MÖSSBAUER STUDIES OF ANION-SUBSTITUTED IRON CHLOROPHYLLS

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The electronic structure of anion-substituted iron chlorophyll a \( \text{[Fe(Chl-a)X]} \) and b \( \text{[Fe(Chl-b)X]} \) (\( X = \text{Cl}^-, \text{NCS}^-, \text{Br}^-, \text{I}^-, \text{CH}_3\text{COO}^- \)) has been characterized by Mössbauer spectroscopy. The central iron ion in these complexes is in a ferric high-spin state. The \( \pi \)-donation from the anion plays an important role in the bonding between the iron ion and the anion. The quadrupole splitting reflects the structural difference between iron chlorophylls and iron porphyrins.

1. Introduction

The electronic structure of chlorophylls has been widely investigated in connection with photosynthesis. However, there have been few reports on iron chlorophylls \( \text{[Fe(Chl)]} \) which have an iron ion as the central ion instead of the magnesium in chlorophylls. In particular, there have been very few Mössbauer studies on these complexes [1]. The structure of iron chlorophylls is closely related to that of iron porphyrins which have interesting electronic properties such as oxygen-binding ability [2]. Hence, it is important to elucidate the electronic structure of the iron chlorophylls and to compare the electronic properties with those of iron porphyrins. In the present work, we prepared several anion-substituted iron chlorophyll a \( \text{[Fe(Chl-a)X]} \) and b \( \text{[Fe(Chl-b)X]} \) and then measured their Mössbauer, electronic, and far-infrared (Fe-X stretching) spectra. The electronic effect of the anion (axial ligand) on the central iron (III) ion of these iron chlorophylls and the difference or the similarity in the electronic structure between the iron chlorophylls and iron porphyrins are reported.

2. Experimental

The methods of preparation of \( \text{Fe(Chl-a)Cl} \) and \( \text{Fe(Chl-b)Cl} \) were described in the previous paper [1]. The complexes, \( \text{Fe(Chl-a)Br, Fe(Chl-a)I, Fe(Chl-a)NCS,} \)
Fe(Chl-a) (CH₃COO), and the corresponding Fe(Chl-b)X were prepared according to the literature method employed for iron porphyrins [3] and purified by the reversed phase HPTLC using acetone-acetonitrile (1:1, V/V) for an eluent. For the bromo complexes, the eluent containing tetrabutylammonium bromide (1 mM) was used. The Mössbauer spectra were measured against a ⁵⁷Co source in Pd using a Wissel constant-acceleration transducer. The spectra obtained were fitted to Lorentzian curves with an iterative least-squares program. The isomer shifts (IS) were referred to the centroid of the Mössbauer spectrum of iron foil. The electronic spectra were measured in CH₂Cl₂ with a Hitachi U-2000 spectrophotometer. The Fe-X stretching frequencies (νFe-X) were recorded on a Bio-Rad DIGILAB FTS-65 spectrophotometer by the polyethylene film method.

### 3. Results and discussion

The Mössbauer parameters, IS and the quadrupole splittings (QS), are listed in table 1. As shown in fig. 2, the two lines of the quadrupole doublet have equal intensity, but each line is broader at the positive velocity side. Comparing these

### Table 1
Mössbauer parameters of Fe(Chl-a)X and Fe(Chl-b)X (77 K)

<table>
<thead>
<tr>
<th>Compd.</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Compd.</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(Chl-a)Cl</td>
<td>0.351</td>
<td>0.893</td>
<td>Fe(Chl-b)Cl</td>
<td>0.375</td>
<td>0.924</td>
</tr>
<tr>
<td>Fe(Chl-a)NCS</td>
<td>0.384</td>
<td>0.960</td>
<td>Fe(Chl-b)NCS</td>
<td>0.401</td>
<td>0.961</td>
</tr>
<tr>
<td>Fe(Chl-a)Br</td>
<td>0.393</td>
<td>1.068</td>
<td>Fe(Chl-b)Br</td>
<td>0.395</td>
<td>0.942</td>
</tr>
<tr>
<td>Fe(Chl-a)I</td>
<td>0.409</td>
<td>1.049</td>
<td>Fe(Chl-b)I</td>
<td>0.410</td>
<td>0.941</td>
</tr>
<tr>
<td>Fe(Chl-a)(CH₃COO)</td>
<td>0.406</td>
<td>0.943</td>
<td>Fe(Chl-b)(CH₃COO)</td>
<td>0.396</td>
<td>0.921</td>
</tr>
</tbody>
</table>