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A convenient synthesis of isocyclam and [16]aneN$_4$ and the photophysics of their dicyanochromium(III) complexes

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ABSTRACT

The syntheses of the tetraazamacrocyclic ligands 1,4,7,11-tetraazacyclotetradecane (isocyclam) and 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$) in two steps starting from the corresponding tetraamine and diethylmalonate is reported. The *trans*-dicyanochromium(III) complexes, *trans*-[Cr(isocyclam)(CN)$_2$]PF$_6$ and *trans*-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$ have also been prepared. Both are ^2E_g emitters with 0–0 band emission wavelengths at 721.2 and 704.8 nm, respectively. The isocyclam complex has a room temperature excited state lifetime of 147 μs in aqueous solution which increases to 215 μs upon macrocyclic N–H deuteration, whereas the corresponding lifetime of the [16]aneN$_4$ complex is 25 μs and is unaffected by macrocyclic N–H deuteration. The implications of the temperature dependence of the excited state lifetimes are also presented.

1. Introduction

Tetraazamacrocyclic ligands have been the subject of a significant number of studies exploiting their metal ion size selectivity, strong binding constants, and ease of functionalization [1,2]. Among potential applications of the metal complexes of these ligands are the selective removal of toxic metals from waste streams [3], radiotherapy [4], and contrast agents for magnetic resonance imaging [5]. Of the simple ligands in this category (Fig. 1), all but isocyclam and [16]aneN$_4$ are commercially available. Our own interest in these ligands revolves around the synthesis and photophysical characterization of their dicyanochromium(III) complexes. We have chiefly been interested in the effect of steric constraint on the mechanism of excited state deactivation [6], but more recently have been interested in preparing a set of closely related complexes with which to study energy transfer as a function of subtle changes in thermodynamic driving force [7]. With respect to this goal, we are interested in complexes of the general formula *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ (where N$_4$ is a tetraazamacrocyclic ligand). Thus, we set out to prepare the two remaining congeners, *trans*-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$ and *trans*-[Cr(isocyclam)(CN)$_2$]PF$_6$ [8].

The literature syntheses for isocyclam [9] and [16]aneN$_4$ [10] involve cyclization reactions using tosyl-protected polyamines, followed by detosylation reactions in concentrated acid solutions. Thus, we initially set out to design streamlined syntheses of these ligands using more benign reaction conditions. Herein we present a convenient synthesis of these ligands along with the new ligand dioxoisocyclam. We also present the synthesis and photophysical characterization of *trans*-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$, *trans*-[Cr(isocyclam)(CN)$_2$]PF$_6$, and for comparison purposes, *cis*-[Cr([13]aneN$_4$)(CN)$_2$]PF$_6$.

2. Experimental

2.1. Materials and methods

3,6-Diaza-1,9-nonanediamine (2,2,3-tet) was prepared according to the literature procedure [11]. *cis*-[Cr([13]aneN$_4$)Cl$_2$]PF$_6$ was prepared by metathesis of *cis*-[Cr([13]aneN$_4$)Cl$_2$]Cl [12]. Chromatography was performed using activated alumina (Neutral, Brockman I, 150 mesh). All measurements were performed under an air atmosphere unless otherwise noted. UV–Vis absorption spectra were recorded using a Varian Cary-50 spectrophotometer. Emission spectra were recorded on an SLM Aminco instrument running DataMax software. Emission lifetimes were measured using as the excitation source a Photon Technology International (PTI) GL-3300 pulsed nitrogen laser fed into a PTI GL-302 dye laser. Data was collected on an OLIS SM-45 EM fluorescence lifetime measurement system and analyzed using OLIS SpectralWorks. The dye laser was operated at 440 nm, corresponding to $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) excitation of the *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes.

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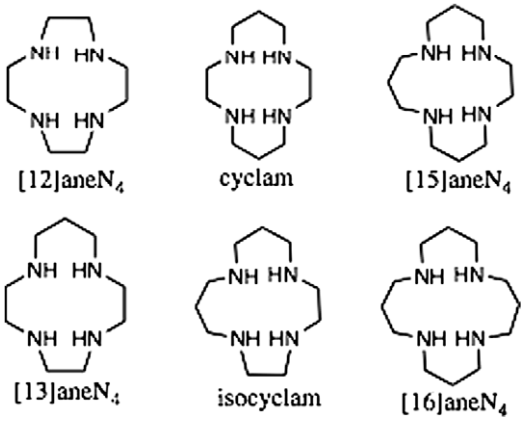

Fig. 1. Simple tetraazamacrocyclic ligands.

2.2. Syntheses

2.2.1. Synthesis of 1,5,9,13-tetraazacyclohexadecane-6,8-dione

A 2 L round bottom flask (RBF) was charged with anhydrous ethanol (1.2 L), 1,5,9,13-tetraazatridecane, (12.15 g, 64.5 mmol) and diethyl malonate (10.33 g, 64.5 mmol). The contents were heated at reflux for seven days under a nitrogen atmosphere, after which the solvent volume was reduced to ~40 mL. The resulting solution was refrigerated at −15 °C for several days to induce crystal growth. White crystals were collected by suction filtration, washed with ice-cold acetonitrile (2 × 5 mL) and cold diethyl ether (2 × 10 mL) and dried in vacuo (3.00 g, 18.1%). ^{1}H NMR ($CDCl_3$): δ 1.66(m, 8H), 2.60(t, 4H), 2.65(t, 4H), 3.15(s, 2H), 3.41(q, 4H), 7.62(bs, 2H). This material is sufficiently pure for the next step. However, the product can be further purified by recrystallization from absolute ethanol. *Anal.* Calc. for $C_{12}H_{24}N_4O_2$: C, 56.23; H, 9.44; N, 21.86. Found: C, 56.37; H, 9.52; N, 21.93%.

2.2.2. Synthesis of 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$)

An oven dried 2-neck 100 mL RBF equipped with a condenser and kept under a positive pressure of nitrogen was charged with 1,5,9,13-tetraazacyclohexadecane-6,8-dione (1.00 g, 3.90 mmol), then BH_3·THF (1.0 M solution in THF, 51.5 mL) was added through a septum. When the evolution of hydrogen had moderated, the rubber septum was replaced with a glass stopper. After 72 h at reflux the contents were cooled to RT and methanol (6 mL) was added dropwise to quench the excess borane. After bubbling ceased, HCl (3.0 M, 10 mL) was added dropwise. The solvent volume was reduced to ~10 mL using rotary evaporation. Methanol (20 mL) was added to the flask and again the solvent volume was reduced to ~10 mL. This process was repeated three more times to aid in the removal of trimethylborate; on the last methanol addition, the solution was evaporated to dryness. The white solid was taken up in HCl (3 M, 40 mL) and the solution was extracted with $CHCl_3$ (2 × 20 mL) to remove organic impurities. The organic layers were discarded and aqueous KOH (15 M, 20 mL) was added dropwise to the aqueous layer to increase the pH > 13. The product was extracted from this basic solution into $CHCl_3$ (5 × 20 mL) and the combined extracts were collected and dried over K_2CO_3. Evaporation of chloroform yielded a white waxy solid (0.444 g, 50%). ^{1}H NMR ($CDCl_3$): δ 1.70(q, 8H), 1.82(bs, 4H), and 2.70(t, 16H). This material is sufficiently pure for use in metal complexation. However, the product can be further purified by sublimation (60 °C, 250 mTorr). *Anal.* Calc. for $C_{12}H_{28}N_4$: C, 63.11; H, 12.36; N, 24.53. Found: C, 62.9; H, 12.10; N, 24.38%.

2.2.3. Synthesis of 1,4,8,12-tetraazacyclotetradecane-5,7-dione (dioxoisocyclam)

This macrocycle was prepared in an analogous fashion to that for 1,5,9,13-tetraazacyclohexadecane-6,8-dione but starting with 2,2,3-tet (10 g, 62.4 mmol), diethyl malonate (9.99 g, 62.4 mmol) in anhydrous ethanol (1 L), yielding 2.68 g (20%) of a white crystalline solid. No further purification was required for this material. ^{1}H NMR ($CDCl_3$): δ 1.60 (bs, 2H), 1.70 (quintet, 2H), 2.66 (m, 6H), 2.76 (t, 2H), 3.18 (s, 2H), 3.37 (quartet, 2H), 3.43 (quartet, 2H), 7.50 (bs, 1H), 7.70 (bs, 1H). *Anal.* Calc. for $C_{10}H_{20}N_4O_2{\cdot}\frac{1}{2}H_2O$: C, 50.61; H, 8.92; N, 23.62. Found: C, 50.69; H, 9.12; N, 23.29%.

2.2.4. Synthesis of 1,4,7,11-tetraazacyclotetradecane (isocyclam)

This was prepared in an analogous fashion to that for [16]aneN$_4$ but starting with 1,4,8,12-tetraazacyclotetradecane-5,7-dione (1.00 g, 4.38 mmol) and BH_3·THF (1.0 M, 57.4 mL) resulting in white waxy solid (0.72 g, 82%). ^{1}H NMR ($CDCl_3$): δ (ppm) 1.66 (q, 4H), 2.10 (bs, 4H), 2.65 (m, 16H). This material is sufficiently pure for metal complexation. However, the material can be further purified by sublimation (75 °C, 300 mTorr). *Anal.* Calc. for $C_{10}H_{24}N_4$: C, 59.96; H, 12.08; N, 27.97. Found: C, 59.98; H, 11.88; N, 27.89%.

2.2.5. Synthesis of trans-[Cr([16]aneN$_4$)Cl$_2$]PF$_6$

The preparation of the crude light-green *trans*-[Cr([16]aneN$_4$)Cl$_2$]Cl using $CrCl_3$ (0.328 g, 2.07 mmol), Zn dust (~0.007 g), and [16]aneN$_4$ (0.472 g, 2.07 mmol) followed the procedure by Eriksen and Mønsted [13] and resulted in 0.442 g of crude *trans*-[Cr([16]aneN$_4$)Cl$_2$]Cl. This solid was dissolved in aqueous NH_4Cl (3 M, ~3 mL) using sonication. The green solution was filtered to remove an insoluble green material that was judiciously rinsed with 3 M aqueous NH_4Cl until the filtrate was colorless. To the green filtrate was added saturated aqueous NH_4PF_6 (~4 mL). The resulting light-green precipitate was collected by filtration and washed with water (2 × 8 mL) and diethyl ether (3 × 5 mL) and dried (0.487 g, 49% overall yield). *Anal.* Calc. for $C_{12}H_{28}N_4CrCl_2PF_6$: C, 29.04; H, 5.69; N, 11.29. Found: C, 28.74; H, 5.55; N, 10.98%.

2.2.6. Synthesis of trans-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$

A 10 mL oven dried RBF was charged with *trans*-[Cr([16]aneN$_4$)Cl$_2$]PF$_6$ (0.100 g, 0.21 mmol) and 1.2 mL anhydrous DMSO. The mixture was heated to 62 °C and upon complete dissolution of the complex, finely ground NaCN (0.084 g, 1.7 mmol) was added. After heating and stirring for 75 min, the contents were filtered (while still warm) to remove insoluble impurities, which were rinsed with an additional 8–10 drops of room temperature DMSO until the filtrate was no longer colored. The product was oiled out by the addition of diethyl ether (30 mL). The supernatant was discarded and this step was repeated to ensure the complete removal of DMSO. To the orange oil was added water (4 mL) followed by saturated aqueous NH_4PF_6 (4 mL), resulting in an orange precipitate. The product was collected by filtration, and washed with water (2 × 1 mL), ethanol (2 × 1 mL), and ether (2 × 5 mL) (0.048 g, 49.5%). *Anal.* Calc. for $C_{14}H_{28}N_6CrPF_6$: C, 35.22; H, 5.91; N, 17.60. Found: C, 35.56; H, 5.84; N, 17.62%. Further purification has been performed by column chromatography using Al_2O_3 and eluting with CH_3CN.

2.2.7. Synthesis of cis/trans-[Cr(isocyclam)Cl$_2$]PF$_6$

A crude mixture of *cis/trans*-[Cr(isocyclam)Cl$_2$]Cl was prepared using isocyclam and $CrCl_3(THF)_3$ according to the method of Swisher et al [14]. For metathesis, *cis/trans*-[Cr(isocyclam)Cl$_2$]Cl (0.526 g, 1.47 mmol) was dissolved in aqueous NH_4Cl (3.0 M, 8 mL). To the filtrate was added saturated aqueous NH_4PF_6 (4 mL) and the olive brown precipitate was collected by filtration and washed with cold distilled water (2 × 5 mL) and diethyl ether

(2 × 4 mL) (0.517 g, 75%). *Anal.* Calc. for $C_{10}H_{24}N_4CrCl_2PF_6$: C, 25.65; H, 5.17; N, 11.97. Found: C, 25.35; H, 5.01; N, 11.69%.

2.2.8. Synthesis of trans-[Cr(isocyclam)(CN)$_2$]PF$_6$

To a 25 mL oven dried RBF was added *cis/trans*-[Cr(isocyclam)Cl_2]PF_6 (0.200 g, 0.427 mmol) and 3.0 mL anhydrous DMSO. The contents in the flask were brought to 65 °C and when the complex was dissolved, NaCN (0.113 g, 2.30 mmol) was added. After 75 min the flask was cooled to room temperature. The DMSO was extracted using diethyl ether (5 × 20 mL). To the orange brown oil that remained was added aqueous NH_4PF_6 (saturated, 4 mL) and the mixture was stirred in an ice bath for 10 min. The orange brown precipitate was collected by filtration and washed with H_2O (2 × 1 mL), ethanol (2 × 1 mL), and diethyl ether (2 × 5 mL). After drying, the crude material (0.118 g) was dissolved in 30 mL CH_3CN and dry loaded onto 3 mL of Al_2O_3 and then eluted down an Al_2O_3 column (7 cm × 2 cm) using CH_3CN. The yellow band was collected and the solvent volume was reduced to ~5 mL. Diethyl ether was added to the concentrated yellow solution and the yellow precipitate was collected by filtration, washed with diethyl ether (3 × 5 mL) and dried (0.0467 g, 24%). *Anal.* Calc. for $C_{12}H_{24}N_6CrPF_6$: C, 32.08; H, 5.38; N, 18.70. Found: C, 32.37; H, 5.28; N, 18.72%.

2.2.9. Synthesis of cis-[Cr([13]aneN$_4$)(CN)$_2$]PF$_6$·H$_2$O

The following procedures were performed in the absence of light. To a 25 mL oven dried RBF was added *cis*-[Cr([13]aneN$_4$)Cl_2]PF_6 (0.200 g, 0.44 mmol) and 3 mL anh. DMSO. The flask was heated to 62 °C and when the complex was completely dissolved finely ground NaCN (0.116 g, 2.38 mmol) was added. The contents were stirred for 75 min. at 62 °C. The DMSO was extracted (5 × 20 mL) with diethyl ether. To the dark brown colored oil was added 8 mL of a 1.0 M solution of NH_4PF_6. The crude orange precipitate was collected by filtration then dissolved using a minimum volume of warm water. NH_4PF_6 (1.4 g) was added and after refrigeration overnight, the orange precipitate was collected by filtration and washed with diethyl ether (0.067 g, 35%). *Anal.* Calc. for $C_{11}H_{22}N_6CrPF_6{\cdot}H_2O$: C, 29.15; H, 5.34; N, 18.54. Found: C, 29.37; H, 5.21; N, 18.56%. UV–Vis(CH_3CN)(ε M^{-1} cm^{-1}): 458 nm(125) and 338 nm (112). Raman shift ν(C≡N) (cm^{-1}): 2144 and 2123.

2.3. N–H deuteration of trans-[Cr(N$_4$)(CN)$_2$]PF$_6$

A 25 mL round bottom flask was charged with the complex (20 mg), D_2O (20 mL), and 1 drop of triethylamine. The solution was stirred for 4 h in the case of the [16]aneN$_4$ complex and 16 h for the isocyclam complex. The solvent was removed on a vacuum line. Deuteration was determined to be >90% by IR spectroscopy.

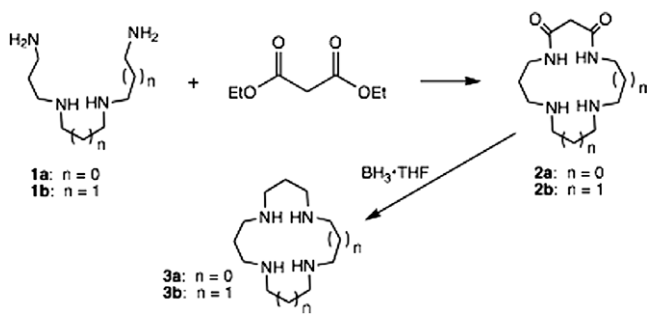

Fig. 2. Synthesis of macrocyclic diamide ligands dioxoisocyclam (**2a**), dioxo-[16]aneN$_4$ (**2b**), isocyclam (**3a**), and [16]aneN$_4$ (**3b**).

3. Results and discussion

3.1. Ligand syntheses

The general scheme for synthesis of the ligands follows a general method first used by Tabushi et al. [15] for the synthesis of C-alkylated cyclams and consists of a cyclization reaction between the appropriate tetraamine and diethylmalonate to obtain the macrocyclic diamide ligands, followed by a borane reduction to give the tetraazamacrocycles (Fig. 2). The ligand dioxoisocyclam has not been previously reported whereas the ligand dioxo-[16]aneN$_4$ was previously reported but without synthetic details or analytical data [16]. The syntheses of the macrocyclic diamides are very reliable with the products simply crystallizing out of the concentrated reaction mixture after several days to a week. Precursor tetraamine, **1b**, used for the synthesis of [16]aneN$_4$ is commercially available, whereas precursor tetraamine, **1a**, for the synthesis of isocyclam can be prepared in large quantities from the condensation of diethylenetriamine with acrylonitrile followed by catalytic hydrogenation [11]. The macrocyclic diamides thus obtained are of sufficient purity for use in the borane reduction. The borane reduction of **2a** to give **3a** (isocyclam) proceeds with good yield, typically between 80% and 90%. The analogous reduction of **2b** to give **3b** ([16]aneN$_4$), on the other hand, consistently gives lower yields, typically near 50%. These macrocyclic tetraamines are of sufficient purity to use in metal complexation reactions. In our hands, we find this synthetic scheme more convenient than the known literature syntheses of isocyclam [9] and [16]aneN$_4$ [10]. It also provides a synthetic strategy for the synthesis of C-functionalized isocyclam and [16]aneN$_4$ ligands by starting with C-alkylated diethylmalonate [15].

3.2. Metal complex syntheses

Initial metallation of the macrocyclic ligands to give the [Cr(N$_4$)Cl_2]Cl follows known literature procedures. For the case of isocyclam [12,14], $CrCl_3(THF)_3$ is used for the metallation according to the method used successfully for cyclam [17], whereas for the case of [16]aneN$_4$ [13], $CrCl_3$ in the presence of catalytic Zn is used for the metallation. We have also attempted the metallation of [16]aneN$_4$ using $CrCl_3(THF)_3$ [12] but have had poor results. To render the complexes soluble in organic solvent for the replacement of Cl^- ligand by CN^-, metathesis of the Cl^- counterion for PF_6^- was performed. An excess of NH_4Cl was added during the metathesis in order to suppress any aquation reactions [6a,18]. We were particularly interested in preparing the dicyano complexes because of the unique photochemical behavior of the known [CrN$_4$(CN)$_2$]$^+$ complexes and our interest in the effect of macrocycle geometry on their photobehavior [6]. Ligand exchange of Cl^- by CN^- using a modification of the literature scheme for *trans*-[Cr(cyclam)(CN)$_2$]$^+$ [8a] gave the desired complexes in moderate yield. Whereas [13]aneN$_4$ has only been observed to form complexes with the *cis*-configuration with Cr(III) (presumably due to the relatively small hole-size) [12], and [16]aneN$_4$ preferentially forms complexes of the *trans*-configuration with Cr(III) [12,13], isocyclam complexes can be either *cis* or *trans* [12,14].

The [Cr(isocyclam)(CN)$_2$]PF_6 initially obtained requires purification using chromatography (neutral Al_2O_3, CH_3CN). Dry loading an acetonitrile solution of the complex onto Al_2O_3 was performed because the crude material does not have good enough solubility in CH_3CN for initial loading onto the column. We are confident that the product from this synthesis and purification is the *trans*-isomer for three reasons. First, the related cyclam complex, *trans*-[Cr(cyclam)(CN)$_2$]ClO_4, is prepared from a *cis/trans* mixture of [Cr(cyclam)Cl_2]ClO_4 and results exclusively in the *trans* isomer [8a].

Second, we have demonstrated that *cis*-[Cr([13]aneN$_4$)(CN)$_2$]PF$_6$ moves more slowly under the column conditions used to purify [Cr(isocyclam)(CN)$_2$]PF$_6$. We expect that this is due to the more polar nature of the *cis*-isomer and expect the same to be true of the *cis*-isomer of [Cr(isocyclam)(CN)$_2$]PF$_6$, were it to form. Third, whereas both *cis*-[Cr([13]aneN$_4$)(CN)$_2$]PF$_6$ and *cis*-[Cr(*rac*-(5,12)-Me$_6$[14]aneN$_4$(CN)$_2$]Cl [8c] are orange solids with notable asymmetry evident in the UV–Vis absorptions, the [Cr(isocyclam)(CN)$_2$]PF$_6$ complex reported herein is bright yellow with two unsplit bands in the UV–Vis (vide infra).

The elemental analysis of the [Cr([16]aneN$_4$)(CN)$_2$]PF$_6$ initially obtained indicates good purity without the need for column chromatography. However, the emission data (vide infra) suggests that this product may be a mixture of isomers or that there may be a trace impurity. The isomeric possibilities are *cis*- and *trans*-isomers, and/or a mixture of isomers relating to the chirality at each nitrogen [13,19]. After column chromatography, the emission data is more consistent with a single isomer.

3.3. Photobehavior

3.3.1. UV–Vis absorption spectra

UV–Vis data for the four *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes (N$_4$ = cyclam, isocyclam, [15]aneN$_4$, [16]aneN$_4$) demonstrates the effect of ring geometry on both ligand field strength and molar absorptivity (Fig. 3, Table 1). For example, the increase in λ_{max} as one proceeds through this series from cyclam to [16]aneN$_4$ is consistent with previous reports of the ligand field strengths of these macrocycles toward chromium(III), namely, cyclam > isocyclam > [15]aneN$_4$ > [16]aneN$_4$, and is consistent with hole-size arguments [12,20]. In addition, it is noteworthy that isocyclam has the largest molar absorptivity, an indication of the reduction of centrosymmetry (and consequent relaxation of the LaPorte selection rule) imposed by the ligand on this complex. Unusually high extinction coefficients were also reported for *trans*-[Cr(1,4-C$_2$-cyclam)(CN)$_2$]PF$_6$ and were related to the lack of centrosymmetry demonstrated by X-ray crystallography [6a].

3.3.2. General excited state behavior

The photophysical data for the *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes are summarized in Table 2 and Fig. 4. The room temperature emission spectra are broad and moderately structured with peak positions similar to that observed for other *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes that have been characterized as ^2E_g (O_h) emitters [21]. Room temperature excitation spectra closely match the UV–Vis spectra, confirming that the observed emission is not due to an impurity. The 77 K spectrum of [Cr(isocyclam)(CN)$_2$]$^+$ is dominated by the 0 → 0 emission band (721.2 nm) as is characteristic of complexes with a lower degree of centrosymmetry as would be imparted by this macrocycle. In contrast, the 77 K emission spectrum of [Cr([16]aneN$_4$)(CN)$_2$]$^+$, shows vibronic structure and, like the centrosymmetric cyclam complex, a relatively weak 0 → 0 band (704.8 nm).

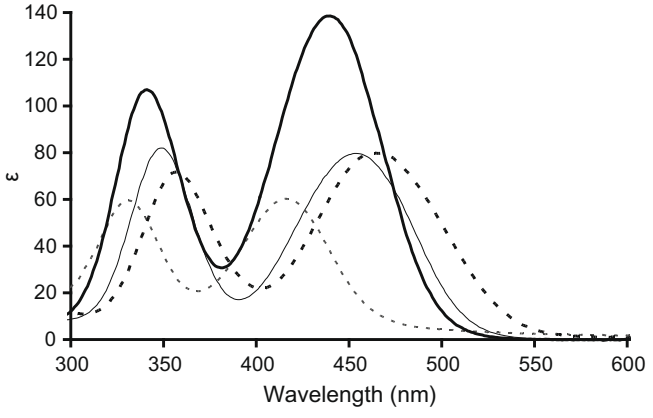

Fig. 3. UV–Vis spectra of *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes: — *trans*-[Cr([15]aneN$_4$)(CN)$_2$]ClO$_4$; - - - *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$; **- -** *trans*-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$; — *trans*-[Cr(isocyclam)(CN)$_2$]PF$_6$.

Table 1
UV–Vis spectral data for Cr(III) tetraazamacrocycle complexes.

Complex	λ_{max} (ε)	Ref.
trans-[Cr(cyclam)(CN)$_2$]ClO$_4$	414 (63), 328 (62)	[8b]
trans-[Cr(isocyclam)(CN)$_2$]PF$_6$	440 (143), 341 (110)	this work
trans-[Cr([15]aneN$_4$)(CN)$_2$]ClO$_4$	452 (80), 348 (82)	[7b,8c]
trans-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$	464 (84), 357 (74)	this work

Table 2
Phosphorescence lifetimes (in μs) for [Cr(N$_4$)(CN)$_2$]$^+$ complexes.[a]

Compound	τ, H$_2$O (20 °C)	τ, DMSO (20 °C)	τ, 1:1 DMSO/H$_2$O (77 K)
trans-[Cr(isocyclam)(CN)$_2$]$^+$	147[b]	215[b]	249
Deutd *trans*-[Cr(isocyclam)(CN)$_2$]$^+$	404[b]		711
trans-[Cr([16]aneN$_4$)(CN)$_2$]$^+$	24	38[c]	217
Deutd *trans*-[Cr([16]aneN$_4$)(CN)$_2$]$^+$	27[d]		2800[e]
trans-[Cr(cyclam)(CN)$_2$]$^+$	335[f]	330[f]	355[f]
Deutd *trans*-[Cr(cyclam)(CN)$_2$]$^+$	1500[f]		3060[f]

[a] Solutions were 0.01 M in HCl to avoid base quenching. This also suppresses H/D exchange of the N-deuterated complexes [6b].
[b] N_2 purged.
[c] Biexponential decay trace with a shorter lifetime of 8 μs.
[d] Biexponential decay trace with a shorter lifetime of 3 μs.
[e] Biexponential decay trace with a shorter lifetime of 860 μs.
[f] Value reported in Ref. [8b].

In addition, these complexes show a significant variation in their room temperature excited state photobehavior in water, particularly when compared with the cyclam complex. For example, the room temperature excited state lifetimes for the complexes of cyclam, isocyclam, and [16]aneN$_4$ are 335, 147, and 25 μs, respectively. Noteworthy also is that the isocyclam complex is slightly quenched by oxygen, i.e., the lifetime drops from 147 μs to 134 μs in air saturated solution. Excited state quenching by oxygen is not observed for the complexes of cyclam or [16]aneN$_4$ and appears to be unique to the isocyclam complex. The lifetimes are slightly longer in acidified DMSO (0.01 M HCl) than in aqueous solution (Table 2). The emission of both the isocyclam and [16]aneN$_4$ complexes is quenched by base, a feature also reported for the analogous cyclam [8b] and [15]aneN$_4$ [8c] complexes. That is, in a pH 9 buffer (phosphate, 0.01 M), the lifetime of the isocyclam complex drops to 22 μs and the lifetime of the [16]aneN$_4$ complex drops to 12 μs.

Aqueous solutions of neither *trans*-[Cr(isocyclam)(CN)$_2$]PF$_6$ nor *trans*-[Cr([16]aneN$_4$)(CN)$_2$]PF$_6$ show perceptible changes in the UV–Vis spectrum after 1 h photolysis in a Rayonet Photochemical Reactor operating with eight 350 nm lamps ($\sim 5 \times 10^{-8}$ ein/s). Thus, these complexes are reasonably photochemically inert, consistent with other *trans* complexes of this type [6,8]. An aqueous solution of the *cis*-[Cr([13]aneN$_4$)(CN)$_2$]PF$_6$ complex, on the other hand, has a very short room temperature lifetime (1 μs) and shows significant decomposition after irradiation for 90 min at 350 nm. Specifically, the absorbance of the peak at 338 nm drops by 30%; the peak at 458 shows a similar drop in absorbance and a concom-

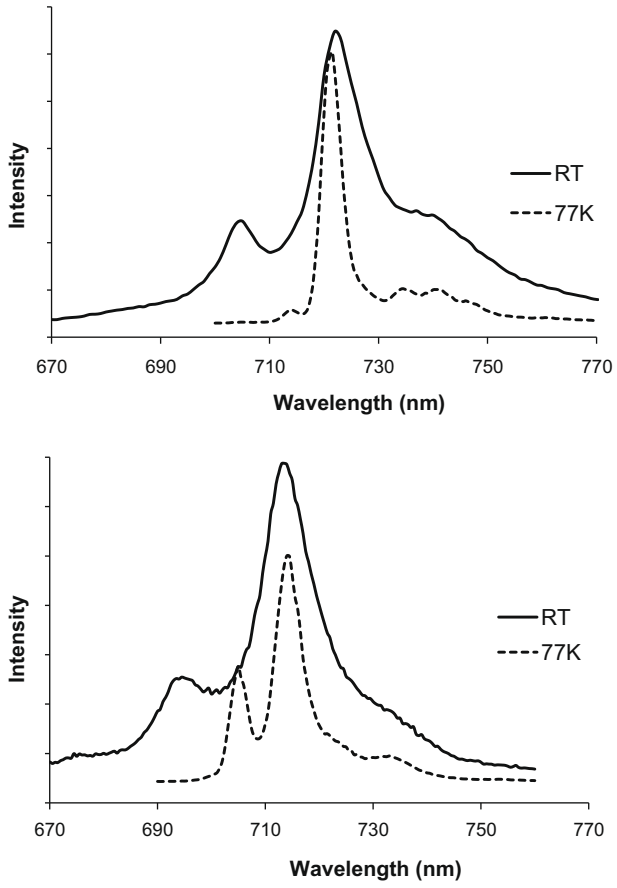

Fig. 4. Emission spectra of *trans*-[Cr(isocyclam)$(CN)_2$]PF_6 (top) and *trans*-[Cr([16]aneN$_4$)$(CN)_2$]PF_6 (bottom).

itant 10 nm redshift; and a new shoulder grows in at 560 nm. These findings are consistent with previous studies on $[Cr(N_4)(CN)_2]^+$ complexes which demonstrate that for *trans* complexes, the dominant ligand field reaction mode is equatorial am(-m)ine loss, whereas for the *cis* complexes, there is also appreciable CN^- loss [22]. For the cases studied herein, productive N-photolabilization is precluded by the macrocyclic ligand effect, leaving only photolabilization of the CN^- ligands as a productive photoreaction.

As discussed with the complex syntheses, the [Cr([16]aneN$_4$)$(CN)_2$]$^+$ initially obtained in the synthesis is often pure as demonstrated by elemental analysis. However, prior to chromatography, the excited state decay trace shows clear biexponential behavior, with lifetimes of approximately 3 and 25 μs. After chromatography, the decay trace is single exponential with a lifetime near 25 μs. If an aqueous solution (20 mg in 20 mL) of this column purified material is stirred at room temperature for 1 h with a drop of triethylamine added, the resulting species has UV–Vis spectra, and room temperature and 77 K emission spectra that are indistinguishable from the column purified material, yet the biexponential behavior has been restored. A likely explanation for this phenomenon is that the triethylamine catalyzes isomerization through amine deprotonation and supports the idea that this material is a mixture of isomers involving the N–H stereochemistry (Fig. 5). Experiments on Cr([16]aneN$_4$)Cl_2^+ [13] and Co([16]aneN$_4$)Cl_2^+ [19] have demonstrated the existence of two stereoisomers for each complex. We have been unable to grow X-ray quality crystals for the unambiguous assignment of the stereochemistry. This triethylamine catalyzed isomerization is likely responsible for the

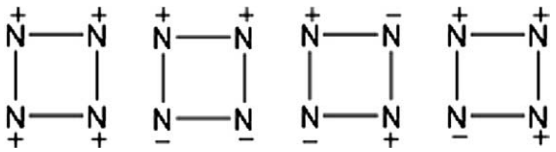

Fig. 5. Possible stereoisomers for [16]aneN$_4$ in *trans*-[Cr([16]aneN$_4$)$(CN)_2$]$^+$.

biexponential excited state decay traces of the deuterated *trans*-[Cr([16]aneN$_4$)$(CN)_2$]$^+$ (Table 2) since triethylamine was used to catalyze the H/D exchange.

In order to more clearly understand the excited state lifetimes of these complexes, we adopt a formalism used extensively for chromium(III) complexes which separates the excited state decay rate constant k_{obs} into temperature dependent and temperature independent components [23].

$$\tau^{-1} = k_{obs} = k^\circ + k(T) \quad (1)$$

Here, τ is the observed lifetime, k° is the nearly temperature independent limiting rate constant for relaxation, and k(T) is the temperature dependent term. The k° term can also be expressed as the sum of a radiative term, k_r°, and a non-radiative term, k_{nr}°, and k(T) takes into account all temperature dependent terms.

Let us first consider the 77 K lifetimes of the complexes (Table 2), the inverse of which approximates k°. For the complexes of the type discussed herein, where the ^2E_g (O_h) and the $^4A_{2g}$ (O_h) electronic states have very similar geometries, the non-radiative relaxation involves tunneling from the excited state to the ground state and is significantly affected by high frequency N–H vibrations, and deuteration of the N–H bonds typically increases the lifetime [24,25]. Note that at 77 K, like the cyclam complex [8b], both the isocyclam and [16]aneN$_4$ complexes demonstrate a significant deuterium isotope effect, consistent with the abovementioned tunneling mechanism. What is curious though, is that the lifetime of the deuterated isocyclam complex is significantly less than either the cyclam or [16]aneN$_4$ complexes. A possible explanation requires consideration that the k° term can be expressed as the sum of a radiative term, k_r°, and a non-radiative term, k_{nr}°, with the non-radiative term being largely due to the aforementioned relaxation involving the N–H oscillators. If k_r° is large enough to compete with k_{nr}° for the isocyclam complex, then the shorter lifetime of the deuterated complex is to be expected. The reason this might be a factor for the isocyclam complex and not for either the cyclam or [16]aneN$_4$ complexes is that the value of k_r should increase with a decrease in centrosymmetry of the complex [26] because of the direct dependence of k_r on the oscillator strength [27]. Given the effect of the Laporte selection rule on the molar absorptivities of the *trans*-$[Cr(N_4)(CN)_2]^+$ discussed previously, it is likely that the oscillator strength of the lower-symmetry isocyclam complex will be the largest, and thus k_r will be the largest. Such an effect has also been observed for the *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6 complex, where the 1,4-C_2-cyclam ligand imposes a reduction of centrosymmetry [6a].

More significant differences in photobehavior are evident in the k(T) term as indicated by the more than tenfold difference in room temperature excited state lifetime between the cyclam and [16]aneN$_4$ complexes. Also, whereas the excited state lifetime of the cyclam complex is nearly identical at 77 K and room temperature, the room temperature excited state lifetime of the isocyclam complex is only a little over half of that at 77 K, and the room temperature excited state lifetime of the [16]aneN$_4$ complex is barely over 10% of that at 77 K. Thus, these new complexes both access a thermally activated decay mechanism at room temperature. Possibilities for thermally activated relaxation include photoreaction,

and back-intersystem crossing to the $^4T_{2g}$ (O_h) excited state. Productive photoreaction has been ruled out by the aforementioned extended photolysis studies and back-intersystem crossing has typically been ruled out for cyano-am(m)ine complexes [8c,22]. Non-productive photoreaction involving Cr–N dissociation followed by reassociation (imposed by the macrocycle) is plausible here and has been suggested for other *trans*-$[Cr(N_4)(CN)_2]^+$ complexes [6b].

Lifetime data for both the [16]aneN_4 and isocyclam complexes was collected over the range of 5–75 °C in 0.01 M HCl(aq). For the [16]aneN_4 complex, plots of $\ln(k - k^\circ)$ versus T^{-1} (Eq. (2), where k° was set to its 77 K value) were linear and gave a value of 39 kJ/mol for E_a and $A = 3 \times 10^{11}$.

$$k = k^\circ + Ae^{-E_a/RT} \quad (2)$$

Even without consideration of k°, the Arrhenius plot was nearly linear, indicating the lifetime of the complex over this temperature range is almost entirely determined by the thermally activated pathway and explains why the [16]aneN_4 complex shows little to no room temperature deuterium isotope effect on its excited state lifetime. A simple Arrhenius plot for the corresponding isocyclam complex data, on the other hand, shows substantial curvature over the temperature range, indicating that the temperature independent term plays a significant role in excited state relaxation at or near room temperature, explaining why this complex shows a significant room temperature deuterium isotope effect on its excited state lifetime. A three parameter fit according to Eq. (2) returned values of $E_a = 39$ kJ/mol, $A = 1 \times 10^{10}$, and $k^\circ = 5900\ s^{-1}$. Thus, the reason that the lifetime of the [16]aneN_4 complex is almost completely determined by the thermally activated mechanism, whereas the k° term is significant for the isocyclam complex lies in the difference in the pre-exponential factor, not the activation energies. It is noteworthy that the activation barriers for both complexes are very similar to the value of 38 kJ/mol determined for *trans*-$[Cr(cyclam)(CN)_2]^+$ [28]. It is also curious that the value for k° for the [16]aneN_4 complex ($5900\ s^{-1}$, which corresponds to $\tau = 170$ μs), is not in good agreement with the 77 K excited state lifetime of 217 μs. This may simply reflect subtle differences in the medium (the 77 K experiments were run in a DMSO/H_2O glass) or may indicate a discontinuity in the lifetime versus temperature behavior that can occur with large changes in solvent mobility as has been observed for other $[Cr(N_4)X_2]^+$ complexes [29].

4. Conclusions

Tetraazamacrocyclic ligands have continued to find applications involving their metal ion binding constants and selectivity. We have provided preparative details for new syntheses of two of the less-utilized ligands in this group that should make these ligands more accessible. Chiefly, we have expanded the set of well-characterized *trans*-$[Cr(cyclam)(CN)_2]^+$ complexes available for our energy transfer studies.

Acknowledgements

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