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Photoemission and Excitation Spectroscopy of *cis*-Difluoro(1,4,8,11-Tetraazacyclotetradecane) Chromium(III) Perchlorate

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The photoemission and excitation spectra of *cis*-[Cr(cyclam)F_2]ClO_4 (cyclam = 1,4,8,11-tetraazacyclotetradecane) taken at 77 K are reported. The 298 K mid- and far-infrared spectra are also measured. The vibrational intervals of the electronic ground state are extracted from the far-infrared and emission spectra. The ten electronic bands due to spin-allowed and spin-forbidden transitions are assigned. The zero-phonon line in the excitation spectrum splits into two components by 169 cm^{-1}, and the large ^2E_g splitting can be reproduced by the ligand field theory. According to the ligand field analysis, we can confirm that nitrogen atoms of the cyclam ligand have a strong σ-donor character, and fluoride ligand also has strong σ- and π-donor properties toward chromium(III) ion.

key words: Chromium(III) complex, vibrational frequencies, electronic transitions

INTRODUCTION

Among the transition metal ions with the $3d^3$ electronic configuration, Cr^{3+} has attracted much attention because of possible applications as laser materials [1]. The trivalent chromium ion prefers octahedral sites and can be incorporated into the variety of halide host lattices [2]. The application of electronic spectroscopy to chromium(III) complexes promises to provide informations concerning ligand field properties as well as metal-ligand geometry [3-9]. It has been found that the splittings of sharp-line electronic transitions are sensitive to the stereochemical environments around the metal. Thus it is possible to extract structural information from sharp-line electronic spectroscopy without a full X-ray structure determination [10,11].

The synthesis, photobehavior and radiative properties of the *cis*-[Cr(cyclam)F_2]ClO_4 (cyclam=1,4,8,11-tetraazacyclotetradecane) have been studied [12,13]. However, the vibrational and electronic energy levels based on the infrared, emission and excitation spectroscopy of title complex have not been published yet.

In the present study, we have measured the 77 K emission and excitation spectra, and the 298 K infrared and visible spectra of *cis*-[Cr(cyclam)F_2]ClO_4. The pure electronic origins were assigned by analyzing the absorption and excitation spectra. Using the observed electronic transitions, a ligand field analysis was performed to determine the metal-ligand bonding properties for the coordinated atoms toward chromium(III) ion. The aim of this research is to create a good spectroscopic basis of knowledge for the further development of new laser materials.

MATERIALS AND METHODS

Materials. The free ligand cyclam was purchased from Strem Chemicals and used as provided. All chemicals were reagent grade materials and used without further purification. The *cis*-[Cr(cyclam)F_2]ClO_4 was prepared as described in the literature [12].

Spectroscopic Measurements. The visible absorption spectrum at room temperature was recorded with a Hewlett-Packard 8452A diode array spectrophotometer. The mid-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer using a KBr pellet. The far-infrared spectra in the region 600-50 cm^{-1} were recorded with a Bruker 113v spectrometer on a microcrystalline sample pressed into a polyethylene pellet. The compound was pressed into a polyethylene pellet (concentration 2 mg in 100 mg polyethylene) by using a Spex 3624B X-Press. These measurements were done at Universität Düsseldorf. The emission and excitation spectra were measured at 77 K on a Spex Fluorolog-2 spectrofluorometer. The spectra at 77 K were obtained by cooling the powder samples in a quartz Dewar flask filled with liquid nitrogen.

RESULTS AND DISCUSSION

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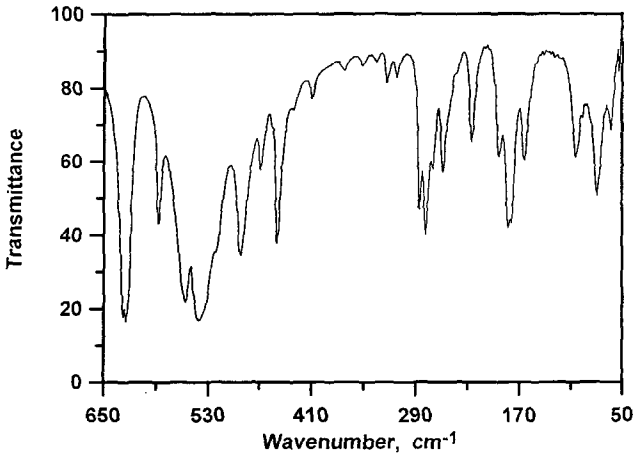

Fig. 1. Far-infrared spectrum of *cis*-[Cr(cyclam)F_2]ClO_4 at 298 K.

Vibrational Intervals. The far-infrared spectra of *cis*-[Cr(cyclam)F_2]ClO_4 recorded at room temperature are presented in Figure 1.

The very strong absorption at 623 cm^{-1} is due to ionic perchlorate. Metal-ligand stretching bands occur in the far infrared range. The peaks in the range 470-405 cm^{-1} can be assigned to the Cr-N stretching mode [14]. A number of absorption bands below 371 cm^{-1} arise from lattice vibration and skeletal bending modes.

An experimental difficulty lies in the assignment of the pure electronic components from the vibronic bands because the vibrational satellites of each electronic origins also appear in the excitation spectrum. It is required that the vibrational intervals of the electronic ground state can be obtained by comparing the emission spectrum with far-infrared spectral data. The 510 nm excited emission spectrum of *cis*-[Cr(cyclam)F_2]ClO_4 at 77 K is shown in Figure 2. The band positions relative to the lowest zero phonon line, R_1, with corresponding infrared frequencies, are listed in Table 1. The emission spectrum was independent of the exciting wavelength within the first spin-allowed transition region.

Table 1. Vibrational frequencies from the 77 K emission and 298 K infrared spectra for *cis*-[Cr(cyclam)F_2]ClO_4[a]

Emission[b]	Infrared	Assignment
-162 w		R_2
0 vs		R_1
52 vw	54 w, 64 w	Lattice vib., and δ(N-Cr-N)
96 sh	80 m, 104 m	
	161 m, 177 m, 181 m	
191 m	193 w, 224 s	
262 sh	256 s, 268 w, 277 vs	
	310 w, 321w, 334 w	δ(F-Cr-N)
350 s	350 vw, 371 vw	
	406 vw, 431 w	ν(Cr-N)
450 vs	446 vs, 466 m	
546 m	535 s, 550 m, 583 s	ν(Cr-F)
635 m	623 vs	ClO_4^-
707 sh	690 w	
805 w	808 vs	$\rho_r(CH_2)$
870 w	854 m, 866 s	ρ_w(NH)
906 vw	901 m	
985 vw	937 m, 998 s	
1015 m	1015 s, 1025 m	

[a]Data in cm^{-1}. [b]Measured from zero-phonon line at 14646 cm^{-1}.

The strongest peak at 14646 cm^{-1} is assigned as the zero-phonon line, R_1, because a corresponding strong peak is found at 14633 cm^{-1} in the excitation spectrum. A hot band at 14808 cm^{-1} may be assigned to the second component of the $^2E_g \rightarrow {}^4A_{2g}$ transition. The vibrational intervals occurring in the spectrum consist of several modes that can be presumed to involve primarily ring torsion and angle-bending modes with frequencies in the range 52-350 cm^{-1}. The bands at 450 and 546 cm^{-1} can be assigned to the Cr-N and Cr-F stretching modes.

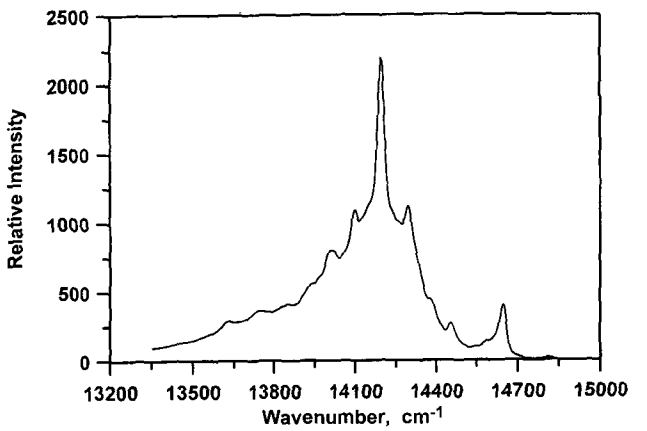

Fig. 2. Emission spectrum of *cis*-[Cr(cyclam)F_2]ClO_4 at 77 K (λ_{ex} = 510 nm).

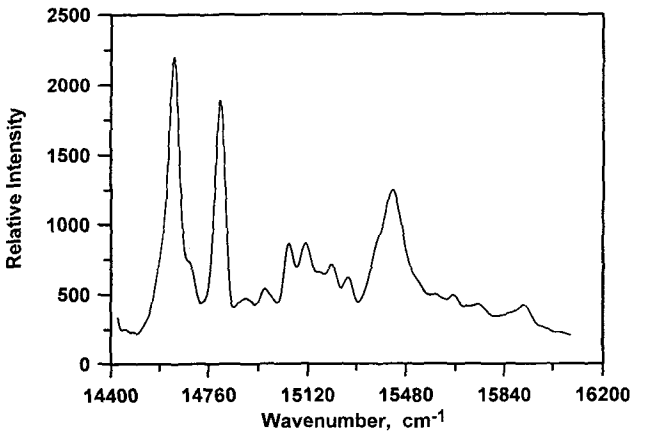

Fig. 3. Excitation spectrum of *cis*-[Cr(cyclam)F_2]ClO_4 at 77 K (λ_{em} = 705 nm).

Table 2. Peak positions in the 77 K sharp-line excitation spectrum of *cis*-[Cr(cyclam)F_2]ClO_4[a]

ν_0-14633	Assignment	(Calcd)[b]		Vibronic frequencies	Ground state frequencies[c]
0 vs	R_1		ν_1	81	80
64 sh	$R_1 + \nu_1$		ν_2	171	177
169 vs	R_2		ν_3	270	268
261 w	$R_1 + \nu_3$	(270)	ν_4	344	350
330 m	$R_2 + \nu_2$	(340)	ν_5	467	466
418 s	$R_1 + \nu_1 + \nu_4$	(425)	ν_6	533	535
480 s	$R_1 + \nu_5$	(467)			
525 vw	$R_1 + \nu_4$			(4533)	
576 s	R_2 + 583 (IR)				
639 m	$R_2 + \nu_5$	(636)			
718 sh					
746 m	T_1				
792 vs	T_2				
830 m	T_3				
876 w	$T_2 + \nu_1$	(873)			
955 vw	$T_2 + \nu_2$	(963)			
1019 m	$T_1 + \nu_3$	(1016)			
1073 vw	$T_2 + \nu_3$	(1062)			
1090 w	$T_1 + \nu_4$	(1090)			
1113 w	$T_3 + \nu_3$	(1100)			
1177 vw	$T_3 + \nu_4$	(1174)			
1280 m	$T_1 + \nu_6$	(1279)			
1352 sh	$T_3 + \nu_6$	(1363)			

[a]Data in cm^{-1}. [b]Values in parentheses represent the calculated frequencies based on the vibrational modes listed. [c]From the emission and infrared spectra (Table 1).

Spin-forbidden Transitions. The excitation spectrum at 77 K is shown in Figure 3. It was recorded by monitoring a relatively strong vibronic peak in the emission spectrum. The spectrum obtained was independent of the vibronic peaks used to monitor it. The peak positions and their assignments are tabulated in Table 2. The calculated frequencies in parentheses were obtained by using the vibrational modes $\nu_1 - \nu_6$ listed in Table 2.

Two strong peaks at 14633 and 14802 cm^{-1} in the excitation spectrum are assigned to the two components (R_1 and R_2) of the $^4A_{2g} \rightarrow {}^2E_g$ transition. The lowest-energy zero-phonon line coincides with the R_1 origin in the emission spectrum within 4 cm^{-1}. The zero-phonon line in the excitation spectrum splits into two components by 169 cm^{-1}, and it can be compared with those of other *cis*-diacidochromium(III) complexes containing tetradentate marcrocyclic cyclam ligand as shown in Table 3 [15-21]. The 169 cm^{-1} of ^2E_g splitting in the excitation spectrum is larger than 139 cm^{-1} and 60 cm^{-1} observed for *cis*-[Cr(cyclam)Cl_2]Cl and *cis*-[Cr(cyclam)$(NO_3)_2$]NO_3, respectively [18,19].

In general, it is not easy to locate positions of the other electronic components because the vibronic sidebands of the ^2E_g levels overlap with the zero phonon lines of $^2T_{1g}$. However, the three components of the $^4A_{2g} \rightarrow {}^2T_{1g}$ electronic origin (T_1, T_2 and T_3) are assigned to relative intense peaks at 746, 792 and 830 cm^{-1} from the lowest electronic line, R_1. Vibronic satellites based on these origins have similar frequencies and intensity patterns to those of the ^2E_g components.

Table 3. The ^2E_g splitting for *cis*-[CrIII(cyclam)X_2]$^{n+}$ complexes

Xa	Splitting[b]	Anion	Ref.
NH_3	83	$(BF_4)_2(NO_3)$	15
en/2	40	$(ClO_4)_3$	16
pn/2	50	$(ClO_4)_3$	17
F^-	169	(ClO_4)	This work
Cl^-	139	(Cl)	18
Br^-	172	(Br)	19
N_3^-	249	(N_3)	20
NCS^-	70	(NCS)	15
ONO^-	93	(NO_3)	15
ONO_2^-	60	(NO_3)	21

[a]en=1,2-diaminoethane; pn=1,2-diaminopropane. [b]Data in cm^{-1}.

The higher energy $^4A_{2g} \rightarrow {}^2T_{2g}$ band was found at 22523 cm^{-1} from the second derivative of the solution absorption spectrum, as shown with dotted line in Figure 4. However, it could not be resolved into the separate components.

Spin-allowed Transitions. The visible absorption spectrum (solid line) of *cis*-[Cr(cyclam)F_2]$^+$ in aqueous solution at room temperature is represented in Figure 5.

It exhibits two bands, one at 19610 cm^{-1} (ν_1) and the other at 27030 cm^{-1} (ν_2), corresponding to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(O_h)$ transitions, respectively.[22] The quartet bands have nearly symmetric profiles. In order to obtain some points of reference for the splittings of the two bands, the band profiles were fitted by using four Gaussian curves (dotted line), as seen in Figure 5. The contribution from outside bands was corrected for the fine deconvolution. A deconvolution pro-

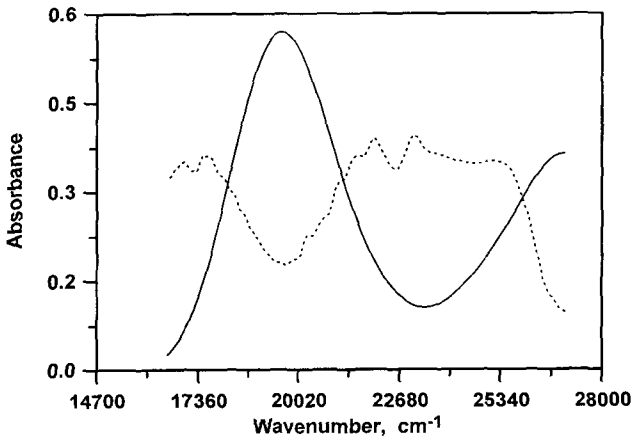

Fig. 4. Absorption spectrum (solid line) and second derivative (dot ted line) of *cis*-[Cr(cyclam)F_2]$^+$ in aqueous solution at 298 K.

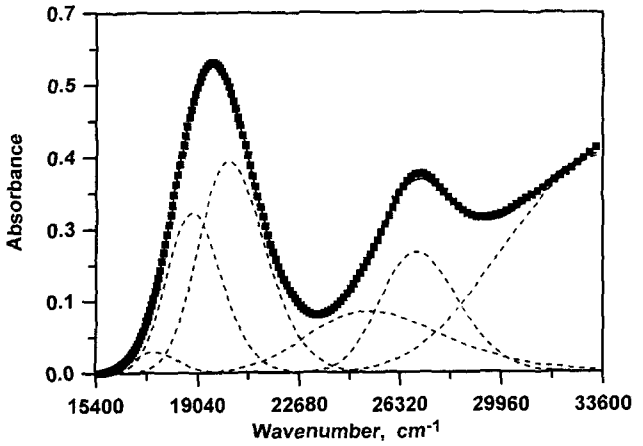

Fig. 5. Resolved electronic absorption spectrum of *cis*-[Cr(cyclam)F_2]$^+$ in aqueous solution at 298 K.

cedure on the experimental band pattern yielded maxima at 18867, 20160, 25125 and 26954 cm^{-1} for the noncubic splittings of $^4T_{2g}$ and $^4T_{1g}$. These peak positions were used as the observed spin-allowed transition energies in the ligand field optimization. In fact, using just one Gaussian curve instead of two yields a least squares error only four times that of the best fit.

Ligand Field Analysis. The ligand field potential matrix was generated for *cis*-[Cr(cyclam)F_2]$^+$ from the coordinated four nitrogen and two fluoride atoms. Although the perchlorate oxygens may also perturbate metal d orbitals, the extent of that interaction was judged too small to warrant any additional adjustable parameters. No crystal structure for any salt of the complex ion is known, thus the positional parameters were adapted from the *cis*-[Cr(cyclam)Cl_2]$^+$, replacing the chlorides with fluorides [18]. The coordinates were then rotated so as to maximize the projections of the six-coordinated atoms on the Cartesian axes centered on the chromium. Angular overlap model parameters provide more chemical insight than the conventional crystal field parameters, and will be used to interpret the electronic spectral transitions [23]. The ligand field analysis was carried out through an optimized fit of experimental to calculated transition energies. Diagonalization of the 120×120 secular matrix yields the doublet and quartet energies with the appropriate degeneracies.[24] Hoggard[11] has described the methods for determining the eigenvalues and eigenfunctions of a d^3 ion in a ligand field from any number of coordinated atoms. The full set of 120 single-term antisymmetrized product wavefunctions was employed as a basis. The Hamiltonian used in the calculation was

$$\hat{H} = \sum_{i<j} \frac{e^2}{r_{ij}} + V_{LF} + \zeta \sum_i \mathbf{l}_i \cdot \mathbf{s}_i + \alpha_T \sum_i \mathbf{l}_i^2 + 2\alpha_T \sum_{i<j} \mathbf{l}_i \cdot \mathbf{l}_j \quad (1)$$

where the terms in the right-hand side represent the interelectronic repulsion, ligand field potential, and spin-orbit coupling, respectively, with the last two representing the Trees correction [25]. The parameters varied during the optimization were the interelectronic repulsion parameters *B*, *C* and the Trees correction parameter α_T, the spin-orbit coupling parameter ζ, the AOM parameters e_σ(F) and e_π(F) for the fluoride-chromium, and e_σ(N) for the cyclam nitrogen-chromium. The π-interaction of amine nitrogens with sp^3 hybridization in the cyclam was assumed to be negligible [16,17]. However, it is noteworthy that the peptide nitrogen with sp^2 hybridization has a weak π-donor character [26]. Schmidtke's π-expansion parameter τ were also included in the treatment of the interelectronic repulsion term. In Schmidtke's approximation, the electrostatic terms are modified by a factor τ for each constituent metal wavefunction that overlaps with a ligand π-orbital. The π-orbital expansion parameter, τ was fixed at the value 0.992. The estimated value was based on the analysis of the type of $[Cr(NH_3)_5X]^{2+}$ (X=NCS^-, CN^-, NCO^-) [6]. All parameters, except e_σ(F) and e_π(F), were constrained to reasonable limits based on the data from other chromium(III) complexes. The seven parameters were used to fit eleven experimental energies: the five $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ components, the average energy of the transition to the 2T2g state, the four $^4A_{2g} \rightarrow \{^4T_{2g}, {}^4T_{1g}\}$ components, and the splitting of the ^2E_g state. Eigenvalues were assigned to states within the doublet and quartet manifolds based on an analysis of the corresponding eigenfunctions. The function minimized was

$$f = 10^3 S^2 + 10^2 \sum D^2 + 10 T^2 + \sum Q^2 \quad (2)$$

where S in the first term is the ^2E_g splitting, and *D*, *T*, and Q represent the differences between experimental and calculated $\{^2E_g, {}^2T_{1g}\}$, $^2T_{2g}$, and $\{^4T_{2g}, {}^4T_{1g}\}$ transition energies, respectively. The Powell parallel subspace optimization procedure [27] was used to find the global minimum. The optimization was repeated several times with different sets of starting parameters to verify that the same global minimum was found. The results of the optimization and the parameter set

Table 4. Experimental and calculated electronic transition energies for *cis*-[Cr(cyclam)F_2]ClO_4[a].

State(O_h)	Experimental	Calculated[b]
^2E_g	14633	14656
	14802	14820
$^2T_{1g}$	15379	15286
	15425	15429
	15463	15542
$^2T_{2g}$	22523	22290
$^4T_{2g}$	18867[c]	18920
	20160[c]	20140
$^4T_{1g}$	25125[c]	25670
	26954[c]	27410

[a]Data in cm^{-1}. [b]e_σ(N) = 7510±26, e_σ(F) = 7705 38, e_π(F)= 1825±32, B = 724 ±6, C = 3150 ±16, α_T = 92±5, ξ = 249 ±29, τ =0.991(fixed). [c]Obtained from the Gaussian component deconvolution.

used to generate the best-fit energies are also listed in Table 4. The fit is very good for the sharp line transitions. The error margins reported for the best-fit parameters in Table 4 are based only on the propagation of the assumed uncertainties in the observed peak positions [28]. The quartet terms were given a very low weight to reflect the very large uncertainty in their position.

The following values were finally obtained for the ligand field parameters: $e_\sigma(N)$ = 7510 ±26, $e_\sigma(F)$ = 7705 ±38, $e_\pi(F)$ =1825 ±32, B = 724 ±6, C = 3150 ±16, α_T = 92 ±5, ζ = 249 ±29 cm^{-1}. A ligand field analysis of the sharp-line excitation and broad-band absorption spectra indicates that the fluoride is strong σ-and π-donor. These values were higher than the values for other coordinated atoms in chromium(III) complexes [3,6,23]. The value of 7510 cm^{-1} for $e_\sigma(N)$ is also comparable to values published for other amines [15-23]. It is suggested that the four nitrogen atoms of the macrocyclic ligand cyclam have strong σ-donor properties toward chromium(III) ion. An orbital population analysis yields a configuration of $(xy)^{0.974}(xz)^{0.979}(yz)^{1.014}(x^2\text{-}y^2)^{0.014}(z^2)^{0.019}$ for the lowest component of the ^2E_g state. The relative d-orbital ordering from the calculation is E(xy) = 1880 cm^{-1} < E(xz) = 2399 cm^{-1} < E(yz) = 3665 cm^{-1} < $E(x^2\text{-}y^2)$ = 22018 cm^{-1} < $E(z^2)$ = 22788 cm^{-1}. These factor plus the AOM parameters are of value in interpreting the photolabilization mode and photostereochemistry of transition metal complexes [29]. The value of the Racah parameter B is about 79% of the value for a free chromium(III) ion in the gas phase. The parameter values reported here appear to be significant, as deduced on the basis of the manifold of sharp line transitions which were obtained from the well resolved excitation spectrum.

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