Spectroscopic Properties of *cis*-(1,4,8,11-Tetraazacyclo-tetradecane)(1,2-propanediamine)chromium(III) Perchlorate[1]

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The 77 K luminescence and excitation spectra, room-temperature FT-infrared and visible absorption spectra of a newly prepared complex *cis*-[Cr(cyclam)(pn)](ClO$_4$)$_3$, where cyclam and pn represent 1,4,8,11-tetraazacyclotetradecane and 1,2-propanediamine respectively, have been measured. Absorption maximum of the first spin-allowed transition in the electronic absorption spectra of *cis*-[Cr(cyclam)(pn)]$^{3+}$ and *cis*-[Cr(cyclam)(en)]$^{3+}$ appears at nearly the same position. The two spin-allowed and six spin-forbidden electronic transitions are assigned from the visible absorption and excitation spectra. It is also shown that the zero phonon line in the excitation spectrum splits into two components by 50 cm^{-1}.

Introduction

Recently there is a growing interest in the synthetic[2], kinetic[3], crystallographic[4], photochemical[5] and photophysical[6] aspects of octahedral chromium(III) complexes with cyclam (1, 4,8,11-tetraazacyclotetradecane) ligand. The octahedral chromium(III) complexes of the tetradentate macrocyclic amine ligand, cyclam, provide two possible geometric isomers. Both *cis*-isomer with folded cyclam and *trans*-isomer with planar form of the ligand have been found.[7]

The UV-visible and infrared spectroscopic investigations of the chromium(III) complexes with the cyclam ligand have been extensively accomplished, but little works have been reported on the luminescence and excitation spectra of the complexes.[2,5-8]

The purpose of this work is to describe various spectroscopic properties in the UV-visible, infrared, luminescence and excitation spectra of a newly prepared *cis*-[Cr(cyclam) (pn)](ClO$_4$)$_3$. The complex is expected to exhibit strong sharp peaks in the luminescence spectra since it contains a CrN$_6$ skeleton analogous to the known species [Cr(NH$_3$)$_6$]$^{3+}$ and [Cr(en)$_3$]$^{3+}$ which show strong phosphorescence in solid state.[9] In this paper, we wish to report the assignments of the pure electronic energies due to spin-allowed and spin-forbidden transitions.

Experimental

Synthesis. The free ligand cyclam was purchased from the Strem Chemicals. All other materials were of reagent grade and used without further purification. The *cis*-[Cr(cyclam)(pn)](ClO$_4$)$_3$ was prepared from the dinitrato complex[10] in a manner similar to that used for the corresponding ethylenediamine(en) analog.[5a] A 0.4 g ground sample of *cis*-[Cr(cyclam)(NO$_3$)$_2$]NO$_2$·1/2H$_2$O was placed in a small beaker and a 3.45 ml of anhydrous racemic 1,2-propane-diamine (pn) was then added. The mixture was stirred with a thin glass rod for 30 min. The precipitate obtained was collected by suction filtration and washed twice with acetone. The crude product was dissolved in 10 ml of water at room-temperature and the resulting orange solution was filtered to remove unreacted materials and impurities. A 5.0 g of NaClO$_4$ was added to the filtrate and placed in a refrigerator overnight. The

yellow microcrystals were collected and air-dried. The compound was recrystallized three times from the aqueous solution for spectroscopic measurements. *Caution* ! Although we have experienced no difficulty with the present perchlorate salt, this should be regarded as a potentially explosive compound and treated with care. Anal. Calcd for [Cr(C$_{10}$H$_{24}$N$_4$) (C$_3$H$_{11}$N$_2$)] (ClO$_4$)$_3$: C, 24.95; H, 5.64; N, 13.43. Found : C, 24.76; H, 5.53; N, 13.07. Analysis for C, H, and N was performed by Korea Basic Science Center with a carlo Erba 11080 analyzer.

Spectroscopic Measurement. Room-temperature absorption spectrum of freshly prepared aqueous solution was recorded with a Hewlett-Packard Model 8451A diode array spectrophotometer.

Infrared spectrum was measured in KBr pellets on a Mattson 2020 Galaxy FT-IR spectrometer. Luminescence and excitation spectra were recorded at 77 K on a Spex Fluorolog-2 Spectro-fluorometer which consists of a 450 W xenon lamp, two spex 1680 220 mm double monochromators and a thermoelectrically cooled R928 photomultiplier tube. For measurements at 77 K the microcrystalline sample was placed in a 4 mm internal diameter quartz tube and directly immersed in an optical flask which was filled with liquid nitrogen. The wavelength scale was calibrated with the lines from a low-pressure mercury lamp, and the accuracy of the monochromator was found to be ± 0.4 nm. The scanning was repeated three times to diminish noise in measurements of luminescence and excitation spectra. N$_2$ gas was also blown to prevent condensation of moisture build up on outside wall of Dewar flask. The exciation spectrum was obtained by monitoring the luminescence intensity of the vibronic sideband at 700 nm. The spectral slit width of 0.5 mm was used for the excitation spectrum. The luminescence spectrum was measured by exciting at 455-475 nm corresponding to the first spin-allowed transition region, and using 0.3 mm monochromater slit width. The luminescence spectrum was independent of wavelength within this range.

Results and Discussion

Absorption Spectrum. The electronic absorption spectrum of *cis*-[Cr(cyclam)(pn)]$^{3+}$ may be interpreted on the basis of an octahedral environment of CrN$_6$$^{3+}$ ion as follows.
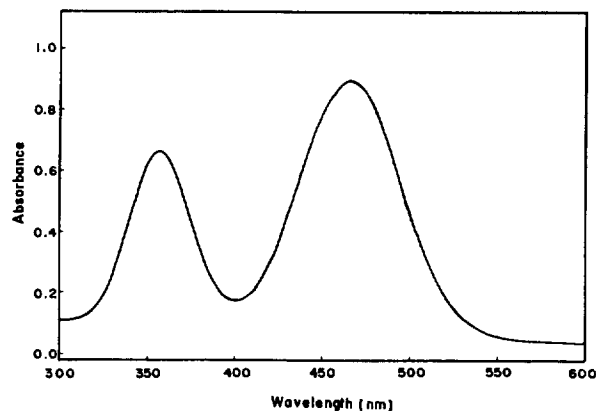
Figure 1. Electronic absorption spectrum of *cis*-[Cr(cyclam)(pn)]$^{3+}$ in aqueous solution at room-temperature.

Table 1. Absorption Maxima of the Spin-allowed Bands in Saturated Hexaaminechromium(III) Ions[a]

Complex ion	$^4A_{2g} \rightarrow ^4T_{2g}$	$^4A_{2g} \rightarrow ^4T_{1g}(F)$	Ref
[Cr(NH₃)₆]$^{3+}$	21600	28490	13
[Cr(en)₃]$^{3+}$	21930	28570	13
[Cr(pn)₃]$^{3+}$	21880	28570	14
[Cr(tn)₃]$^{3+}$	21550	28170	15
[Cr(tacn)₂]$^{3+}$	22780	29410	16
[Cr(diammac)]$^{3+}$	23420	29850	16
[Cr(NH₃)₄(en)]$^{3+}$	21645	28490	13
[Cr(NH₃)₄(tn)]$^{3+}$	21460	28410	15
cis-[Cr(en)₂(NH₃)₂]$^{3+}$	21740	28490	13
cis-[Cr(tn)₂(NH₃)₂]$^{3+}$	21645	28490	15
cis-[Cr(cyclam)(NH₃)₂]$^{3+}$	21280	28090	5a
cis-[Cr(cyclam)(en)]$^{3+}$	21410	28010	5a
cis-[Cr(cyclam)(pn)]$^{3+}$	21460	28090	This work

[a] Data in cm^{-1}.

The hexacoordinate octahedral chromium(III) complexes exhibit three spin-allowed transitions from the ground state $^4A_{2g}(F)$ to $^4T_{2g}(v_1)$, $^4T_{1g}(F)$ (v_2) and $^4T_{1g}(P)(v_3)$.[11] The third v_3 band expected to appear at above 30030 cm^{-1} (333 nm) is usually observed by the charge transfer band in the ultraviolet region.[12] The room-temperature electronic absorption spectrum of *cis*-[Cr(cyclam)(pn)](ClO₄)₃ in aqueous solution is represented in Figure 1.

It exhibits two bands; one at 466 nm (21460 cm^{-1}, v_1) and the other at 356 nm (28090 cm^{-1}, v_2), assigned the $^4A_{2g} \rightarrow ^4T_{2g}$ and $^4A_{2g} \rightarrow ^4T_{1g}$ (O_h) transitions, respectively. These bands are quite similar to those observed for other octahedral CrN₆$^{3+}$ complexes. The band maxima of ligand field transitions for some hexaaminechromium(III) complexes are also summarized in Table 2. Especially, the absorption spectral data of *cis*-[Cr(cyclam)(pn)]$^{3+}$ and *cis*-[Cr(cyclam)(en)]$^{3+}$ are very similar, so that the average ligand field strength of coordinated nitrogen atoms is nearly indentical in both complexes, in spite of the additional methyl group in pn ligand. The energy of the first spin-allowed transition, $^4A_{2g} \rightarrow ^4T_{2g}(v_1)$ directly gives the value of ligand field splitting parameter, $10Dq$. The value of ratio, v_2/v_1 is 1.309. We can find that
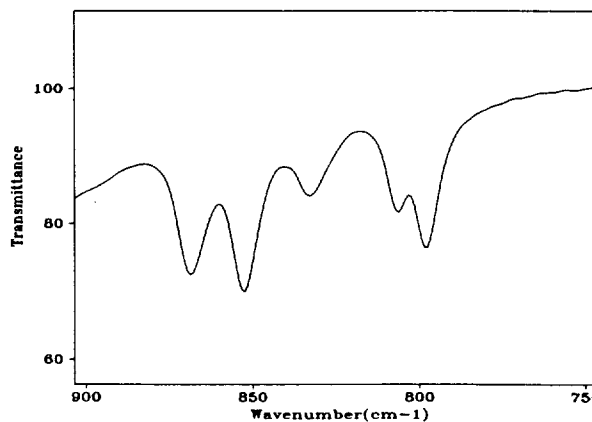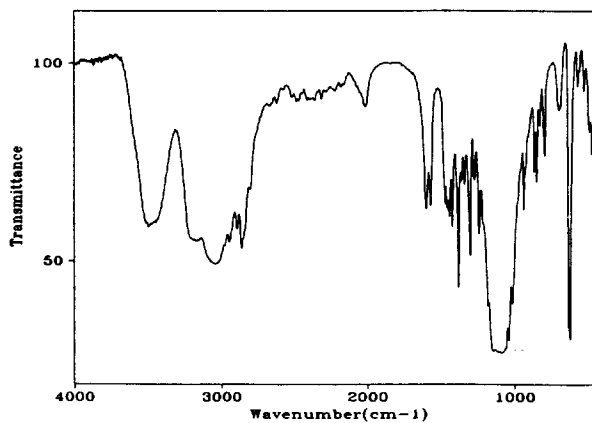

Figure 2. (a) FT-infrared spectrum of *cis*-[Cr(cyclam)(pn)](ClO₄)₃ at room-temperature; (b) Expanded portion of the infrared spectrum in the frequency range 750-900 cm^{-1}.

this value corresponds with $Dq/B = 3.45$, $v_3/B = 73.341$, $v_3/v_1 = 2.126$ and $v_3/v_2 = 1.624$ from the table[11] of transition energy ratios for A_2 ground term in the cubic complexes. The nephelauxetic ratio parameter, β can be calculated using the formula, $\beta = B(\text{complex})/B(\text{free ion})$ where the free ion value[11] for Cr(III) is 918 cm^{-1}. The angular overlap model parameter, e_σ is readily obtained from the relation, $10Dq = 3e_\sigma - 4e_\pi$ because the π-bonding for the amine nitrogen is zero approximately. However, it is noteworthy that the π-bonding ability of nitrogen with sp^2 hybridization such as peptide nitrogen is a weak π-donor.[17] The deduced ligand parameters for *cis*-[Cr(cyclam)(pn)]$^{3+}$ are $Dq = 2146$, $B = 622$ and $e_\sigma(N) = 7153$ cm^{-1}. There is a reduction in the interelectronic repulsion parameter in the complex to about 68% of the free ion value. The transition to the $^4T_{1g}(P)$ state is also predicted to lie at about 45620 cm^{-1}. The third band corresponding to this transition has not been detected in the UV-visible spectrum.

Infrared Spectrum. Figure 2(a) presents the FT-infrared spectrum at room temperature of complex *cis*-[Cr(cyclam)(pn)](ClO₄)₃. The positions and their assignments of infrared absorption peaks are listed in Table 2.

The infrared spectrum shows a strong broad absorption centred at 3480 cm^{-1} which may be assigned to the O-H stretching of the contained water molecule in the complex. The strong bands in the 3200-3000 cm^{-1} and 3000-2800 cm^{-1} regions are due to the N-H and C-H stretching modes,

Table 2. Infrared Spectral Data for *cis*-[Cr(cyclam)(pn)](ClO₄)₃[a]

ν/cm⁻¹	Assignment
440s, 479m, sp	ν(Cr-N)
532w, 574m, sp	ν(Cr-N)+Ring def.
628vs, 700m	ClO₄⁻
798s, 806w, sp	ρ(CH₂)
832w, 854m, 868m, sp	ρ(NH₂)
939m	γ(NH₂)
1043vs	ν(C-C) and ν(C-N)
1102s, br	ClO₄⁻
1276w	γ(CH₂)
1306s, 1344vw	ω(NH₂)
1385s	ω(CH₂)
1427m, 1449m, sp	δ(CH₂)
1577s, 1606s, sp	δ(NH₂)
2017s	
2861vs, 2894w	ν(C-H)
3045s, br 3187s	ν(N-H)
3480s, br	ν(O-H)

[a] Intensities estimated as follows: vs, very strong; s, strong; m, medium; w, weak; br, broad; sp, split.

respectively. The two strong absorption bands at 1607 and 1577 cm⁻¹ and the medium bands in the region 1480-1420 cm⁻¹ can be assigned to the NH₂ and CH₂ bending modes, respectively. The positions are quite similar to those of free ethylenediamine reported by Sabatini and his coworker.[18] A number of absorption bands in the regions of 1400-1200 cm⁻¹ are due to the wagging modes of CH₂ and NH₂. The very strong absorption at 628 cm⁻¹ and strong broad band at 1103 cm⁻¹ are assigned to ionic perchlorate.[19] Metal-nitrogen stretching bands occur in the far infrared range. As seen in Figure 2(a), these Cr-N stretching bands were detected at 440 and 479 cm⁻¹, indicating that nitrogen is coordinated to chromium(III). In the case of [Cr(NH₃)]Cl₃, this peak was found to be at 469 cm⁻¹ frequency.[20]

The infrared spectroscopy is frequently useful in assigning configuration of *cis*- and *trans*-isomers of cyclam chromium (III) complexes. It is well known that *cis*-isomer exhibits at least three bands in the 830-890 cm⁻¹ region due to the NH₂ rocking modes while the methylene vibration splits into two peaks in the 790-830 cm⁻¹ region. However, *trans*-isomer shows two groups of bands, a doublet near 890 cm⁻¹ arising from the secondary amine vibration and only one band near 810 cm⁻¹ due mainly to the methylene vibration[21]. Indeed the present complex exhibits three bands at 832, 854 and 868 cm⁻¹ in the NH₂ rocking frequency region. Two CH₂ rocking bands at 806 and 798 cm⁻¹ are also observed. The expanded portion of the spectrum in those regions is shown in Figure 2(b). As expected, the infrared spectrum of the new complex is clearly consistent with a *cis*-configuration.

As seen in Table 2, our results also support the view that the assignment of NH₂ and CH₂ deformation follows the sequence according to which these vibrational modes have the energetic order[22]: bending>wagging>twisting>rocking.

Luminescence Spectrum. The 77 K luminescence spectrum of *cis*-[Cr(cyclam)(pn)](ClO₄)₃ is shown in Figure
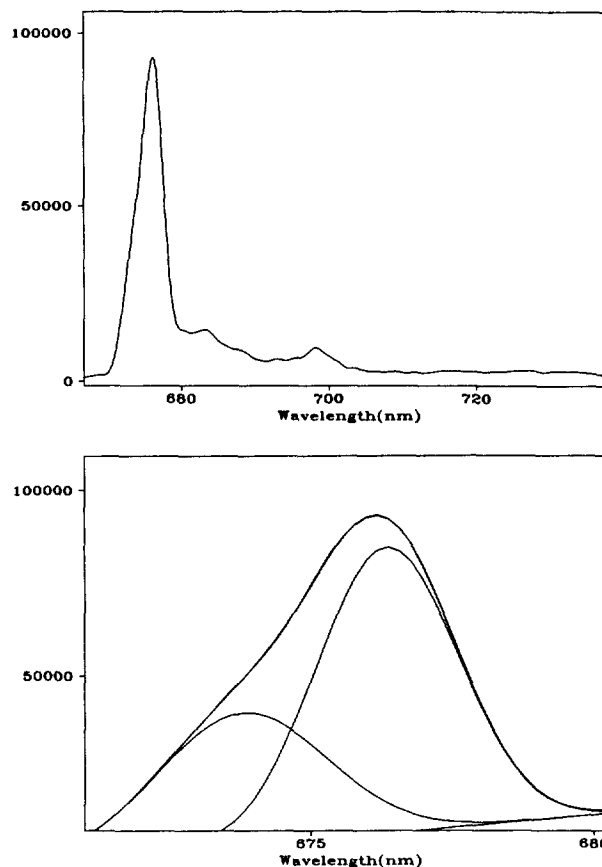

Figure 3. (a) Luminescence spectrum of *cis*-[Cr(cyclam)(pn)] (ClO₄)₃ at 77 K; (b) Expanded portion of the zero phonon line and its resolved Gaussian components in the luminescence spectrum.

Table 3. Luminescence Data for *cis*-[Cr(cyclam)(pn)](ClO₄)₃[a]

λ/nm	ν̄/cm⁻¹	ν̄₀−ν̄/cm⁻¹	Assignment
674.5	14826	−53sh	R₂
676.9	14773	0vs	R₁
681.3	14678	96vw	Lattice mode
684.0	14620	153m	
688.7	14520	254w	δ(N-Cr-N)
693.7	14415	359w	
696.3	14362	413vw	ν(Cr-N)
698.9	14308	466m	
703.9	14207	568vw	ν(Cr-N)+Ring def.
707.1	14142	633vw	ClO₄⁻
709.7	14090	685vw	
712.5	14035	740vw	
716.3	13961	815vw	ρ(CH₂)
717.9	13930	846vw	ρ(NH₂)
720.9	13872	904vw	

[a] Data in cm⁻¹.

3(a). The peak positions and vibronic intervals are also given in Table 3.

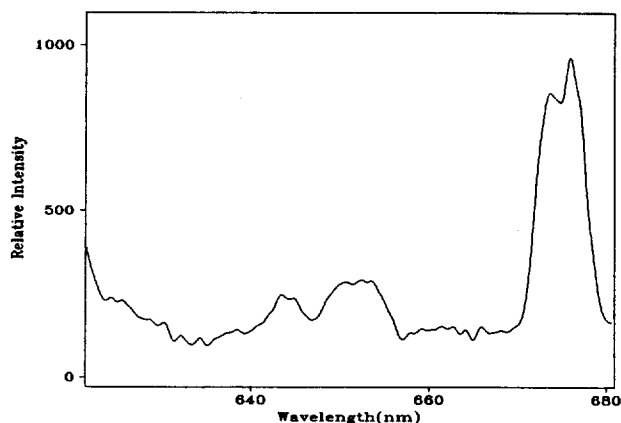The strongest narrow peak at 14773 cm⁻¹ in the luminescence spectrum is assigned to the zero phonon line, R₁ be-

Figure 4. Excitation spectrum of cis-[Cr(cyclam)(pn)](ClO₄)₃ at 77 K.

Table 4. Peak Positions in the 77 K Sharp Line Excitation Spectrum of cis-[Cr(cyclam)(pn)](ClO₄)₃[a]

$\bar{v}$-14791	Assignment	(Calcd)[b]	Vibronic frequenceis		Ground state frequencies
0vs	R_1		v_1	174	153
50s	R_2		v_2	254	254
175vw	R_1+v_1	(174)	v_3	362	359
226m	R_2+v_1	(224)	v_4	471	466
267w					
299w	R_2+v_2	(304)			
328w					
379w					
407vw					
509s	T_1				
535m	R_1+532 (ir)				
572sh	R_1+573 (ir)				
577m	T_2				
715m	T_3				
749m	T_2+v_1	(751)			
871w	T_1+v_3	(871)			
974m	T_1+v_4	(980)			
1029w	T_2+v_4	(1048)			
1077w	T_3+v_3	(1077)			
1120sh	$T_2+v_1+v_3$	(1113)			
1196w	T_3+v_4	(1186)			
1230w					

[a]Data in cm⁻¹. [b]Values in parentheses represent the calculated frequency of the vibrational mode listed. [c]From the luminescence spectrum (Table 3).

cause the corresponding strong peak is found at 14791 cm⁻¹ in the excitation spectrum. A hot band appears as a shoulder on the zero phonon line, which may be assigned to the second component of the $^2E_g{\rightarrow}^4A_{2g}$ transition. The splitting of zero phonon line in the spectrum was obtained by deconvolution to be 53 cm⁻¹ as shown in Figure 3(b). The vibronic intervals below 360 cm⁻¹ are probably to be assigned as lattice vibrations, ring torsion and angle bending modes. The Cr-N stretching modes are found at 413 and 466 cm⁻¹. The
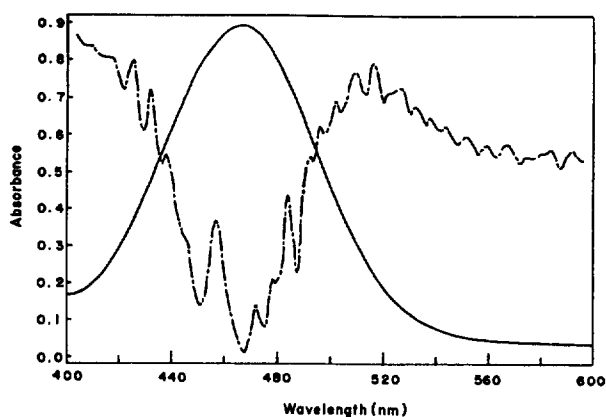

Figure 5. Absorption spectrum (solid line) and second derivative (solid-dashed line) spectrum of cis-[Cr(cyclam)(pn)]³⁺ in aqueous solution.

Table 5. Observed Electronic Transition Energies for cis-[Cr(cyclam)(pn)](ClO₄)₃ in O_h Symmetry[a]

Spin-forbidden		Spin-allowed	
Assignment	Observed	Assignment	Observed
$^4A_{2g}{\rightarrow}^2E_g$	14791	$^4A_{2g}{\rightarrow}^4T_{2g}$ (avg)	21459
	14841		
$\rightarrow^2T_{1g}$	15300	$\rightarrow^4T_{1g}$ (avg)	28090
	15368		
	15506		
$\rightarrow^2T_{2g}$ (avg)	22173		

[a]Data in cm⁻¹.

spectrum did not change with the exciting wavelength within the first spin-allowed band.

Excitation Spectrum. The 77 K excitation spectrum is shown in Figure 4. The peak positions and their assignments are given in Table 4.

The two strong sharp line peaks at 14791 and 14841 cm⁻¹ separated by 50 cm⁻¹ are assigned to the two components of the $^4A_{2g}{\rightarrow}^2E_g$ transition. The zero phonon splitting of 50 cm⁻¹ observed is larger than the 18 and 10 cm⁻¹ observed for [Cr(en)₃]³⁺ and [Cr(tacn)₂]³⁺ complexes, respectively.[9b,23] In general, an experimental problem lies with the difficulty in distinguishing pure electronic transitions from the vibronic bands that also appear in the spectrum. The two components (T_1 and T_3) of $^4A_{2g}{\rightarrow}^2T_{1g}$ transitions are assigned to the two relatively intense peaks at 509 and 715 cm⁻¹ from the lowest electronic line (R_1) because they have no correspondence in the luminescence and infrared spectra. As expected, a greater difficulty was experienced in the assignment of one component of the $^4A_{2g}{\rightarrow}^2T_{1g}$ electronic origin. However, the peak at 557 cm⁻¹ with medium intensity which is assigned as T_2 component of the $^4A_{2g}{\rightarrow}^2T_{1g}$ transition because a few same vibrational structures were observed on this band as on the other electronic origins. The electronic origin was also more intense than the vibronic peaks in the same region.

The higher energy $^4A_{2g}{\rightarrow}^2T_{2g}$ band was found at 451 nm

from the second derivative of the solution absorption spectrum of *cis*-[Cr(cyclam)(pn)]$^{3+}$, as shown with solid-dashed line in Figure 5 and could not be resolved into the separate components.

In conclusion, on the basis of UV-visible, infrared, luminescence and excitation spectral data of *cis*-[Cr(cyclam)(pn)] (ClO$_4$)$_3$, the pure electronic origins due to spin-allowed and spin-forbidden transitions have been located, as given in Table 5. It is shown that the splitting of the zero phonon line in the excitation spectrum is 50 cm^{-1}. A modern ligand field analysis on the electronic spectral data is in progress. The *cis*-configuration of the complex is also confirmed by the infrared spectrum which has five bands in the region 750-900 cm^{-1} due to CH$_2$ and NH$_2$ rocking modes. It is observed that there is not much difference in the ligand field strength of the title complex comparing to those for other hexaamine-chromium(III) complexes. However, we believe that the splitting and peak position of sharp line transitions vary because they are very sensitive to the metal-ligand geometry.[24]

References

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