Synthesis of a Dysprosium(III) Complex with a Hexadentate Amine Ligand †

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Abstract: The use of polydentate macrocyclic Lewis bases is a way to contribute to determine the coordination number of metal complexes. In this sense, hexadentate N₆ donors can help to achieve lanthanoid complexes with coordination number 8. But the geometry of these complexes depends on the flexibility of the bases. Accordingly, in this communication we present the synthesis and crystallographic characterization of the dysprosium complex [DyL₆Cl₂]Cl·2H₂O, where L₆ is a flexible hexaaza donor.

Keywords: hexaaza donor; dysprosium; flexible macrocycle

1. Introduction

Hexaaazamacrocycles are Lewis bases widely utilized in coordination chemistry. In fact, these ligands are very broadly used in obtaining lanthanoid metal complexes [1–4], even though Ln³⁺ ions are hard Pearson acids and should have a preference for hard oxygen donor ligands. But the macrocycle effect makes lanthanoids easily coordinated to these nitrogenous ligands. The greater or lesser flexibility of these hexaaazamacrocycles, as well as the number and volume of auxiliary ligands, predetermine the coordination number of the metal center. In this sense, it has been described that if the auxiliary ligands are small, the coordination index normally exceeds the value of 8 [4], but that if such ligands are bulky, the coordination index 8 is the usual one [4]. However, the geometry seems to depend largely on the flexibility of the macrocycle. But this is a factor that is so far little explored. With these considerations in mind, we have focused on a previously described N₆ amine macrocyclic ligand [5,6], for which only two lanthanoid metal complexes exist [6], in which the ligand provides a rather flat N₆ environment to the metal, despite its high flexibility. Accordingly, in this communication we report a new dysprosium complex of this N₆ donor, with the aim of analyzing the effect of such flexibility on the geometry about of the lanthanoid ion as a function of its size and the coordinated auxiliary donors.

2. Materials and Methods

2.1. Materials and General Methods

All chemical reagents and solvents were purchased from commercial sources and used as received without further purification. Single X-ray diffraction data for [DyL₆Cl₂]Cl·2H₂O (1·2H₂O) were collected at 100 K on a Bruker d8 VENTURE PHOTON III-14 diffractometer, employing graphite monochromated Mo-ka (λ = 0.71073 Å) radiation. Multi scan absorption corrections were applied using SADABS [7]. The structure was
solved by standard direct methods, employing SHELXT [8], and then refined by full matrix least-squares techniques on F², using SHELXL [9] from the program package SHELX.

2.2. Synthesis

The hexadentate amine ligand LN⁶ was obtained as previously reported [5,6], and satisfactorily characterized by ¹H NMR spectroscopy. ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 7.53 (t, 2H, H aromatic), 7.16 (d, 2H, H aromatic), 7.03 (d, 2H, H aromatic), 3.73 (s, 4H, HCH₂-py), 3.57 (s, 4H, HCH₂-py), 2.73 (t, 4H, HCH₂-N), 2.59 (t, 4H, HCH₂-N), 2.27 (s, 6H, HCH₃).

[DyLN⁶Cl₂]Cl·2H₂O (1·2H₂O): to a solution of LN⁶ (0.040 g, 0.113 mmol) in acetonitrile (20 mL), dysprosium chloride hexahydrate (0.043 g, 0.113 mmol) and dry methanol (10 mL) were added. The mixture was refluxed for 4 h, and then the solvent was removed under vacuum up to half of its initial volume. Colourless single crystals were isolated by layering the solution with diethyl ether in the fridge at ~5 °C. Yield: 0.030 g (40%). Crystal data (at 100(2) K): monoclinic, P2₁/n, C₂₀H₃₄Cl₃DyN₆O₂, MW = 659.38, with a = 10.3146(8) Å, b = 16.4037(13) Å, c = 14.8724(11) Å, α = 90°, β = 91.920(3)°, γ = 90°, V = 2515.0(3) Å³, Z = 4, R₁ = 0.0159 and ωR₂ = 0.0390 (I > 2σ(I)).

3. Results and Discussion

3.1. Synthesis

[DyLN⁶Cl₂]Cl·2H₂O (1·2H₂O) was prepared by a classical reaction synthesis, from dysprosium(III) chloride hexahydrate and the amine neutral ligand LN⁶, using acetonitrile and dry methanol as solvents, as shown in Scheme 1. The metal complex was obtained in the form of colourless single crystals, which corroborates the high purity with which it was isolated.

Accordingly, 1·2H₂O was unequivocally characterized by single X-ray diffraction studies.

Scheme 1. Reaction scheme for isolation of complex 1·2H₂O. Solvent molecules and the flexion of the LN⁶ ligand have been omitted, for clarity.

3.2. Single X-ray Diffraction Studies

A ball and sticks diagram for 1 is shown in Figure 1, and main bond distances and angles are recorded in Table 1.

The crystal structure of 1·2H₂O shows that it is composed of one mononuclear cation [DyLN⁶Cl₂]⁺ and a Cl⁻ anion. In addition, water as solvate is present in the unit cell.

In the cation (Figure 1), the dysprosium ion is surrounded by a neutral hexadentate amine ligand, which links the metal through all the nitrogen atoms of the pyridine and the amine functions. The coordination sphere of the dysprosium atom is completed by two chloride ligands. Accordingly, the lanthanoid ion is in an octacoordinated N₆Cl₂ environment.
Figure 1. Ball and sticks diagram for the cation [DyL₆Cl₂]⁺ in 1.

Table 1. Main bond distances (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1-N1</td>
<td>2.6186(13)</td>
</tr>
<tr>
<td>Dy1-N2</td>
<td>2.5079(13)</td>
</tr>
<tr>
<td>Dy1-N3</td>
<td>2.5064(13)</td>
</tr>
<tr>
<td>Dy1-N4</td>
<td>2.6326(13)</td>
</tr>
<tr>
<td>Dy1-N5</td>
<td>2.4903(13)</td>
</tr>
<tr>
<td>Dy1-N6</td>
<td>2.5096(13)</td>
</tr>
<tr>
<td>Dy1-Cl1</td>
<td>2.6523(4)</td>
</tr>
<tr>
<td>Dy1-Cl2</td>
<td>2.6196(4)</td>
</tr>
<tr>
<td>N1-Dy1-N4</td>
<td>155.43(4)</td>
</tr>
<tr>
<td>N2-Dy1-N5</td>
<td>104.82(4)</td>
</tr>
<tr>
<td>N3-Dy1-N6</td>
<td>108.12(4)</td>
</tr>
<tr>
<td>Cl1-Dy1-Cl2</td>
<td>101.626(14)</td>
</tr>
</tbody>
</table>

Due to ligand folding, and despite the coordination index 8, it can be clearly seen in Figure 1 that the geometry of the compound is far from being hexagonal bipyramidal. In fact, calculations of the degree of distortion of the DyN₆Cl₂ core with respect to an ideal eight vertex polyhedron with the SHAPE software [10–12], shows that the geometry is closer to a triangular dodecahedron, but highly distorted towards a biaugmented trigonal prism.

In this structure, it is noticeable that the L N₆ donor bends in half, with the methyl groups on both nitrogen atoms adopting a syn-syn disposition. This clearly differs from the previously reported lanthanoid complexes of L₆⁺ ([LnL₆(NO₃)₂]NO₃, Ln = Ce, Sm), where the ligand is almost planar [6]. The very different conformation of the ligand is demonstrated by the dihedral angle between the pyridine units, which is less than 20° in related complexes and 45.35° in 1·2H₂O, and by the NPy-Dy-NPy angles, which tend to 180° in related compounds, and it is ca. 105° in 1·2H₂O. Accordingly, this work shows that the size of the metal ion and the nature of the auxiliary ligands are definite factors to be taken into account in ligand folding, and that the geometry that can be induced by this type of flexible ligands is not as predetermined as with rigid N₆ macrocyclic ligands [4].

In addition, both protonated amine groups establish weak interactions with the chloride counterions (distances N···Cl of ca. 3.29 Å), expanding the mononuclear complex into a chain (Figure 2). In this chain, the shortest distance between adjacent dysprosium ions is 10.3146(9) Å.
4. Conclusions

This work reports the synthesis and structural characterization of a Dy\textsuperscript{III} complex with a flexible hexaaza donor. The high flexibility of this ligand makes it to fold in half, with the methyl groups adopting a \textit{syn-syn} disposition. This leads to the dysprosium atom being in an \textit{N}\textsubscript{6}Cl\textsubscript{2} environment, with a distorted geometry between triangular dodecahedron and biaugmented trigonal prism. This clearly contrasts with the nearly planar character of the ligand described for Ce\textsuperscript{III} or Sm\textsuperscript{III} complexes with nitrate auxiliary ligands. In fact, this work shows that the coordination chemistry of this ligand is structurally very versatile, and that the arrangement adopted by the ligand in the environment of the metal center seems to depend largely on the size of the metal ion itself and the auxiliary ligands. Indeed, this is the first metal complex of this ligand in which a fully folded arrangement of this \textit{N}\textsubscript{6} macrocycle is observed.

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