Infrared Spectra of Some Er³⁺ β-Diketonates in the Region 4000—250 cm⁻¹

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IR Spectra, β-Diketonates

The infrared spectra of four erbium β-diketonates have been recorded in KBr phase on a Perkin-Elmer model 521 double grating spectrophotometer. About thirty bands in each case have been observed and assigned to different modes of vibration. Single ring analysis has been used in interpretation of the bands.

Introduction

The recent research in the laser action and in the fluorescence spectra of rare-earth chelates suggests that a detailed infrared study of these chelates would be interesting. The infrared study helps in interpretation of vibronic contribution to the electronic spectra. This study also throws light on the structure of the chelates ring, interaction among the rings, nature of the metal-oxygen frequencies and force constants associated with these frequencies. Recently authors have reported infrared spectra of some tris-rare-earth β-diketone chelates and studied the nature of the force constants associated with the metal-oxygen frequencies.

In the present paper the infrared spectra of tris-chelates of Er³⁺ with acetylacetone (AA), thenoyl trifluoro acetylacetone (TFA), benzoylacetone (BA) and dibenzylmethide (DBM) are reported and discussed. Single ring analysis has been used in interpretation of most of the bands, since the interaction among the different rings is very small.

Experimental Procedure

The hydrated tris-chelates of Er³⁺ with AA, TFA, BA, and DBM were prepared in the following way:

ErCl₄·6H₂O, the respective ligand and ammonia were dissolved in a molar ratio of 1:3:1 in ethanol. After partial evaporation of the solvent, the crystals precipitate was collected, washed with ethanol and air dried. The erbium chloride used was of 99.9% purity and was obtained from Leico Industries, New York. Ligands were obtained from BDH, England, and were used without further purification. The reagents used were of A.R. grade.

The solid state IR spectra of all these chelates in KBr discs at 25 °C were recorded in the region 4000–250 cm⁻¹ on a Perkin-Elmer model 521 double grating spectrophotometer. The instrument was calibrated against indene and was swept with dry air while the spectra were being recorded. The maximum uncertainty in the reported frequencies is estimated to be less than 5 cm⁻¹.

Discussions

The IR frequencies of the hydrated chelates studied are listed in Tables I and II. The spectra may be interpreted by considering a 1:1 (metal/ligand) complex of the chelates, since the simplicity of the spectra reveals that the vibrational coupling between different rings is small. The assignments have been made by comparing the observed spectra with those reported in literature for similar species.

1. CH₃ and CF₃ group vibrations

The asymmetric and symmetric stretching and asymmetric and symmetric in-plane bending vibrations of CH₃ group appear around 2920, 2850; 1390 and 1360 cm⁻¹, respectively. On substitution of a CF₃ group in place of CH₃ group in the TFA chelate the corresponding frequencies of the CF₃ group appear at 1300, 1132; 610 and 570 cm⁻¹. The rocking frequency of the CH₃ group appears at 1020 cm⁻¹ whereas that of the CF₃ group has been observed at 780 cm⁻¹. The band near ~ 670 cm⁻¹ may be assigned to stretching mode of (C-CH₃). The corresponding mode for (C-CF₃) appears at 640 cm⁻¹.
Table I. IR frequencies [cm$^{-1}$] of AA and TFA chelates and their assignments.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>3370 (bs)</th>
<th>3380 (bs)</th>
<th>3400 (w)</th>
<th>3425 (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(O-H)</td>
<td>$\nu$(C-H)</td>
<td>$\nu$(C=O)</td>
<td>$\nu$(C=O)</td>
<td>$\nu$(C=O)</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>$\delta$(CH$_3$)</td>
<td>$\delta$(CH$_3$)</td>
<td>$\delta$(CH$_3$)</td>
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<tr>
<td>$\delta$(C-F$_3$)</td>
<td>$\delta$(C-F$_3$)</td>
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<td>$\delta$(C-F$_3$)</td>
<td>$\delta$(C-F$_3$)</td>
</tr>
<tr>
<td>$\pi$(C-H) + low freq.</td>
<td>$\pi$(C-H) + low freq.</td>
<td>$\pi$(C-H) + low freq.</td>
<td>$\pi$(C-H) + low freq.</td>
<td>$\pi$(C-H) + low freq.</td>
</tr>
</tbody>
</table>

Table II. IR frequencies [cm$^{-1}$] of BA and DBM chelates and their assignments.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>3065 (w)</th>
<th>3058 (m)</th>
<th>3050 (w)</th>
<th>3050 (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(C=H)</td>
<td>$\nu$(C=H)</td>
<td>$\nu$(C=H)</td>
<td>$\nu$(C=H)</td>
<td>$\nu$(C=H)</td>
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<td>$\nu$(C=H)</td>
<td>$\nu$(C=H)</td>
</tr>
<tr>
<td>$\pi$(C=H) + low freq.</td>
<td>$\pi$(C=H) + low freq.</td>
<td>$\pi$(C=H) + low freq.</td>
<td>$\pi$(C=H) + low freq.</td>
<td>$\pi$(C=H) + low freq.</td>
</tr>
</tbody>
</table>

Relative intensity: vs = very strong, s = strong, bs = broad strong, m = medium, sh = shoulder, w = weak, vw = very weak.

Assignment: $\nu$ = stretching, $\delta$ = in-plane bending, $\pi$ = out of plane bending, $\varphi$ = rocking, s = symmetric, as = asymmetric.

The in-plane bending vibration of (C=CH$_3$) is observed at 530 cm$^{-1}$. (C=CF$_3$) in-plane bending vibration probably lies below 250 cm$^{-1}$. Mixed modes of the (C=CH$_3$) group with C=C and C=O appear in the region 1240-1285 and 925 cm$^{-1}$ respectively, whereas the mixed modes of the (C=CF$_3$) group with C=C and C=O appear at 1180 and 930 cm$^{-1}$ respectively.

2. C-H group vibrations

Stretching vibration due to the C-H group appears in the region 2990-3070 cm$^{-1}$. The bending in-plane and out of plane vibrations of this group absorb in the regions 1370-1400 and 750-770 cm$^{-1}$, respectively. Mixed modes consisting of out-of-plane bending and some low frequencies appear in the region 1020-1080 cm$^{-1}$ in case of AA and TFA chelates. However, the regions of these vibrations have shifted to 940-965 cm$^{-1}$ in the case of BA and DBM chelates. Similar mixed modes of in-plane bending vibrations with (C=O) stretching have been observed in the regions (a) 1440-1460 cm$^{-1}$ and (b) 1130-1220 cm$^{-1}$ (BA, DBM); 1185-1225 cm$^{-1}$ (AA, TFA).

$\phi$ = phenyl ring.
3. C=C and C=O vibrations
The coupled vibrations of the two acetone molecules bounded together by chemical linkage give four stretching frequencies, two C=O and two C=C. These have been observed at ~1600, ~1450 cm\(^{-1}\); ~1520 and 1240–1285 cm\(^{-1}\), respectively. All these four frequencies are found to shift from those of the free ligands. This is caused by the perturbation due to complex formation. The lowering of the C=O stretching frequencies may be taken as indication of the nature of coordination in the complex. An appreciable shift has been noted in C=O and C=C frequencies when the CH\(_3\) group is replaced by CF\(_3\) or a benzene ring.

4. Phenyl C–H vibrations
The band at 2920 cm\(^{-1}\) (DBM) may be assigned to a C–H stretching mode of the benzene ring. The bending in-plane vibration have been observed in the region 1052–1075 cm\(^{-1}\) and the bending out-of-plane vibrations have been observed at 850 and 718 cm\(^{-1}\). In pure benzene or its derivatives three stretching and four bending vibrations are observed. However, in our complexes only one stretching and three bending vibrations have been observed.

5. Phenyl ring stretching and breathing vibrations
All the four C–C stretching vibrations appearing in the benzene or its derivatives appear in our complexes. They appear at 1570, 1540, 1480 and 1300 cm\(^{-1}\). The ring breathing vibration occurs at 1000 cm\(^{-1}\). It is seen that there is a small effect of complexation on this mode of vibration.

A band appearing in the region 680–695 cm\(^{-1}\) is due to the presence of five adjacent hydrogen atoms vibrating in phase and out-of-plane of the ring.

The stretching and in-plane bending modes of vibrations due to (C–O) group have been observed at 810 and 425–520 cm\(^{-1}\) respectively.

6. Sulphur group vibrations
On substitution of S for C, thiophene bands have been observed at 1500 and 1350 cm\(^{-1}\). A mixed mode of S–O stretching and C–H bending in-plane vibration appears at 1405 cm\(^{-1}\). The C–S stretching vibration has been observed at 710 cm\(^{-1}\). The presence of sulphur group lowers the frequency of the asymmetric C–H bending vibrations.

7. Metal-oxygen vibrations
Theoretically, it has been found that the number of IR active vibrations depend on the geometry of the complex, e.g., 4 for tetrahedral and 3 for octahedral. Experimental studies on a large number of \(\beta\)-diketonates reveal that vibration appearing in the region 390–415 cm\(^{-1}\) is metal-oxygen vibration. The other two vibrations are expected to appear in the region 250–100 cm\(^{-1}\).

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