

Proceeding Paper

# Dysprosium(III)-Mediated Carboxylate Formation from a Schiff Base †

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**Abstract:** This work describes an uncommon new case of imine hydrolysis, leading to the formation of a carboxylate group. The conditions of the media that favor this conversion, which seem to be mediated by the presence of Dy<sup>III</sup>, are analyzed. The process brings about the formation of a dysprosium complex of formula  $\{[(DyL_2)_2Na_2(H_2O)_8][Et_3NH]_2[DyL_2]_2\} \cdot 14H_2O$  (**1**). Single X-ray characterization of the final product is reported.

**Keywords:** Schiff base; carboxylate; hydrolysis; Dy<sup>III</sup>



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## 1. Introduction

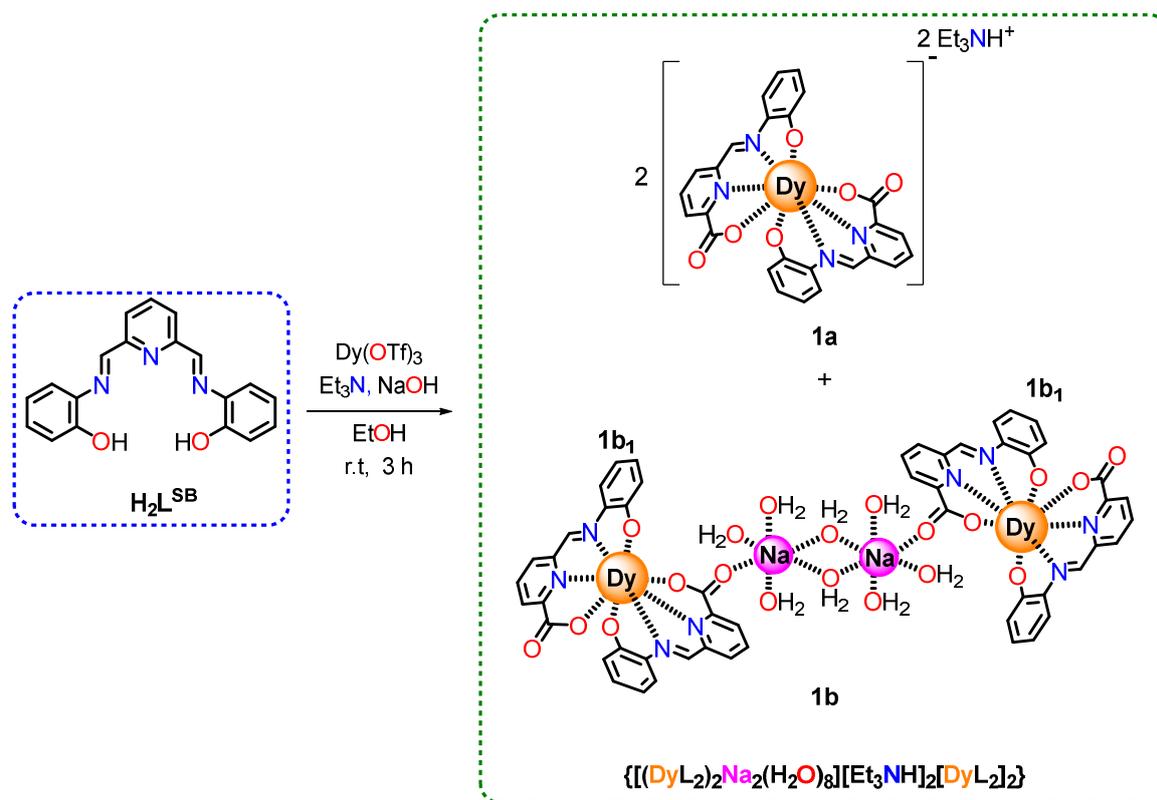
Hydrolysis of Schiff bases usually produces the amine and aldehyde starting materials [1]. In Schiff bases containing two imine groups, partial hydrolysis is quite common, and it can generate imine–amine [2,3] or imine–aldehyde derivatives [4]. However, although it is unusual, sometimes it is observed that such hydrolysis does not stop in the mentioned products, and they continue reacting to form new compounds. In light of this, we recently described the synthesis and stabilization of a hemiacetal from a Schiff base [5]. As a continuation of this work, we describe the formation of an imine–carboxylate ligand from a diimine donor. The obtention of carboxylic acids from aldehydes is well known, and some synthetic methods that do not use any oxidants in addition to the air itself are reported for this organo-catalyzed [6,7] or metal-catalyzed [8] reaction. Additionally, the Cannizzaro reaction also leads to the isolation of carboxylates by aldehyde disproportionation, usually in a strong basic medium [9].

Nevertheless, in spite of these well-known processes, as far as we know, no partial hydrolysis of Schiff base metal complexes has been previously reported to yield coordination compounds containing imine–carboxylate ligands. Accordingly, the herein reported in situ transformation of a diimine donor into an imine–carboxylate ligand, in the presence of Dy<sup>III</sup>, is an uncommon reaction.

## 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. The Schiff base H<sub>2</sub>L<sup>SB</sup> (Scheme 1) was obtained as previously reported [5] and satisfactorily characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy.



**Scheme 1.** Reaction scheme for the isolation of complex 1.

Single X-ray data for **1** were collected at 100 K on a Bruker D8 VENTURE PHOTON III-14 diffractometer, employing graphite monochromated Mo- $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Multiscan absorption corrections were applied using SADABS [10]. The structure was solved by standard direct methods, employing SHELXT [11], and then refined by the full matrix least-squares techniques on  $F^2$ , using SHELXL [12] from the program package SHELX.

## 2.2. Syntheses

$\left\{ \left[ \text{DyL}_2 \right]_2 \text{Na}_2(\text{H}_2\text{O})_8 \right\} \left[ \text{Et}_3\text{NH} \right]_2 \left[ \text{DyL}_2 \right]_2 \cdot 14\text{H}_2\text{O}$  (**1**): to a solution of  $\text{H}_2\text{L}^{\text{SB}}$  (0.154 g, 0.487 mmol) in ethanol (20 mL), NaOH (0.038 g, 0.969 mmol) and triethylamine (0.098 g, 0.969 mmol) were added. The newly obtained solution was mixed with an ethanol (10 mL) solution of dysprosium triflate (0.295 g, 0.487 mmol). The mixture was stirred for 3 h. During this time, an orange solid formed. The suspension was centrifuged, and the orange solid collected and recrystallized in ethanol. The formed single crystals of **1**, suitable for X-ray diffraction studies, were collected by filtration and air dried. Yield: 0.216 g (55% based on Dy). Crystal data (at 100(2) K): triclinic,  $P-1$ ,  $\text{C}_{116}\text{H}_{140}\text{Dy}_4\text{N}_{18}\text{Na}_2\text{O}_{46}$ , MW = 3218.43, with  $a = 10.264(2) \text{ \AA}$ ,  $b = 13.553(4) \text{ \AA}$ ,  $c = 23.507(6) \text{ \AA}$ ,  $\alpha = 95.859(8)^\circ$ ,  $\beta = 91.785(8)^\circ$ ,  $\gamma = 106.110(7)^\circ$ ,  $V = 3119.0(14) \text{ \AA}^3$ ,  $Z = 1$ ,  $R_1 = 0.0966$  and  $wR_2 = 0.2061$  ( $I > 2\sigma I$ ).

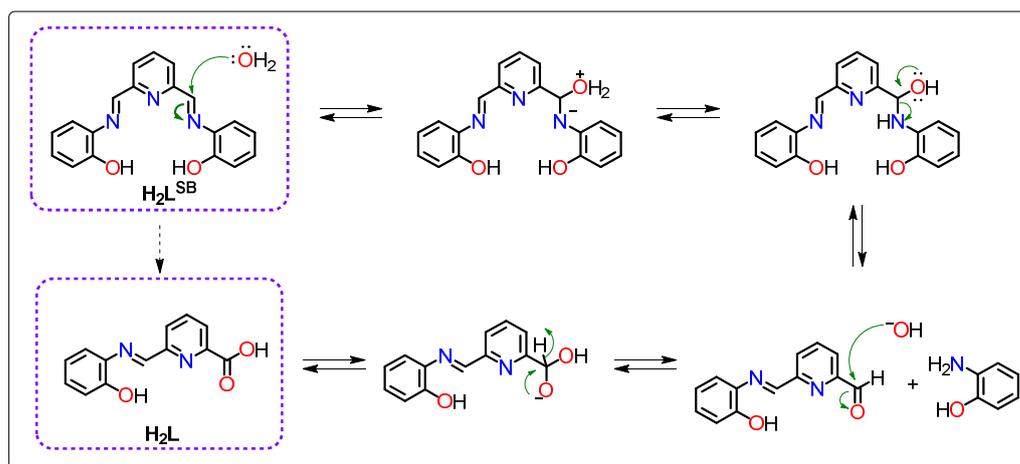
## 3. Results and Discussion

### 3.1. Synthesis and Spectroscopic Characterization

The reaction of the dysprosium(III) triflate with a solution of  $\text{H}_2\text{L}^{\text{SB}}$  in ethanol and basified with triethylamine and sodium hydroxide leads to the isolation of the complex  $\left\{ \left[ \text{DyL}_2 \right]_2 \text{Na}_2(\text{H}_2\text{O})_8 \right\} \left[ \text{Et}_3\text{NH} \right]_2 \left[ \text{DyL}_2 \right]_2 \cdot 14\text{H}_2\text{O}$  (**1**) (Scheme 1).

This compound contains the newly generated in situ ligand  $[\text{L}]^{2-}$ , which derives from the Schiff base  $[\text{L}^{\text{SB}}]^{2-}$  (Scheme 1) by partial hydrolysis and where a carboxylate functional group is present. The hydrolysis of imines giving rise to aldehydes is well known, but,

seemingly, there are not previous examples of the transformation of coordinated imines into carboxylates. This reaction, summarized in Scheme 2, seems to be catalyzed by the coordination to the Dy<sup>III</sup> ion as no evidence of such hydrolysis is observed when a basic ethanolic solution of H<sub>2</sub>L<sup>SB</sup> is left to stand for one week. Accordingly, the initial step in the formation of the carboxylate group should be the partial hydrolysis of the Schiff base, due to the presence of small amounts of water in the reaction medium (Scheme 1), followed by a nucleophilic attack of the hydroxide ion on the recently generated aldehyde function [9,13]. This leads to the formation of the acidic function, which, in a basic medium, is deprotonated, and all the steps seem to be promoted by Dy<sup>III</sup>.



**Scheme 2.** Proposed mechanism for the formation of carboxylate from the imine functional group.

Complex 1 was an orange solid, apparently stable in air in a solid state and in the solution, which was unequivocally characterized by single X-ray diffraction studies.

### 3.2. Single X-ray Diffraction Studies

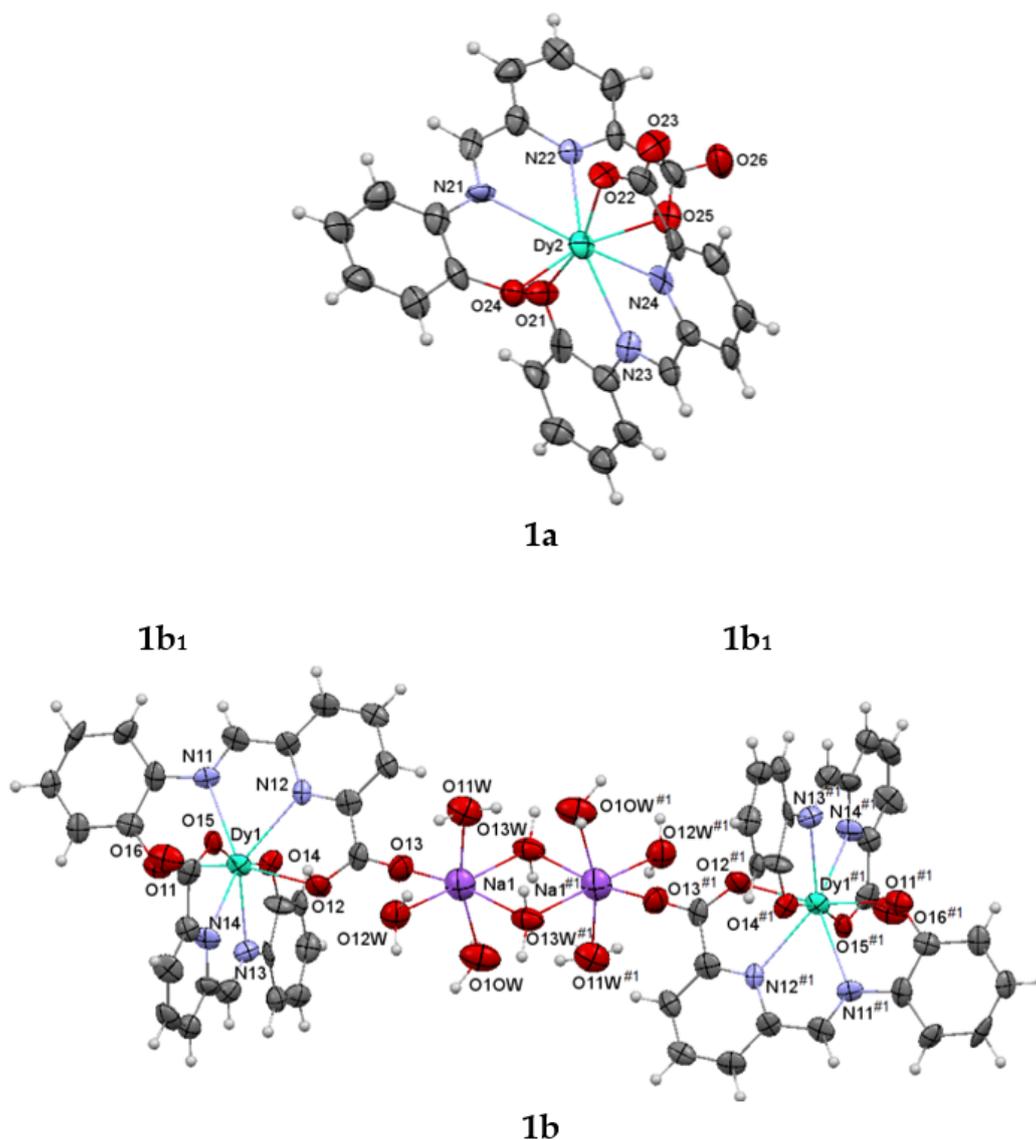
Single crystals of  $\{[(DyL_2)_2Na_2(H_2O)_8][Et_3NH]_2[DyL_2]_2\} \cdot 14H_2O$  (1) were obtained as detailed above. An ellipsoid diagram for 1 is shown in Figure 1, and the main distances and angles are recorded in Table 1.

The crystal structure of 1 shows that it is composed of two  $Et_3N^+$  cations, two crystallographically identical mononuclear  $[DyL_2]^-$  anions, which are called 1a, and a neutral  $[(DyL)_2Na_2(H_2O)_8]$  moiety, which is called 1b. In addition, water as a solvate is present in the unit cell.

In the 1a anion (Figure 1), the dysprosium ion is surrounded by two imine–carboxylate ligands that act as dianionic tetradentate  $N_2O_2$  donors, linking the metal ion through both nitrogen atoms of the imine and pyridine functions, the deprotonated phenolic oxygen atom and the deprotonated oxygen atom of the carboxylic group. Accordingly, the dysprosium ion is octacoordinated in an  $N_4O_4$  environment. Calculations of the degree of distortion of the  $DyN_4O_4$  core, with respect to an ideal eight-vertex polyhedron with the SHAPE software [14–16], gives rise to shape measurements closer to a snub diphenoid but distorts towards a triangular dodecahedron. The  $[DyL_2]^-$  moieties develop an intricate hydrogen bond scheme with the  $[Et_3NH]^+$  cations and the water solvates, which involves the phenolate and carboxylate oxygen donors of the anions. Thus, a zig-zag double chain of  $[DyL_2]^-$  anions is formed, and both chains are joined by hydrogen bonds between them. In addition, the double chain holds the  $[Et_3NH]^+$  cations through hydrogen bonds via water molecules (Scheme 2). In this assembly, the shortest intrachain and interchain  $Dy_2 \cdots Dy_2$  distances are 10.264(2) Å and 7.583(2) Å, respectively.

The  $[(DyL)_2Na_2(H_2O)_8]$  (1b) moiety can be understood as two crystallographically related  $[DyL_2]^-$  anions (named 1b<sub>1</sub>, Figure 1), assembled through a  $[Na_2(OH)_2]^{2+}$  moiety.

In the  $[\text{DyL}_2]^-$  block, both imine–carboxylate ligands act as in **1a**, providing an  $\text{N}_4\text{O}_4$  environment to the  $\text{Dy}^{\text{III}}$  ion.



**Figure 1.** Ellipsoid (50% probability) diagram for the anion  $[\text{Dy}(\text{L})_2]^-$  (**1a**) and the moiety  $[(\text{DyL})_2\text{Na}_2(\text{H}_2\text{O})_8]$  (**1b**) in **1**. Water solvate and  $\text{Et}_3\text{N}^+$  cations are omitted for clarity.

Once more, SHAPE calculations for the octacoordinated  $\text{Dy}^{\text{III}}$  indicate that the geometry around the metal (Figure 1) is a snub diphenoid distorted towards a triangular dodecahedron.

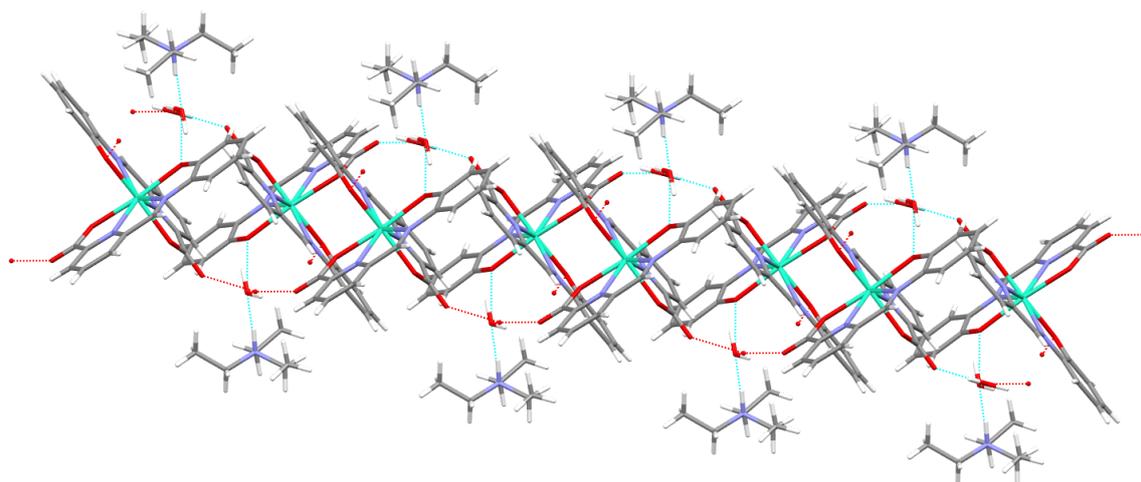
The  $[\text{Na}_2(\text{OH}_2)_8]^{2+}$  moiety can be understood as two symmetry-related  $[\text{Na}(\text{OH}_2)_4]^+$  cations, where the sodium atoms are surrounded by four water molecules. Two of these cations are bridged through the oxygen atom of one of the water ligands (O13W), thus giving rise to an  $\text{O}_5$  environment for the sodium ion. This generates the  $[\text{Na}_2(\text{OH}_2)_8]^{2+}$  cation, where each one of the  $\text{Na}^+$  centres additionally binds to the uncoordinated carboxylate oxygen atom of one of the  $[\text{L}]^{2-}$  ligands belonging to the  $[\text{DyL}_2]^-$  anion. Accordingly, this joins the two  $[\text{DyL}_2]^-$  blocks through the  $[\text{Na}_2(\text{OH}_2)_8]^{2+}$  glue and gives rise to an  $\text{O}_6$  environment for the sodium centres. This leads to  $\text{Na}\cdots\text{Na}$  distances of 3.52(2) Å and  $\text{Dy1}\cdots\text{Dy1}$  distances of 16.452(3) Å within the **1b** assembly.

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

Dy1-O11	2.216(15)	Dy2-O21	2.285(13)
Dy1-O12	2.354(14)	Dy2-O22	2.388(12)
Dy1-O14	2.297(12)	Dy2-O24	2.263(13)
Dy1-O15	2.349(13)	Dy2-O25	2.317(13)
Dy1-N11	2.502(14)	Dy2-N23	2.514(16)
Dy1-N12	2.494(15)	Dy2-N24	2.502(14)
Dy1-N13	2.475(15)	Dy2-N21	2.501(16)
Dy1-N14	2.496(14)	Dy2-N22	2.508(15)
Na1-O1OW	2.34(2)	Na1-O13	2.347(18)
Na1-O11W	2.392(19)	Na1-O13W	2.614(18)
Na1-O12W	2.383(17)	Na1-O13W #1	2.436(17)
N12-Dy1-N11	63.5(5)	N24-Dy2-N23	63.1(5)
O14-Dy1-O15	163.7(5)	O24-Dy2-O25	165.2(5)

#1:  $-x, -y + 2, -z$ .

Both 1a and 1b blocks are also connected through an intricate hydrogen bond scheme (Figure 2), which involves the coordinated water, the water solvate and the phenolate oxygen atoms, which results in the shortest intermolecular Dy1...Dy2 distances of 7.531(2) Å.

**Figure 2.** Hydrogen bond scheme among the 1a units, involving the  $\text{Et}_3\text{NH}^+$  cations and water solvate.

#### 4. Conclusions

This work reports the formation and stabilization of an imine–carboxylate donor from a diimine ligand in a basic medium and in the presence of dysprosium(III). Accordingly, this work contributes to increasing the number of functional groups that can be produced from the hydrolysis of imine metal complexes, given that, as far as we know, there are no reports of previous examples of carboxylate donors obtained from imine ligands.

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

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