynyl and cyano ligands being of similar ligand-field strength. In contrast, the same band for *trans*-$Cr(cyclam)(C{\equiv}CC_6H_{11})_2^+$ is red-shifted by 22 nm relative to that of the dicyano analogue.[9]

In addition, the energy and fine structure of the very weak emission (Figure 3) is indicative of phosphorescence from the $^2E_g(O_h)$ state, as is observed for **2b**.[17] This is in stark contrast with the $Cr(cyclam)(C{\equiv}CR)_2^+$ complexes, which show broad, structureless, red-shifted emission from the $^2T_{1g}(O_h)$ state (R = aryl) or mixed emission from both the $^2T_{1g}$ and ^2E_g states (R = cyclohexyl). For those $Cr(cyclam)(C{\equiv}CR)_2^+$ complexes, emission from the $^2T_{1g}(O_h)$ state was attributed to the alkynyl ligands acting as π donors, a characteristic that appears to be absent when R = CF_3.[9] The phosphorescence lifetime of **2a** (Table 2) in a degassed aqueous solution is slightly longer than that of **2b** and also increases significantly in response to

Table 2. Photophysical Data for *trans*-$[Cr(cyclam)X_2]^+$ Compounds in a Room-Temperature Aqueous Solution

	λ_{max}, nm	τ, N_2 (air),[a,b] μs
$[Cr(cyclam)(CCCF_3)_2]OTf$	725[c]	460 (345)
$[Cr(cyclam\text{-}d_4)(CCCF_3)_2]OTf$		1950 (800)
$[Cr(cyclam)(CN)_2]ClO_4$	716[c]	(335)[d]
$[Cr(cyclam\text{-}d_4)(CN)_2]ClO_4$		(1500)[d]

[a] Phosphorescence lifetimes of nitrogen-purged samples are given, followed by lifetimes in air-saturated solutions in parentheses; λ_{ex} = 440 nm. [b] The phosphorescence lifetime of **2a** exhibits a mild concentration dependence, as has been observed for **2b**.[18] The lifetimes reported for **2a** are at a concentration of ~0.5 mM in water. [c] These are the highest-intensity peaks from the fine structure observed in Figure 3. [d] Reference 7.

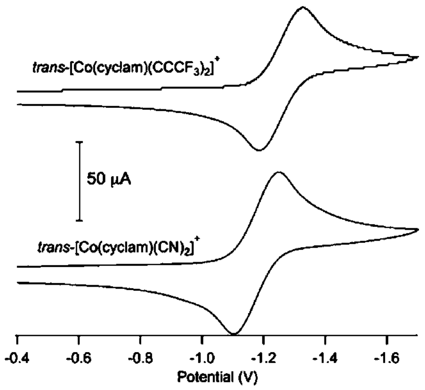

Figure 4. Cyclic voltammograms of **3a** and **3b** (6 mM in DMSO; 0.1 M TBAP), Ag/AgCl reference and glassy carbon working electrodes, 100 mV/s. Under these conditions, ferrocene has a $Fe^{III/II}$ potential of 0.52 V.

deuteration of the cyclam amines. It is also noteworthy that emission from **2a** is somewhat quenched by dissolved oxygen, showing a 25% decrease in the lifetime in an air-saturated aqueous solution. Although this contrasts with **2b**, which shows no excited-state quenching by dissolved oxygen,[7] the quenching of **2a** is notably less than that for other $Cr(cyclam)(C{\equiv}CR)_2^+$ complexes, which are quenched by greater than 40% in an air-saturated aqueous solution.[9]

Cobalt Complexes. The lowest-energy metal-centered absorption band of **3a** (426 nm) is red-shifted by 5 nm from that of **3b** (see the Supporting Information). Again, this is in contrast with the phenylethynyl complex, *trans*-$Co(cyclam)(C{\equiv}CPh)_2^+$, whose lowest-energy absorption band occurs at 463 nm.[3d] Given the typical lack of emission from Co(III) complexes, we additionally compared the cyclic voltammograms of **3a** and **3b** (Figure 4). Each shows chemically reversible $Co^{III/II}$ reduction waves, in contrast with *trans*-$Co(cyclam)(CCPh)_2^+$, which exhibits a nonreversible reduction wave.[3d] The fact that the reduction of **3a** occurs at a potential 80 mV more cathodic than that of **3b** indicates that, in this case, the trifluoropropynyl ligand is slightly more electron-donating than the cyano ligand.

SUMMARY

For each comparison herein, the trifluoropropynyl ligand is a close electronic analogue to the cyano ligand and a much better surrogate than other $:C{\equiv}CR^-$ ligands (where R = cyclohexyl or aryl). Although the small red shifts in UV−vis spectra might suggest that the trifluoropropynyl ligand is a slightly weaker field ligand than cyanide, low-temperature UV−vis would be necessary to reveal the split-band components (under D_{4h} symmetry) that would be necessary for a more definitive statement. Most remarkable is that phosphorescence from **1a** is readily visible by eye with a quantum yield greater than 0.1, which, to our knowledge, is the largest ever observed for metal-centered phosphorescence from a Rh(III) complex. Photophysical studies are ongoing to determine the mechanism by which the trifluoropropynyl ligand enhances phosphorescence.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, IR spectra of **1a**−**3a**, excitation spectra of **1a** and **2a**, and UV−vis spectra of **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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