Electronic and Vibrational Spectroscopy of cis-Diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III) Thiocyanate

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The emission and excitation spectra of cis-[Cr(cyclam)(NCS)₂]NCS (cyclam = 1,4,8,11-tetraazacyclotetradecane) taken at 77 K are reported. The infrared and visible spectra at room temperature are also measured. The vibrational intervals due to the electronic ground state are extracted from the far-infrared and emission spectra. The ten pure electronic origins due to spin-allowed and spin-forbidden transitions are assigned by analyzing the absorption and excitation spectra. Using the observed transitions, a ligand field analysis has been performed to determine the bonding properties of the coordinated ligands in the title chromium(III) complex. According to the results, it is found that nitrogen atoms of the cyclam ligand have a strong σ-donor character, while the NCS ligand has medium σ- and π-donor properties toward chromium(III) ion.

Key Words: Electronic transitions, Vibrational intervals, Chromium(III) complex, Ligand field analysis

Introduction

In the past several years, the preparation,1-2 kinetics,3 photochemistry,4,5 photophysics,6,7 and structural analysis8-10 of the cis-diacidochromium(III) complexes containing the tetradeptate macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) have been studied extensively. We also have described the vibrational and electronic energy levels based on the emission, far-infrared and electronic spectroscopy.11-18 The application of electronic spectroscopy to chromium(III) complexes promises to provide information concerning metal-ligand bonding properties as well as molecular geometry.1,2 With the use of excitation or absorption spectroscopy the narrow intraconfigurational transitions due to the spin-forbidden in chromium(III) system can be located with a precision two orders of magnitude greater than can the broad spin-allowed bands. Especially, the splittings of sharp-line electronic transitions are very sensitive to the exact bond angles around the metal. Thus it is possible to extract structural information from the electronic spectroscopy without a full X-ray structure determination.19,20

The NCS group may coordinate to a transition metal through the nitrogen or the sulfur or both. In general, Cr, Ni and Co metals tend to form M-N bonds, while as metals of the second transition series, such as Rh, Pd and Ir tend to form M-S bonds.21 However, the oxidation state of the metal, the nature of other ligands in a complex and steric factor also influence the mode of coordination. When the isothiocyanato group coordinates to a chromium(III) ion, it is found that the Cr-N-C and N-C-S angles fall in the range 172.5°-173.5° and 177.2°-179.6°, respectively.10 So far literature gives no information on the detailed ligand field properties of coordinated atoms in the title chromium(III) complex.

In this work the 77 K emission and excitation spectra, and the room temperature infrared and visible spectra of cis-[Cr(cyclam)(NCS)₂](NCS) have been measured. The vibrational intervals of the electronic ground state were determined from the far-infrared and emission spectra. The pure electronic origins were assigned by analyzing the absorption and excitation spectra. With the electronic transitions, a ligand field analysis was performed to determine the metal-ligand bonding properties for the coordinated atoms of isothiocyanato and cyclam ligands toward chromium(III) ion.

Experimental Section

The free ligand cyclam was purchased from Strem Chemicals. All chemicals were reagent grade materials and used without further purification. The cis-[Cr(cyclam)(NCS)₂](NCS) was prepared as described in the literature."³

The far-infrared spectrum in the region 600-50 cm⁻¹ was recorded with a Bruker 113v spectrometer on a microcrystalline sample pressed into a polyethylene pellet. The mid-infrared spectrum was obtained with a Mattson Infini- ties series FT-IR spectrometer using a KBr pellet. The room-temperature visible absorption spectrum was recorded with a HP 8453 diode array spectrophotometer. The emission and excitation spectra at 77 K were measured on a Spex Fluorolog-2 spectrofluorometer. The Nitrogen Dewar accessory was used for the low-temperature scan.²¹,²²

Results and Discussion

Absorption Spectrum. The visible absorption spectrum (solid line) of cis-[Cr(cyclam)(NCS)₂]⁴⁺ in aqueous solution at room temperature is represented in Figure 1.

It exhibits two bands, one at 20410 cm⁻¹ (ν₁) and the other at 27025 cm⁻¹ (ν₂), corresponding to the ¹A₂g → ¹T₂g and
$^2A_g \rightarrow ^4T_{1g} (O_h)$ transitions, respectively. The quartet bands have nearly symmetric profiles. In order to have some point of reference for the splittings of the two bands, we have fit the band profiles to four Gaussian curves, as seen in Figure 1. The contribution from outside bands was corrected for fine deconvolution. A deconvolution procedure on the experimental band pattern yielded maxima at 19765, 20795, 25840 and 27810 cm$^{-1}$ for the noncubic split levels of $^4T_{2g}$ and $^4T_{1g}$, respectively. These resolved 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 (dotted line) shown in Figure 1.

**Infrared Spectra.** The infrared spectroscopy is 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 890-830 cm$^{-1}$ region due to the N-H wagging 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. The present complex exhibits three bands at 892, 861 and 850 in the N-H wagging frequency region. Two CH$_2$ rocking bands at 797 and 808 cm$^{-1}$ are also observed. These vibrational modes are not affected by differing counteranions. The infrared spectrum of the title complex was clearly consistent with the cis configuration.

Metal-ligand stretching bands occur in the far infrared range. The far-infrared spectrum of cis-[Cr(cyclam)(NCS)$_2$](NCS) recorded at room temperature are presented in Figure 2. The peaks in the range 471-408 cm$^{-1}$ can be assigned to the Cr-N (cyclam) stretching mode. A number of absorption bands below 399 cm$^{-1}$ arise from lattice vibration, skeletal bending and the Cr-NCS stretching modes.

**Emission Spectrum.** An experimental problem lies with the difficulty in distinguishing pure electronic components from the vibronic bands that also appear in the excitation spectrum. It is required that the vibrational intervals of the electronic ground state be obtained by comparing the emission spectrum with far-infrared spectral data. The 19920 cm$^{-1}$ (502 nm) excited 77 K emission spectrum of cis-[Cr(cyclam)(NCS)$_2$](NCS) is shown in Figure 3. 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.

The strongest peak at 13589 cm$^{-1}$ is assigned as the zero-phonon line, $R_1$, because a corresponding strong peak is found at 13602 cm$^{-1}$ in the excitation spectrum. A hot band at 13660 cm$^{-1}$ may be assigned to the second component of the $^2E_g \rightarrow ^4A_{2g}$ transition. The vibronic 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 150-264 cm$^{-1}$. The band at 424 cm$^{-1}$ can be assigned to a Cr-N(cyclam) stretching mode.

**Excitation Spectrum.** The 77 K excitation spectrum is shown in Figure 4. It was recorded by monitoring a relatively strong vibronic peak in the emission spectrum. The spectrum obtained was independent of the vibronic peak used to monitor it. The peak positions and their assignments are
Table 1. Vibrational frequencies from the 77 K Emission and 298 K infrared spectra for cis-[Cr(cyclam)(NCS)$_2$](NCS)

<table>
<thead>
<tr>
<th>Emission$^a$</th>
<th>Infrared</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-71 w</td>
<td>R$_1$</td>
<td></td>
</tr>
<tr>
<td>0 vs</td>
<td>R$_2$</td>
<td></td>
</tr>
<tr>
<td>150 w</td>
<td>60 w, 74 m, 109 s</td>
<td>Lattice vib., skeletal bends</td>
</tr>
<tr>
<td>214 vw</td>
<td>205 vw, 221 w, 231 w</td>
<td>and</td>
</tr>
<tr>
<td>264 w</td>
<td>259 m, 280 s, 300 s</td>
<td>(Cr-N) and (NCS)</td>
</tr>
<tr>
<td>359 m</td>
<td>312 m, 322 s, 331 s, 346 w</td>
<td>ν(Cr-N) and ν(NCS)</td>
</tr>
<tr>
<td>424 vw</td>
<td>408 sh, 431 m, 439 sh</td>
<td>ν(Cr-N)$_{ring}$ def.</td>
</tr>
<tr>
<td>542 vs</td>
<td>531 vs, 572 w, 580 m</td>
<td>ν(Cr-N)</td>
</tr>
<tr>
<td>799 vs</td>
<td>757 m, 797 m, 808 w</td>
<td>δ(CH)$_3$</td>
</tr>
<tr>
<td>1016 sh</td>
<td>1030 vs, 1056 vs</td>
<td>γ(NH)</td>
</tr>
</tbody>
</table>

$^a$Data in cm$^{-1}$, $^b$Measured from zero-phonon line at 13589 cm$^{-1}$.

Figure 4. The 12804 cm$^{-1}$ monitored excitation spectrum of cis-[Cr(cyclam)(NCS)$_2$](NCS) at 77 K.

Tabulated in Table 2. The calculated frequencies in parentheses were obtained by using the vibrational modes ν$_1$-ν$_5$ listed in Table 2.

Two strong peaks at 13602 and 13672 cm$^{-1}$ in the excitation spectrum are assigned to the two components (R$_1$ and R$_2$) of the $^4$A$_{2g}$ → $^2$E$_g$ transition. The lowest-energy zero-phonon line coincides with the emission origin within 3 cm$^{-1}$. The zero-phonon line in the excitation spectrum splits into two components 70 cm$^{-1}$ apart, and it can be compared with those$^{11-18}$ of the $^4$A$_{2g}$ → $^2$E$_g$ system (X = NH$_3$, en/2, pn/2, F$^-$, Cl$^-$, Br$^-$, N$_3^-$, ONO$^-$, ONO$_2^-$), as shown in Table 3. In general, it is not easy to locate positions of the other electronic components because the vibronic sidebands of the $^2$E$_g$ levels overlap with the zero phonon lines of $^2$T$_{1g}$. However, the three components of the $^4$A$_{2g}$ → $^2$T$_{1g}$ electronic origin (T$_1$, T$_2$ and T$_3$) can be found with strong intensities 803, 853 and 933 cm$^{-1}$ from the lowest electronic line, R$_1$ because the vibronic satellites based on these origins also have similar frequencies and intensity patterns to those of the $^2$E$_g$ components.

The higher energy $^4$A$_{2g}$ → $^2$T$_{2g}$ band was found at 20660 cm$^{-1}$ from the second derivative of the solution absorption spectrum, as shown with a dotted line in Figure 5.

Ligand Field Analysis. The ligand field potential matrix was generated for cis-[Cr(cyclam)(NCS)$_2$]$^+$ from the coordinated six nitrogen atoms. The angular positions of ligating six atoms and adjacent two carbons were taken from the X-ray crystal structure$^{10}$ of cis-[Cr(cyclam)(NCS)$_2$(ClO$_4$)$_3$], which was determined to be monoclinic with the space group P2$_1$/c. The coordinates were then rotated so as to maximize the projections of the six-coordinated atoms on the Cartesian axes centered on the chromium. The resulting Cartesian and spherical coordinates are shown in Table 4.
yields the doublet and quartet energies with the appropriate \( \pi \) perpendicular directions, denoted e. The following values were finally obtained for the ligand field potential, and spin-orbit coupling, respectively, with the last two representing the Trees correction. The parameters varied during the optimization were the interelectronic repulsion parameters B, C, and the Trees correction parameter \( \alpha \), the spin-orbit coupling parameter \( \zeta \), plus the AOM parameters \( e_\pi \) (NCS) and \( e_\sigma \) (NCS) for the isothiocyanato nitrogen-chromium, and \( e_\sigma (N) \) for the cyclam nitrogen-chromium. The \( \pi \)-interaction of amine nitrogens with \( sp^2 \) hybridization has a weak \( \pi \)-donor character. All parameters, except \( e_\sigma (NCS) \) and \( e_\sigma (NCS) \), 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 \( ^1T_2 \rightarrow ^1T_2 ^T \) components, identified in Table 5, the lowest energy of the transition to the \( ^2T_2 ^c \) state, the four \( ^1A_2 \rightarrow ^1T_2 ^c \) 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

\[
f = 10^{-5}S^2 + 10^6D^2 + 10^7T + \Sigma Q^2
\]

where \( S \) in the first term is the \( ^2E_g \) splitting, and \( D, T, \) and \( Q \) represent the differences between experimental and calculated \( ^2E_g, ^2T_1 ^c, ^2T_2 ^c, \) and \( ^1T_2 ^c, ^1T_1 ^c \) transition energies, respectively. The Powell parallel subspace optimization procedure 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 5. The fit is good for the sharp line transitions. The error margins reported for the best-fit parameters in Table 5 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

Table 5. Experimental and calculated electronic transition energies for cis-[Cr(cyclam)(NCS)]\(_2\)NCS\(^a\)

<table>
<thead>
<tr>
<th>State ((O_h))</th>
<th>Expt</th>
<th>Calcd (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^2E_g)</td>
<td>13602</td>
<td>13817</td>
</tr>
<tr>
<td>(^2T_1 ^c)</td>
<td>13672</td>
<td>13874</td>
</tr>
<tr>
<td>(^2T_2 ^c)</td>
<td>14405</td>
<td>14186</td>
</tr>
<tr>
<td>(^2T_2 ^c)</td>
<td>14455</td>
<td>14323</td>
</tr>
<tr>
<td>(^2T_1 ^c)</td>
<td>14535</td>
<td>14437</td>
</tr>
<tr>
<td>(^1T_2 ^c)</td>
<td>20660</td>
<td>20728</td>
</tr>
<tr>
<td>(^1T_2 ^c)</td>
<td>19765</td>
<td>19858</td>
</tr>
<tr>
<td>(^1T_1 ^c)</td>
<td>20795</td>
<td>20890</td>
</tr>
<tr>
<td>(^1T_1 ^c)</td>
<td>25840</td>
<td>25998</td>
</tr>
</tbody>
</table>

\(^a\)Data in cm\(^{-1}\); \(^*\)expt\((N) = 7512 \pm 45; \ e_\sigma (NCS) = 6112 \pm 58; \ e_\sigma (NCS) = 632 \pm 28; \ B = 588 \pm 6; \ C = 2992 \pm 38; \ \alpha = 66 \pm 10; \ \zeta = 277 \pm 54. \ ^{*}\)Obtained from the Gaussian component deconvolution.
field parameters: \( e_0(N) = 7512 \pm 45 \), \( e_0(NCS) = 6112 \pm 58 \), \( e_0(NCS) = 632 \pm 28 \), \( B = 588 \pm 6 \), \( C = 2992 \pm 38 \), \( \alpha_{\text{ef}} = 66 \pm 10 \) and \( \zeta = 277 \pm 54 \text{ cm}^{-1} \). A ligand field analysis of the sharp-line excitation and broad-band absorption spectra indicates that the isothiocyanato nitrogen has a medium \( \sigma \)-and \( \pi \)-donor properties toward chromium(III) ion. These values for \( e_0(NCS) \) and \( e_0(NCS) \) parameters can be compared with the values for other coordinated atoms in the chromium (III) complexes.\(^{32-39} \) The value of 7512 cm\(^{-1} \) for \( e_0(N) \) of the cyclam is slightly larger than 7285 cm\(^{-1} \) for the cis-

\[ \text{Cr(cyclam)(N}_3\text{)}_2\text{][N}_3\text{].} \]

It is safe to conclude that the four nitrogen atoms of the macrocyclic ligand cyclam are a strong \( \sigma \)-donor. The AOM parameters can be used in interpreting the photobehavior of transition metal complexes.\(^{30} \) The observed \( ^2E_g \) splitting, 70 cm\(^{-1} \) in the excitation spectrum can compared with the values\(^{11-18} \) of cis-diacidochromium (III) complexes with the cyclam, as seen in Table 3. An orbital population analysis yields a configuration of \((xy)^{0.992}(xz)^{1.010}(yz)^{0.972}(x^2-y^2)^{0.008}(z^2)^{0.018}\) for the lowest component of the \( ^2E_g \) state.

The relative \( d \)-orbital ordering from the calculations \( E(xy) = 154 \text{ cm}^{-1} < E(zx) = 519 \text{ cm}^{-1} < E(yz) = 1162 \text{ cm}^{-1} < E(x^2-y^2) = 20312 \text{ cm}^{-1} < E(z^2) = 21389 \text{ cm}^{-1} \). The value of the Racah parameter \( B \) is about 64% of the value for a free chromium(III) ion in the gas phase, and it is confirmed that electron repulsions are weaker in the complex than the free ion. The ligand field 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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References

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