chemistry proceedings

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Proceeding Paper

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

Cristina González-Barreira [1,]*, Julio Corredoira-Vázquez [1,2], Ana M. García-Deibe [1] and Matilde Fondo [1]

[1] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain; julio.corredoira.vazquez@usc.es (J.C.-V.); ana.garcia.deibe@usc.es (A.M.G.-D.); matilde.fondo@usc.es (M.F.)

[2] Phantom-g, CICECO—Aveiro Institute of Materials, Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal; julio.corredoira.vazquez@usc.es

* Correspondence: cristina.gonzalez.barreira@rai.usc.es; Tel.: +34-881814248

† Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: https://ecsoc-27.sciforum.net/.

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 N_6 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 $[DyL^{N6}Cl_2]Cl \cdot 2H_2O$, where L^{N6} is a flexible hexaaza donor.

Keywords: hexaaza donor; dysprosium; flexible macrocycle

Citation: González-Barreira, C.; Corredoira-Vázquez, J.; García-Deibe, A.M.; Fondo, M. Synthesis of a Dysprosium(III) Complex with a Hexadentate Amine Ligand. *Chem. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: 15 November 2023

1. Introduction

Hexaazamacrocycles 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 Ln^{III} 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 hexaazamacrocycles, 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 N_6 amine macrocyclic ligand [5,6], for which only two lanthanoid metal complexes exist [6], in which the ligand provides a rather flat N_6 environment to the metal, despite its high flexibility. Accordingly, in this communication we report a new dysprosium complex of this N_6 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 $[DyL^{N6}Cl_2]Cl \cdot 2H_2O$ (**1**·$2H_2O$) were collected at 100 K on a Bruker d8 VENTURE PHOTON III-14 diffractometer, employing graphite monochromated Mo-kα (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 F^2, using SHELXL [9] from the program package SHELX.

2.2. Synthesis

The hexadentate amine ligand L^{N6} was obtained as previously reported [5,6], and satisfactorily characterized by ^{1}H NMR spectroscopy. ^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm): 7.53 (t, 2H, $H_{aromatic}$), 7.16 (d, 2H, $H_{aromatic}$), 7.03 (d, 2H, $H_{aromatic}$), 3.73 (s, 4H, $H_{CH2\text{-}py}$), 3.57 (s, 4H, $H_{CH2\text{-}py}$), 2.73 (t, 4H, $H_{CH2\text{-}N}$), 2.59 (t, 4H, $H_{CH2\text{-}N}$), 2.27(s, 6H, H_{CH3}).

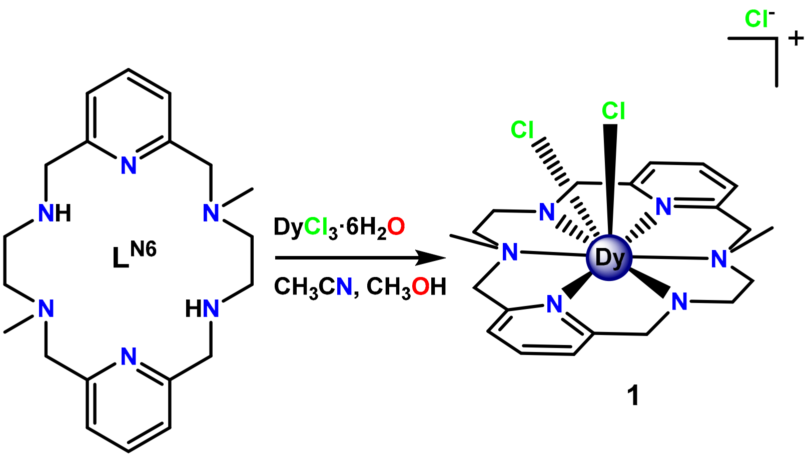
$[DyL^{N6}Cl_2]Cl\cdot 2H_2O$ (**1**$\cdot 2H_2O$): to a solution of L^{N6} (0.040 g, 0.113 mmol) in acetonitrile (20 mL), dysprosium chloride hexahydrate (0.043 g, 0.113 mmol) and dry methanol (10 mL) were added. The mixture was refluxed for 4 h, and then the solvent was removed under vacuum up to half 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, $C_{20}H_{34}Cl_3DyN_6O_2$, MW = 659.38, with a = 10.3146(8) Å, b = 16.4037(13) Å, c = 14.8724(11) Å, $\alpha = 90^\circ$, $\beta = 91.920(3)^\circ$, $\gamma = 90^\circ$, V = 2515.0(3) Å^3, Z = 4, $R_1 = 0.0159$ and $\omega R_2 = 0.0390$ ($I > 2\sigma I$).

3. Results and Discussion

3.1. Synthesis

$[DyL^{N6}Cl_2]Cl\cdot 2H_2O$ (**1**$\cdot 2H_2O$) was prepared by a classical reaction synthesis, from dysprosium(III) chloride hexahydrate and the amine neutral ligand L^{N6}, 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**$\cdot 2H_2O$ was unequivocally characterized by single X-ray diffraction studies.



Scheme 1. Reaction scheme for isolation of complex **1**$\cdot 2H_2O$. Solvent molecules and the flexion of the L^{N6} 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**$\cdot 2H_2O$ shows that it is composed of one mononuclear cation $[DyL^{N6}Cl_2]^+$ 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 N_6Cl_2 environment.

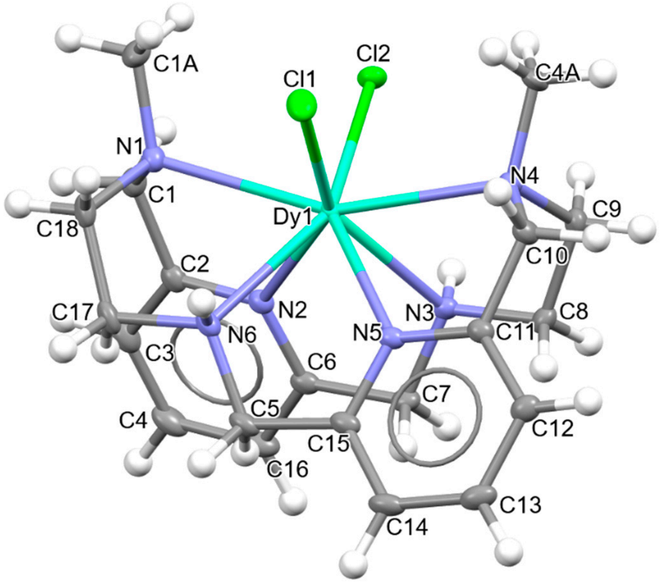


Figure 1. Ball and sticks diagram for the cation $[DyL^{N6}Cl_2]^+$ in **1**.

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

Dy1-N1	2.6186(13)
Dy1-N2	2.5079(13)
Dy1-N3	2.5064(13)
Dy1-N4	2.6326(13)
Dy1-N5	2.4903(13)
Dy1-N6	2.5096(13)
Dy1-Cl1	2.6523(4)
Dy1-Cl2	2.6196(4)
N1-Dy1-N4	155.43(4)
N2-Dy1-N5	104.82(4)
N3-Dy1-N6	108.12(4)
Cl1-Dy1-Cl2	101.626(14)

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 DyN_6Cl_2 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 L^{N6} ($[LnL^{N6}(NO_3)_2]NO_3$, 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**$\cdot 2H_2O$, and by the N_{Py}-Dy-N_{Py} angles, which tend to 180° in related compounds, and it is ca. 105° in **1**$\cdot 2H_2O$. 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 N_6 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.

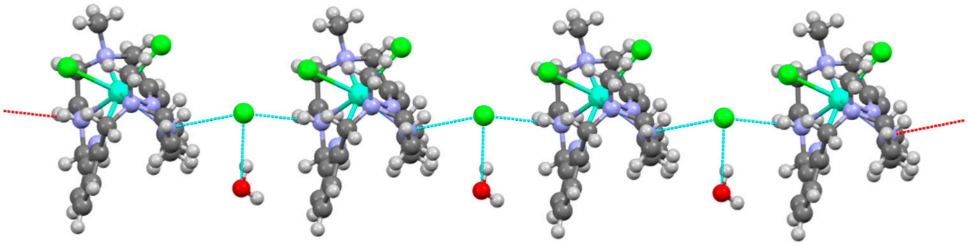


Figure 2. Ball and sticks diagram showing the weak interactions that lead to the chain disposition of **1**·$2H_2O$.

4. Conclusions

This work reports the synthesis and structural characterization of a Dy^{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 a *syn-syn* disposition. This leads to the dysprosium atom being in an N_6Cl_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^{III} or Sm^{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 N_6 macrocycle is observed.

Author Contributions: Conceptualization, M.F. and J.C.V.; methodology, C.G.B., J.C.V. and M.F.; formal analysis, M.F., A.G.D. and C.G.B.; investigation, M.F., J.C.V. and C.G.B.; writing—original draft preparation, M.F. and C.G.B.; writing—review and editing, M.F.; supervision, M.F. and J.C.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: J. Corredoira-Vázquez acknowledges Xunta de Galicia for his postdoctoral fellowship (ED481B 2022-068).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mitewa, M.; Bontchev, P.R. Coordination chemistry of N_6 macrocycles. *Coord. Chem. Rev.* **1994**, *135–136*, 129–163. https://doi.org/10.1016/0010-8545(94)80067-7.
2. Rezaeivala, M.; Keypour, H. Schiff base and non-Schiff base macrocyclic ligands and complexes incorporating the pyridine moiety—The first 50 years. *Coord. Chem. Rev.* **2014**, *280*, 203–253. https://doi.org/10.1016/j.ccr.2014.06.007.
3. Gavey, E.L.; Pilkington, M. Coordination complexes of 15-membered pentadentate aza, oxoaza and thiaaza Schiff base macrocycles “Old Complexes Offer New Attractions”. *Coord. Chem. Rev.* **2015**, *296*, 125–152. https://doi.org/10.1016/j.ccr.2015.03.017.
4. Corredoira-Vázquez, J.; González-Barreira, C.; Oreiro-Martínez, P.; García-Deibe, A.M.; Sanmartín-Matalobos, J.; Fondo. M. Lanthanoid complexes of pentadentate and hexadentate N_5 and N_6 macrocycles: Synthesis and applications. *J. Rare Earths* **2023**, *in press*. https://doi.org/10.1016/j.jre.2023.03.013.
5. Lamelas, R.; García, V.; Liñares, A.; Bastida, R.; Labisbal, E.; Fernández-Lodeiro, A.; Lodeiro, C.; Núñez, C.; Valencia, L. Novel trans-disubstituted hexaaza-macrocyclic ligands containing pyridine head units: Synthesis, disubstitution and colorimetric properties. *Sens. Actuators B Chem.* **2016**, *225*, 481–491. https://doi.org/10.1016/j.snb.2015.11.090.
6. Lamelas, R.; Bastida, R.; Labisbal, E.; Macías, A.; Pereira, T.; Pérez-Lourido, P.; Valencia, L.; Vila, J.M.; Núñez, C. A new series of lanthanide complexes with the trans-disubstituted $Py_2[18]aneN_6$ macrocyclic ligand: Synthesis, structures and properties. *Polyhedron* **2019**, *160*, 180–188. https://doi.org/10.1016/j.poly.2018.12.006.

7. Siemens Industrial Automation, Inc. *SADABS: Area-Detector Absorption Correction*; Siemens Industrial Automation, Inc.: Madison, WI, USA, 1996.
8. Sheldrick, G.M. SHELXT-integrated space-group and crystal-structure determination. *Acta Cryst*. **2015**, *71*, 3–8. https://doi.org/10.1107/S2053273314026370.
9. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst*. **2015**, *71*, 3–8. https://doi.org/10.1107/S2053229614024218.
10. Llunell, M.; Casanova, D.; Cirera, J.; Bofill, J.M.; Alemany, P.; Alvarez, S.; Pinsky, M.; Avnir, D. *SHAPE v1.1b*; Publish: Barcelona, Spain, 2005.
11. Ruiz-Martínez, A.; Casanova, D.; Alvarez, S. Polyhedral structures with an odd number of vertices: Nine-coordinate metal compounds. *Chem. Eur. J.* **2008**, *14*, 1291–1303. https://doi.org/10.1002/chem.200701137.
12. Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. *SHAPE: Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools*; University of Barcelona: Barcelona, Spain, 2010.