

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 favour this conversion, which seems to be mediated by the presence of Dy^{III}, are analysed. 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; dysprosium(III)

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1. Introduction

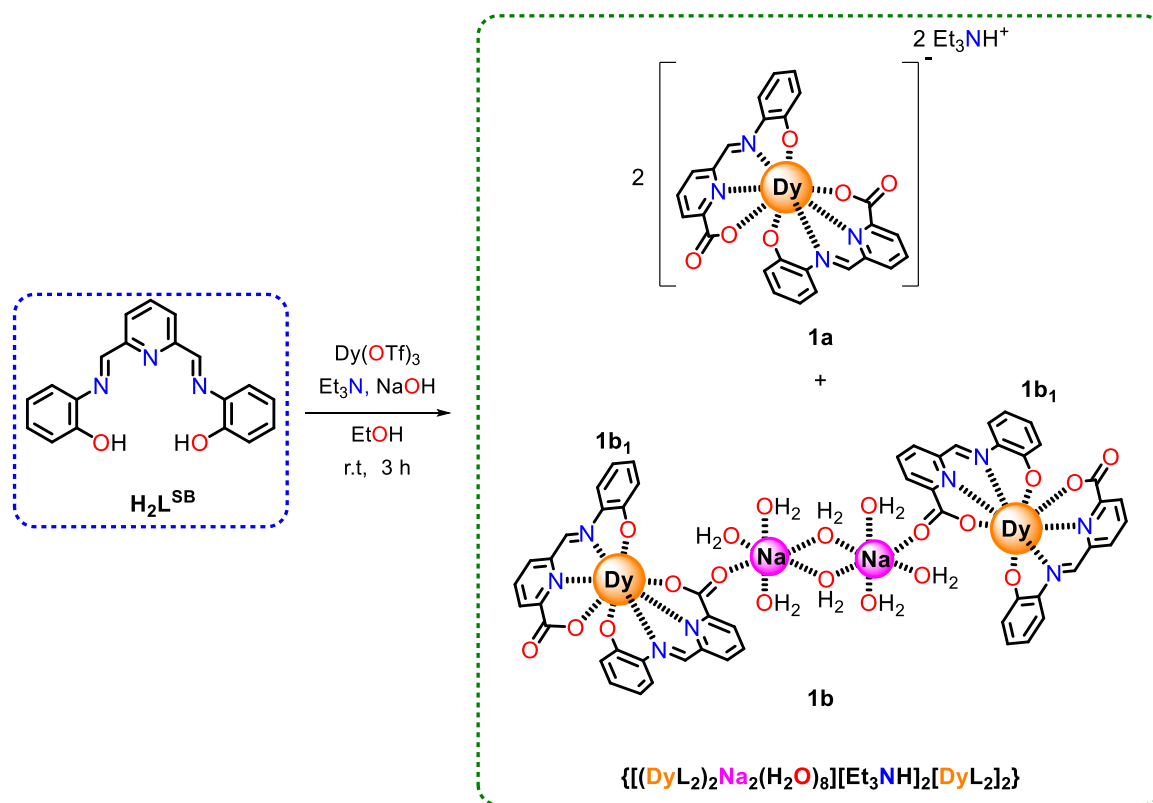
Hydrolysis of Schiff bases usually produces the amine and aldehyde starting materials [1]. In Schiff bases containing two imine groups, partial hydrolysis is quite common, and it can generate imine-amine [2,3] or imine-aldehyde derivatives [4]. However, although it is unusual, sometimes it has been observed that such hydrolysis does not stop in the mentioned products, and these continue reacting to form new compounds. In this way, we ourselves have 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 were reported for this organocatalyzed [6,7] or metal-catalyzed [8] reaction. Besides, the Cannizzaro reaction also leads to the isolation of carboxylates by aldehydes 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 dysprosium(III), 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 H₂L^{SB} (Scheme 1) was obtained as previously reported [5], and satisfactorily characterized by elemental analysis, IR and ¹H NMR spectroscopy.



Scheme 1. Reaction scheme for 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- α ($\lambda = 0.71073 \text{ \AA}$) radiation. Multi scan absorption corrections were applied using SADABS [10]. The structure was solved by standard direct methods, employing SHELXT [11], and then refined by full matrix least-squares techniques on F^2 , using SHELXL [12] from the program package SHELX.

2.2. Syntheses

$\{[(\text{DyL}_2)_2\text{Na}_2(\text{H}_2\text{O})_8][\text{Et}_3\text{NH}]_2[\text{DyL}_2]_2\} \cdot 14\text{H}_2\text{O}$ (**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) are added. The new obtained solution is mixed with an ethanol (10 mL) solution of dysprosium triflate (0.295 g, 0.487 mmol). The mixture is stirred for 3 h. During this time, an orange solid is formed. The suspension is centrifuged and the orange solid collected and recrystallized in ethanol. The formed single crystals of **1**, suitable for X-ray diffraction studies, are collected by filtration and dried in air. 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 $wR_2 = 0.2061$ ($I > 2\sigma I$).

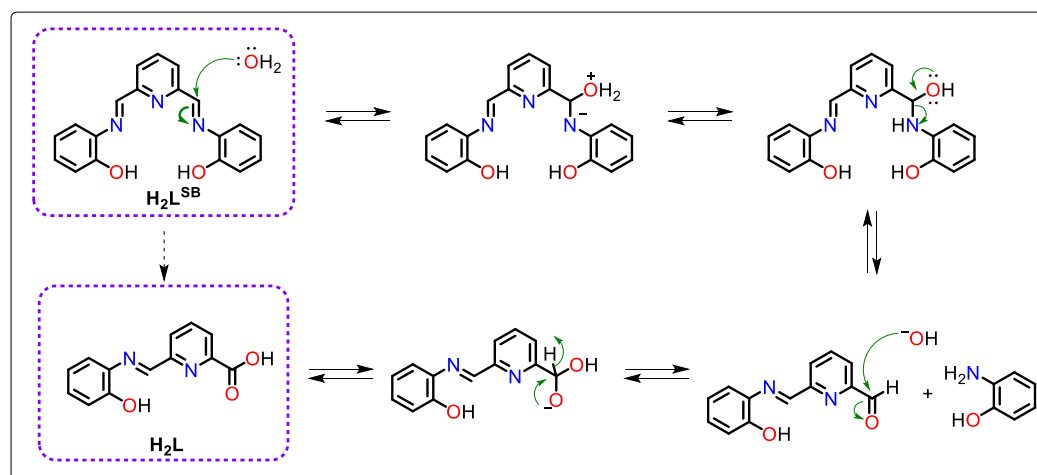
3. Results and Discussion

3.1. Synthesis and Spectroscopic Characterisation

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

This compound contains the new in situ generated 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 to give rise to aldehydes is well-known but,

seemingly, there are not previous examples of transformation of coordinated imines into carboxylates. This reaction, summarized in Scheme 2, seems to be catalyzed by coordination to the Dy^{III} ion, as no evidence of such hydrolysis is observed when a basic ethanolic solution of H₂L^{SB} 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^{III}.



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

Complex **1** is an orange solid, apparently stable in air in solid state and in 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 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 will be called **1a**, and a neutral $[(DyL)_2Na_2(H_2O)_8]$ moiety, which will be called **1b**. In addition, water as 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 a 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 distorted towards 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 between them by hydrogen bonds. In addition, the double chain holds the $[Et_3NH]^+$ cations through hydrogen bonds via water molecules (Figure 2). In this assembly, the shortest intrachain and interchain Dy²...Dy² 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 as **1b₁**, Figure 1), assembled through a $[Na_2(OH_2)_8]^{2+}$ moiety.

In the $[\text{DyL}_2]^-$ block, both imine-carboxylate ligands act as in **1a**, providing an N_4O_4 environment to the Dy^{III} ion.

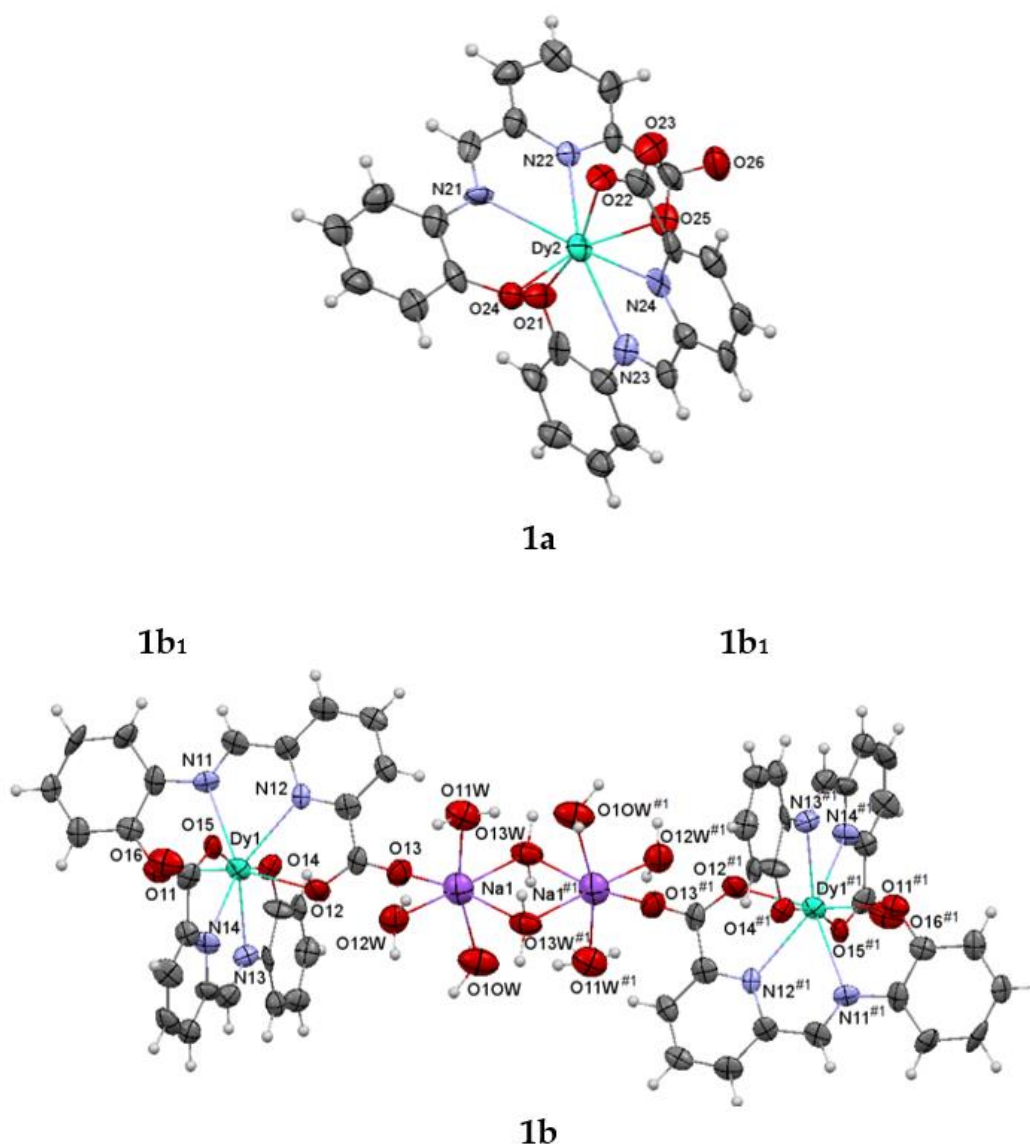


Figure 1. Ellipsoid (50% probability) diagram for the anion $[\text{Dy}(\text{L})_2]^-$ (**1a**) and the moiety $[(\text{DyL})_2\text{Na}_2(\text{H}_2\text{O})_8]$ (**1b**) in **1**. Water solvate and Et_3N^+ cations are omitted for clarity.

Table 1. Main bond distances (\AA) and angles ($^\circ$) 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)

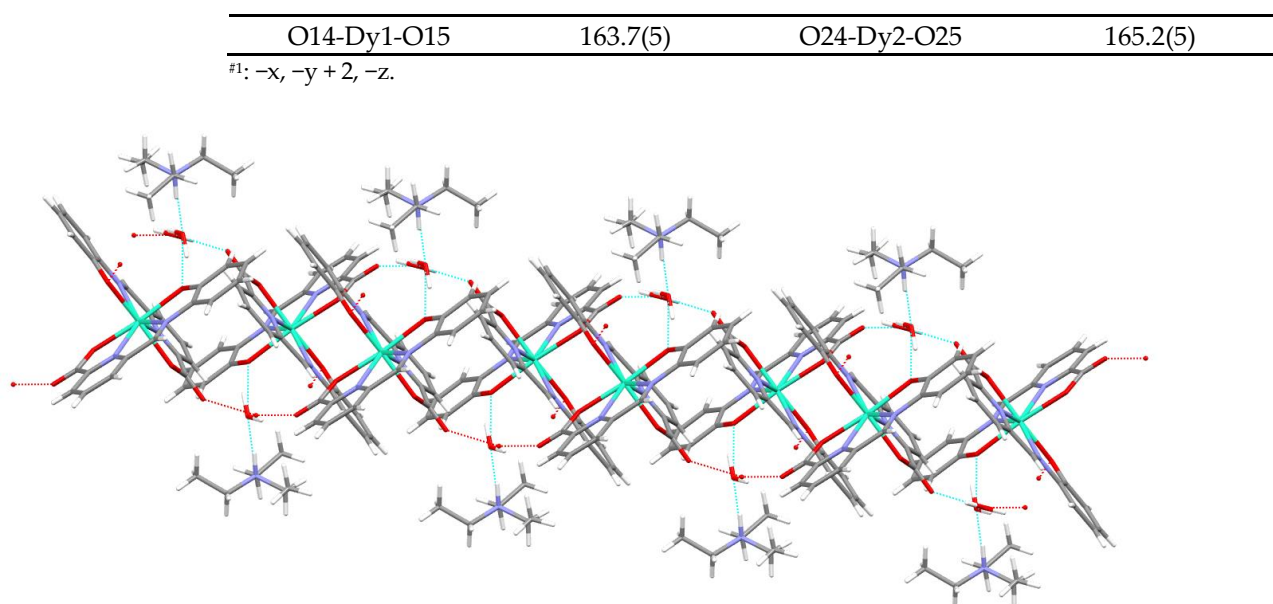


Figure 3. Hydrogen bond scheme among the **1a** units, involving the Et_3NH^+ cations and water solvate.

Once more, SHAPE calculations for the octacoordinated Dy^{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 joined two 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 O_5 environment for the sodium ion. This generates the $[\text{Na}_2(\text{OH}_2)_8]^{2+}$ cation, where each one of the Na^+ centres additionally bind 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 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.

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

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 increase the number of functional groups that can be produced from hydrolysis of imine metal complexes, given that, as far as we know, no previous examples of carboxylate donors were reported to be obtained from imine ligands.

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