NMR Study of Brominated Yttrium Acetylacetonate

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Bromination of Y(acac)3 by NBS (where acac = acetylacetone and NBS = N-bromosuccinimide) in chloroform medium yields a bromo product. Analysis of the CMR and PMR spectra based on symmetry consideration helps in fixing the exact number of diketone rings that undergo flipping as two.

We have previously reported1−3 the unusual phenomenon of ring flipping upon bromination of lanthanide-β-diketonates/β-ketoesters by N-bromosuccinimide (NBS). The near and far IR spectra of the reaction products exhibited bands at 1780 (νC = C), 1700 (νCO) acetyl, 1200 (νC−O) and 180 cm−1 (νM−Br) indicating molecular rearrangement. As it is impossible to decide the exact number of flipped diketone rings in the product from IR data only, we envisaged that the changes in the environment of ligand protons and carbons as a result of rearrangement would be reflected in 1H and 13C NMR chemical shifts of the reaction product, leading to identification of number of flipped rings. The results of such a study are reported in this note.

For convenience, the following nomenclature is introduced; M(AA)3 refers to tris-chelate with unflipped bromoacetylacetone ring and O, O coordinating sites; M(AA)(AB) refers to chelate in which only one ring is flipped with O and Br coordinating sites; M(AA)AB refers to chelate with two flipped rings; and M(AB)3 refers to chelate in which all the three bromoacetylacetone rings undergo flipping with O and Br becoming the coordinating sites.

The 200 MHz PMR spectrum of Y(acac)3·2H2O in DMSO-d6 exhibits only one signal due to the methyl protons at δ 1.77 (ref. 4), the other signals appearing at 3.35 (H2O) and 5.32 (γ−CH) [O6 or D3 geometry neglecting water molecules]. The 50.32 MHz 13C NMR spectrum of this chelate displays signals at δ 27.16 (CH3)5, 100.72 (CH) and 188.52 (C=O). The above tris-chelate of the type M(AA)3 has a C3 axis which renders each atom in each ligand ring environmentally equivalent and hence the chemical shifts inherent for a given ligand molecule would appear as such without an increase in number.

Since the molecule M(AA)3(AB) has no C3 and C2 axes, there will be two separate chemical shifts, one for the (AA)3 part and the other for the (AB) part. In the chelate M(AA)(AB)2, which can exist in cis and trans forms, the C2 axis renders the two unsymmetrical bidentate ligands environmentally equivalent. Thus PMR or CMR chemical shifts of AB will not show an increase in the number of signals. Also the NMR spectra of the cis and trans forms will not be different.

Considering now the molecule M(AB)3, which is an unsymmetrical octahedral tris-chelate, it can exist in facial and meridional forms. Facial form of M(AB)3 has a characteristic C3 symmetry making (AB)3 interchangeable and hence environmentally equivalent. On the contrary, the meridional isomer is totally asymmetric and all the three ligand moieties (AB)3 are environmentally non-equivalent. The spectra will therefore show an increased number of NMR signals. Thus 200 MHz PMR spectrum of Y(acac-Br)3·H2O in DMSO-d6 exhibits signals at δ 1.84 (CH3, six-membered ring), 2.58 (CH3CO), 2.83 (CH3, five-membered ring) and 3.5 (H2O). The 50.32 MHz 13C NMR spectrum of this chelate in DMSO-d6 exhibits signals at δ 24.29 (CH3, six-membered ring), 29.70 (CH3CO), 29.89 (CH3, five-membered ring), 100.74 (C=O, five-membered ring), 178.39 (C=O of CH3CO), 179.61 (C=O, five-membered ring), 186.07 and 186.47 (C−Br in two different rings).

Table 1—Total Number of PMR and CMR Signals Expected and Observed for Different Configurations (Water Signals excluded)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetry</th>
<th>Expected</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(AA)3</td>
<td>C3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>M(AA)(AB)</td>
<td>NO C2</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>M(AB)3</td>
<td>C3</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>M(AB)3</td>
<td>Asymmetric</td>
<td>6</td>
<td>15</td>
</tr>
</tbody>
</table>

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Employing a dynamic model developed by Ramalingam et al., it is possible to carry out various symmetry operations on an octahedral complex and to examine the changes in the ligand environment for different arrangements. The above discussion centres around this model and the details of such an observation are summarised in Table 1.

It is clear from Table 1 that for a chelate of the type M(αA)(βAB), the observed and expected signals agree. Thus it may be concluded that the bromo product obtained as a result of bromination of lanthanide-β-diketonates/β-ketoesters contains two flipped rings with O and Br in coordinating sites and one unflipped ring with O and O coordinating sites.

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References