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Synthesis and Characterization of *cis-* and *trans-*Dicyano(1,4,8,11-Tetraazacyclotetradecane)rhodium(III) Perchlorate

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Studies employing macrocyclic tetradentate amine ligands have contributed significantly to our understanding of transition metal (TM) substitution [1], redox [2], and biological chemistry [2]. The macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) has played a prominent role in these investigations. The photochemical behavior of cyclam complexes of chromium(II) [3] and rhodium(III) [4] have also provided valuable mechanistic insight into TM photosubstitution chemistry. Furthermore, we have recently observed [5] remarkable photochemical and photophysical properties for the chromium(III) species, *trans*-Cr(cyclam)(CN)$_2^+$. Although a wide range of rhodium(III) species of the type Rh(cyclam)X$_2^+$ have been reported [6], the analogous *trans*-Rh(cyclam)(CN)$_2^+$ species has not been previously described. We report here the preparation and characterization of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ and its corresponding *cis*-isomer. The photobehavior of these rhodium(III) complexes will be described elsewhere.

Experimental Section

Reagents

The free ligand cyclam was purchased from Strem Chemicals, while RhCl$_3$·3H$_2$O was obtained from Alfa/Ventron. *Cis*-[Rh(cyclam)Cl$_2$]ClO$_4$ was prepared following the literature procedure [6]. The perchlorate salt of the corresponding *trans*-complex was isolated by addition of NaClO$_4$ to an aqueous solution of the reported chloride salt [6]. All other reagents were of analytical grade quality (Fisher Scientific), and were used without further purification.

Measurements

Electronic absorption spectra were recorded on a Cary 118C spectrophotometer, and infrared data were collected on a Perkin-Elmer 283 using KBr pellets. All NMR spectra were obtained on a Varian FT-80A spectrometer; ^{1}H spectra were obtained at 80 MHz, and ^{13}C spectra at 20 MHz. The ^{1}H spectra are referenced to internal sodium 2,2-dimethyl-2-silapentane sulfonate. The ^{13}C spectra were run in 10 mm tubes as saturated solutions in D$_2$O; 50,000 to 500,000 transients were collected depending on the solubility of the complex in question. The ^{13}C chemical shifts are reported relative to TMS, using internal dioxane as a reference. Conductance measurements in water were determined using a Markson Electromark Analyzer (Model 4403). Elemental Analyses were performed by Midwest Microlabs.

Syntheses

trans-*[Rh(cyclam)(CN)$_2$]ClO$_4$*

A 300 mg sample (6.5 × 10^{-4} mol) of *trans*-[Rh(cyclam)Cl$_2$]ClO$_4$ was dissolved in 30 ml water, 3.50 g ground NaCN (7.1 × 10^{-2} mol) was added, and the solution refluxed for 4 h. After cooling in an ice-bath, a white crystalline product was collected and washed with acetone and ether (135 mg). Further product (70 mg) was obtained on addition of solid NaClO$_4$ to the filtrate. The two solid fractions were then combined, dissolved in the minimum volume of hot water, the solution filtered, and solid NaClO$_4$ added with scratching to the filtrate. The white precipitate was filtered off, washed with acetone and ether, and suction dried (154 mg, 53%). *Anal.* Calcd. for hemihydrate RhC$_{12}$H$_{24}$N$_6$ClO$_4$·½H$_2$O: C, 31.08; H, 5.35; N, 18.00; Cl, 8.01%. Found: C, 31.25; H, 5.43; N, 18.12; Cl, 7.65%.

cis-*[Rh(cyclam)(CN)$_2$]ClO$_4$*

A 300 mg sample (6.5 × 10^{-4} mol) of *cis*-[Rh(cyclam)Cl$_2$]ClO$_4$ was dissolved in 15 ml water, 3.50 g ground NaCN (7.1 × 10^{-2} mol) was added, and the solution refluxed for 3 h. After cooling, a small amount of brown impurity was filtered off, and a large excess of solid LiClO$_4$ added to the filtrate. Cooling 15 min yielded an off-white precipitate, which was filtered and washed with acetone and ether (179 mg). This crude product was recrystallized from a minimum volume of hot water, and solid LiClO$_4$ again added to assist in the reprecipitation. The final white crystalline product was collected, washed with acetone and ether, and suction dried (111 mg, 35%). *Anal.* Calcd for hemihydrate RhC$_{12}$H$_{24}$N$_6$ClO$_4$·½H$_2$O: C, 31.08; H, 5.35; N,

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TABLE I. Ultraviolet Spectral Data for Rh(cyclam)X_2^+ Complexes in Aqueous Solution.

Complex	λ (nm)	ε (L cm^{-1} mol^{-1})	Ref.
cis-Cl_2^+	354, 299, 207	223, 308, 33900	6
trans-Cl_2^+	406, 310sh, 242sh, 204	78, 80, 3300, 37100	6
cis-$(CN)_2^+$	281, 218	465, 1830	this work
trans-$(CN)_2^+$	267, 218	270, 1620	this work

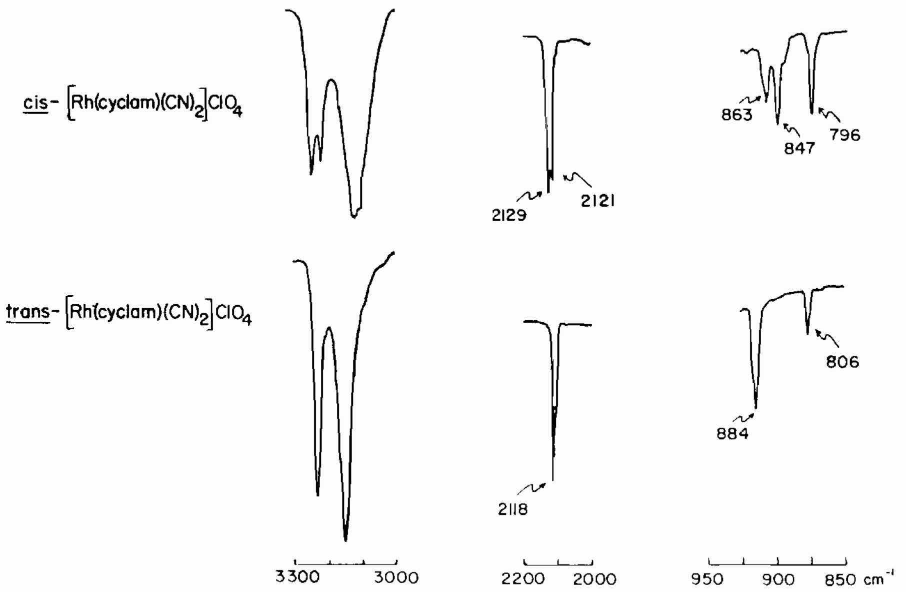

Fig. 1. Infrared spectra (KBr disk) of *cis*- and *trans*-[Rh(cyclam)$(CN)_2$]ClO_4.

18.00; Cl, 8.01%. Found: C, 31.21; H, 5.38; N, 18.19; Cl, 7.84%. *CAUTION:* Although we have encountered no problems with these compounds, perchlorate salts of TM complexes should be handled with care.

Results and Discussion

Syntheses

Bounsall and Koprich have reported [6] the synthesis of 9 different *cis–trans* pairs of Rh-(cyclam)X_2^+ complexes. The *cis* and *trans* products were in each instance obtained from the respective *cis*- or *trans*-Rh(cyclam)Cl_2^+ complex, by heating at reflux temperature in an aqueous solution of the desired anion. Of these products only the *cis*-diiodo species showed any tendency for isomerization. We therefore adopted their synthetic approach in the present study, refluxing aqueous solutions of *cis*- and *trans*-[Rh(cyclam)Cl_2]ClO_4 in the presence of excess CN^- for several hours. Spectroscopic analysis of the compounds isolated provides compelling evidence for cyanide substitution proceeding with retention of geometric configuration (*vide infra*).

Characterization

The molar conductances of 1 X 10^{-3} *M* aqueous solutions of the *cis* and *trans* isomers (89 and 90 ohm^{-1} cm^{-2} mol^{-1}, respectively) are in the range found for 1:1 TM complex electrolytes. Both complexes are resistant to acid or base hydrolysis to the known *cis* and *trans* diaquo or bis(hydroxy) species. The assignment of geometric configuration has therefore been made on the basis of uv, ir and nmr spectral analysis. In Table I the *UV spectra* of the new dicyano species are compared with the literature values for the corresponding dichloro complexes. For both dicyano compounds the band appearing at longest wavelength is assigned as a ligand-field (d–d) transition; the high energy of this transition is in accord with the position of CN^- in the spectrochemical series. There is considerable

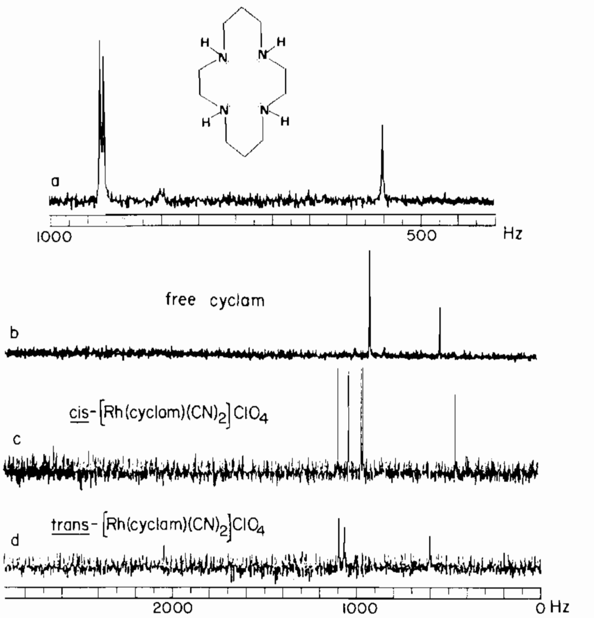

Fig. 2. Proton decoupled 20 MHz ^{13}C NMR spectra in D_2O: (a) free cyclam, at an expanded scale to emphasize the separation of the N-bound methylene carbons (*ca.* 15,000 scans); (b) free cyclam; (c) the *cis* complex (*ca.* 100,000 scans), with peaks at 23.4, 48.6; 49.1; 52.6 and 55.4δ; (d) the *trans* complex (*ca.* 500,000 scans), with peaks at 30.0, 53.5, and 55.0δ. In all cases, peak positions were determined relative to dioxane added subsequently, and are referenced relative to TMS.

precedent for our assumption that the *cis* complex is the compound with the larger molar absorptivity for this long wavelength absorption; however, the energy ordering is the reverse of that for the *cis–trans* pairs described by Bounsall and Koprich [6]. The second d–d transition frequently observed at higher energy for octahedral Rh(III) species is overlain in the present dicyano complexes by the absorption tail of an intense charge transfer (CT) transition centered at 218 nm for both the *cis* and *trans* isomers. These CT transitions are interpreted as metal-to-ligand $d(t_{2g}) \rightarrow \pi^*$, CN^- bands (*i.e.*, MLCT transitions) [7]. The corresponding MLCT band for $Rh(CN)_6^{3-}$ is observed at 192 nm [7].

The use of IR spectroscopy for *cis–trans* isomeric discrimination has been explored extensively by Poon and co-workers [8–10] for a variety of cyclam complexes. They report diagnostic distinctions between *cis* and *trans* isomers in the 790–910 cm^{-1} region; these variations have been found to be independent of the central metal ion, other ligands, and counterions. *Trans* complexes are characterized by two groups of bands – one band (often a doublet) near 890 cm^{-1} due primarily to the secondary amine vibration, and a singlet near 810 cm^{-1} arising predominantly from the methylene vibrations. The amine vibration for the *cis* species invariably occurs at lower frequency, and considerably more splitting is generally observed. The IR spectra of our two dicyano isomers in this region (Fig. 1) also display these anticipated differences. In addition, other regions of the IR spectrum show more splitting in the case of the *cis* species, most evidently in the N–H and C≡N stretch regions (Fig. 1).

As expected [11], the *proton NMR* spectra of both isomers in D_2O–D_2SO_4 solution consist of complex multiplets in the methylene region. These proton spectra are, however, of greater diagnostic value in the amine proton region; the *trans* species shows only one resonance at 5.8δ indicative of four equivalent amine protons, whereas the *cis* complex displays two resonances at 5.3 and 6.6δ. The application of *carbon-13 NMR* as a structural probe has received comparatively little attention in TM cyclam systems [12], despite its demonstrated value in differentiating between *cis-* and *trans*-bis(ethylenediamine) complexes of Co(III) and Rh(III) [13]. In Fig. 2 the ^{13}C NMR spectra of *cis-* and *trans-*[Rh(cyclam)(CN)$_2$]ClO$_4$ in D_2O solution are compared with that of the uncomplexed cyclam ligand. This latter spectrum is characterized by a simple pattern – two nearly coincident downfield resonances at 47.0 and 47.1δ associated with the N-bound methylene carbons, and a smaller upfield resonance at 27.8δ assigned to the central carbon of the propylenediamine ring fragments. In accord with expectations, the *trans* complex displays a peak pattern essentially identical to that of the free cyclam (but with considerably more pronounced differentiation of the N-bound methylenes), while the N-bound methylene carbons of the *cis* complex show four distinct resonances, consistent with a folded geometry for the macrocyclic ring. Under our experimental conditions, no signals for the cyanide carbons were observed.

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