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OPTICAL SPECTROSCOPY AND LIGAND FIELD PARAMETERS OF *CIS*-DIBROMO(1,4,8,11-TETRAAZACYCLOTETRADECANE) CHROMIUM(III) BROMIDE

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Abstract – The 77 K emission and excitation, and room-temperature visible spectra of *cis*-[Cr(cyclam)Br_2]Br (cyclam=1,4,8,11-tetraazacyclotetradecane) are reported. The mid- and far-infrared spectra at room-temperature 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. It is found that nitrogen atoms of the cyclam ligand have strong σ- donor characters, but bromide ligand has weak σ- and π-donor properties toward chromium(III) ion. The zero-phonon line in the excitation spectrum splits into two components by 172 cm^{-1}, and the large ^2E_g splitting can be reproduced by the ligand field theory.

INTRODUCTION

The optical properties and ligand field states of trivalent chromium complexes have received considerable attention due to their interesting photochemical and photophysical behaviors.[1,2] Absorption, excitation, emission and infrared spectra allow determination of vibrational interval and ligand field parameter of great importance for spectroscopy, photochemistry and photophysics.[3-5] The sharp line transitions due to the spin-forbidden and their splittings in chromium(III) system are strongly affected by the angular positions and orientations of the ligands.[6] Thus it is possible to deduce particular bond angles from electronic and excitation spectroscopy without a X-ray structure determination.[7,8]

While preparation and visible absorption maxima of *cis*-[Cr(cyclam)Br_2]Br were reported,[9] there have been no reports on other spectral properties and ligand field analysis of *d-d* transitions.

In this study the 77 K emission and excitation, and room-temperature visible spectra of *cis*-[Cr(cyclam)Br_2]Br were measured. The pure electronic origins were assigned by analyzing the absorption and excitation spectra. Using the observed electronic transitions, a ligand field analysis has been performed to determine the metal-ligand bonding properties for the coordinated bromide and nitrogen atoms toward chromium(III).

MATERIALS AND METHODS

The free ligand cyclam was purchased from Strem Chemicals. All other chemicals were reagent grade materials and used without further purification. The *cis*-[Cr(cyclam)Br_2]Br was prepared according to published procedure.[9] The compound was recrystallized three times for spectroscopic measurements.

The room-temperature visible absorption spectrum was recorded with a Varian CARY5G UV-VIS-NIR spectrophotometer. The mid-infrared spectrum was obtained with a Mattson Infinity series FT-IR spectrometer on a CsI pellet. The far-infrared spectrum in the region 600-50 cm^{-1} was recorded with a Bruker 113V spectrometer on a sample pressed into a polyethylene pellet. The emission and excitation spectra were measured 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.[10]

RESULTS AND DISCUSSION

Absorption Spectrum

Figure 1 displays the visible absorption spectrum (solid line) of *cis*-[Cr(cyclam)Br_2]$^+$ in aqueous solution at room temperature. The one ligand field maximum at 18730 cm^{-1} (ν_1) and the other shoulder at 24270 cm^{-1} (ν_2) correspond to the $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$ transitions in the O_h approximation, respectively.[10] 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 Fig. 1. The contribution from outside bands was

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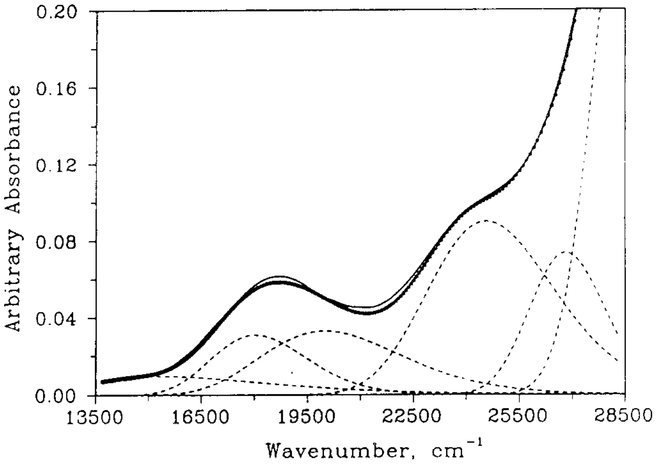

Figure 1. Electronic absorption spectrum of *cis*-[Cr(cyclam)Br$_2$]Br in aqueous solution at 298 K.

corrected for the fine deconvolution. A deconvolution procedure on the experimental band pattern yielded maxima at 17945, 20025, 24445 and 26710 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. The energy $^4A_{2g}\rightarrow{}^2T_{2g}$ band was also found at 20242 cm^{-1} from the second derivative of the solution absorption spectrum, but it could not be resolved into the separate components.

Infrared Spectra

The mid- and far-infrared spectra of *cis*-[Cr(cyclam)Br$_2$]Br recorded at room temperature are presented in Figs. 2 and 3. The mid-infrared spectrum shows a strong broad absorption centered at 3417 cm^{-1} which may be assigned to the O-H stretching of the contained water molecule in the complex. The two strong absorption at 3151 and 3078 cm^{-1} and the strong bands in the region 3000-2800 cm^{-1} are due to the symmetric and antisymmetric N-H and C-H stretching modes, respectively. The two strong absorptions at 1612 cm^{-1} and 1454 cm^{-1} can be assigned to the NH$_2$ and CH$_2$ bending modes, respectively.[10] A number of absorption bands in the regions of 1400-1200 cm^{-1} are due to the wagging modes of CH$_2$ and NH$_2$. The infrared spectroscopy is frequently useful in elucidating structures of *cis*- and *trans*-isomers of cyclam chromium(III) complexes. It is well known that *cis*-isomer exhibits at least three bands in the 890-830 cm^{-1} region due to the NH$_2$ rocking modes while the methylene vibration split into two peaks in the 830-790 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.[11] Indeed, the present complex exhibits three bands at 887, 864 and 853 cm^{-1} in the NH$_2$ rocking frequency region. Two CH$_2$ rocking bands at 816 and 796 cm^{-1} are also observed. The infrared spectrum of the complex is clearly consistent with a *cis*-configuration. Metal-ligand stretching bands occur in the far infrared range. As seen in Fig. 3, the four bands in the range 410-475 cm^{-1} can be assigned to Cr-N stretching modes. A number of absorption bands below 386 cm^{-1} arise from lattice vibration, skeletal bending and the Cr-Br stretching mode.

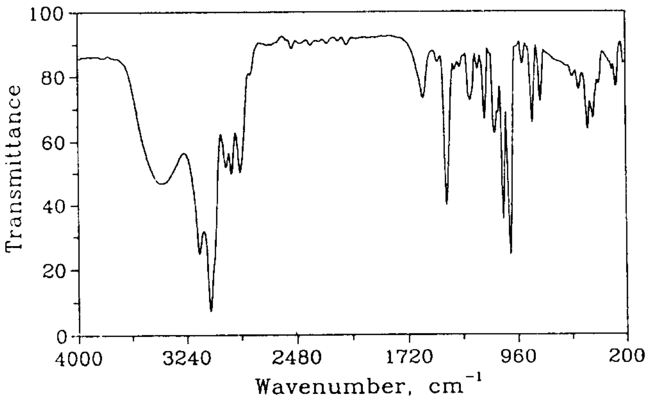

Figure 2. Mid-infrared spectrum of *cis*-[Cr(cyclam)Br$_2$]Br at 298 K.

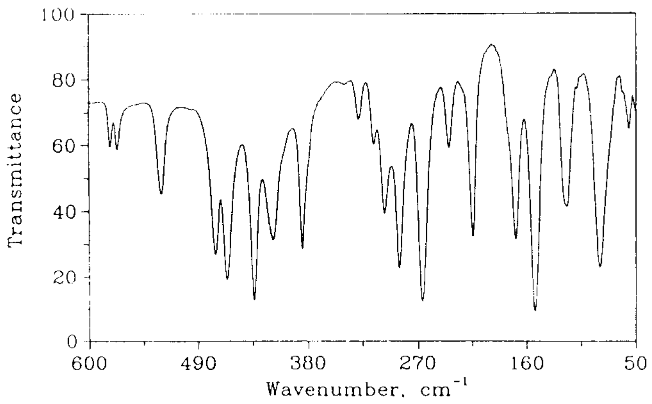

Figure 3. Far-infrared spectrum of *cis*-[Cr(cyclam)Br$_2$]Br at 298 K.

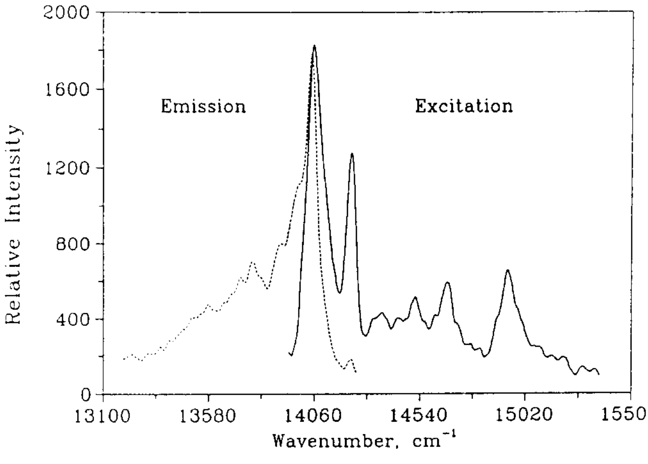

Figure 4. Emission (······) and excitation (——) spectra of *cis*-[Cr(cyclam)Br$_2$]Br at 77 K.

Table 1. Vibrational frequencies from the 77 K luminescence and 298 K infrared spectra for *cis*-[Cr(cyclam)Br$_2$]Br[a]

Luminescence[b]	Infrared	Assignment
-178 m		R_2
0 vs		R_1
59 sh	57 w, 86 m	Lattice vib. and Ring def.
141 w	120 m, 152 s, 171 m	
225 vw	215 m, 239 w	
269 m	267 s, 289 m	
320 m	303 w, 314 vw	ν (Cr-Br)
	329 vw	
365 vw	386 m	
399 w		
469 m	415 w, 434 s	ν (Cr-N)
	461 s, 473 m	
504 vw	527 m	ν (Cr-N) + Ring def.
543 w		
586 vw	571 w, 578 w	
646 w	621 vw	
687 w	710 vw	
742 vw	796 m	ρ (CH$_2$)
823 w	816 w	
	853 w, 864 w, 887 w	ρ (NH$_2$)

[a] Data in cm^{-1}. [b] Measured from zero-phonon line at 14047 cm^{-1}.

Table 2. Assignment of sharp-line positions in the 77 K excitation spectrum of *cis*-[Cr(cyclam)Br$_2$]Br[a]

$\bar{\nu}_0$-14057	Assignment	Calcd[b]		Vibronic frequencies[c]	Ground state frequencies[d]
0 vs	R_1		ν_1	96	86
95 sh	$R_1 + \nu_1$	96	ν_2	144	141
172 vs	R_2		ν_3	274	269
274 w	$R_1 + \nu_3$	274	ν_4	335	329
309 m	$R_2 + \nu_2$	316	ν_5	390	386
334 sh	$R_1 + \nu_4$	335	ν_6	472	473
381 w	$R_1 + \nu_5$	390			
419 vw	$R_1 + \nu_2 + \nu_3$	418			
461 m	$R_2 + 2\nu_2$	460			
508 sh	$R_2 + \nu_4$	507			
552 w	$R_2 + \nu_5$	562			
608 s	T_1				
655 sh	$R_2 + \nu_6$	644			
694 vw	$T_1 + \nu_1$	704			
714 w	$R_2 + 2\nu_3$	720			
756 w	$T_1 + \nu_2$	752			
830 m	T_2				
879 s	T_3				
931 sh	$T_2 + \nu_1$	926			
1003 vw	$T_1 + \nu_5$	998			
1026 sh	$T_3 + \nu_2$	1023			
1081 w	$T_1 + \nu_6$	1080			
1134 w	$T_1 + \nu_2 + \nu_3$	1026			
1224 w	$T_2 + \nu_5$	1220			
1278 w	$T_3 + \nu_5$	1269			

[a] Data in cm^{-1}. [b] Values in parentheses represent the calculated frequencies based on the vibrational modes listed. [c] From the excitation spectrum. [d] From the luminescence and infared spectra.

Luminescence Spectrum

An experimental problem lies with the difficulty in distinguishing pure electronic components from the vibronic bands that also appear in the excitation spectrum. The vibrational intervals of the electronic ground state can be obtained by comparing the emission spectrum with far-infrared spectral data. The 530 nm excited 77 K luminescence spectrum (dotted line) of *cis*-[Cr(cyclam)Br$_2$]Br is shown in Fig. 4. The band positions relative to the lowest zero phonon line, R_1, with corresponding infrared frequencies, are listed in Table 1. The luminescence spectrum was independent of the exciting wavelength within the first spin-allowed transition region.

The strongest peak at 14047 cm^{-1} is assigned as the zero-phonon line, R_1, because the corresponding strong peak is found at 14057 cm^{-1} in the excitation spectrum. A well defined hot band at 14225 cm^{-1} may be assigned to the second component of the $^2E_g \rightarrow {}^4A_{2g}$ transition. The Cr-N stretching band was detected at 469 cm^{-1}. The vibronic intervals occurring in the spectrum can be presumed to involve primarily ring torsion, angle-bending and Cr-Br stretching modes with frequencies in the range 50-400 cm^{-1}.

Excitation Spectrum

The 77 K excitation spectrum (solid line) is also shown in Fig. 4. It was recorded by monitoring a relatively strong vibronic peak in the luminescence spectrum. The spectrum obtained was independent of the vibronic peak 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 ν_1-ν_6 listed in Table 2. Two strong peaks at 14057 and 14229 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 luminescence origin within 10 cm^{-1}. The zero-phonon line in the excitation spectrum splits into two components by 172 cm^{-1}, and it can be compared with those of the chromium(III) complexes with tetragonal symmetry.[12] 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 608, 830 and 879 cm^{-1} from the lowest electronic line, R_1. Vibronic satellites based on these origins also have similar frequencies and intensity

Table 3. Experimental and calculated electronic transition energies for *cis*-[Cr(cyclam)Br$_2$]Br^a

State(O$_h$)	Exptl	Calcd^b
^2E_g	14057	14056
	14229	14227
$^2T_{1g}$	14665	14747
	14887	14841
	14936	14881
$^2T_{2g}$(avg)	20242	20276
$^4T_{2g}$	17945^c	17872
	20005^c	19505
$^4T_{1g}$	24445^c	24993
	26710^c	26490

^{a}Data in cm^{-1}, ^{b}e$_\sigma$(N) =7506 ± 23,e$_\sigma$(Br) = 4819 ± 34, e$_\pi$(Br) = 592 ± 36, B = 756 ± 2, C = 2457 ± 6, α_T = 237 ± 3, ζ= 275 ± 23, ^{c}Obtained from the Gaussian component decomvolution.

patterns to those of the ^2E_g components.

Ligand Field Analysis

The ligand field potential matrix was generated for *cis*-[Cr(cyclam)Br$_2$]$^+$ from the coordinated four nitrogen and two bromide atoms. 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 bromides.[13] The ligand field analysis was carried out through an optimized fit of experimental to calculated transition energies. There are 120 microstates derived from the d^3 configuration. Diagonalization of the 120 × 120 secular matrix yields the doublet and quartet energies with the appropriate degeneracies. Hoggard 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.[14] The full set of 120 single-term antisymmetrized product wavefunctions was employed as a basis. The Hamiltonian used in the calculation was

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

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.[15] 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$_\sigma$(Br) and e$_\pi$(Br) for the bromide-chromium, and e$_\sigma$(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.[18] Schmidtke's π-expansion parameter τ was 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 0.9917. The estimated value was based on the analysis of [Cr(NH$_3$)$_5$Cl]Cl$_2$.[19] The Racah parameter A was also fixed at 5000 cm^{-1}. The value of the Racah parameter A has little effect on the calculated transition energies. All parameters, except e$_\sigma$(Br) and e$_\pi$(Br), 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 $^2T_{2g}$ 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[20] 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 used to generate the best-fit energies are also listed in Table 3. The fit is good for the sharp line transitions. The error margins reported for the best-fit parameters in Table 3 are based only on the propagation of the assumed uncertainties in the observed peak positions. 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) = 7506 ± 23, e$_\sigma$(Br) = 4819 ± 34, e$_\pi$(Br) = 594 ± 36, B = 756 ± 2, C = 2457 ± 6, α_T = 237 ± 3, and ζ = 275 ± 23 cm^{-1}. A ligand field analysis of the sharp-line excitation and broad-band absorption spectra indicates that the bromide is weak σ-and π-donor. These values were lower than the values for other coordinated atoms in chromium(III) complexes.[6,21] It appears that the very weak bonding properties of bromide are due to size effect of the ligand.

The value of 7506 cm^{-1} for $e_\sigma(N)$ is comparable to values for other amines.[7,16] It is suggested that the four nitrogen atoms of the macrocyclic ligand cyclam have strong σ-donor properties toward chromium(III). The AOM parameters can be used in interpreting the preferential photosolvation and photostereochemistry of transition metal complexes.[1,3,22] The 172 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.[13,23] An orbital population analysis yields a configuration of $(xy)^{0.988}(xz)^{0.986}(yz)^{0.984}(x^2\text{-}y^2)^{0.024}(z^2)^{0.017}$ for the lowest component of the ^2E_g state. The relative *d*-orbital ordering from the calculation is $E(xy)$ = 314 cm^{-1} < $E(xz)$ = 605 cm^{-1} < $E(yz)$ = 683 cm^{-1} < $E(x^2\text{-}y^2)$ = 18449 cm^{-1} < $E(z^2)$ = 20787 cm^{-1}. The value of the Racah parameter B is about 82 % 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 highly resolved excitation spectrum.

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