

# The influence of the counterion in the behavior of a *trans*-diacetate dysprosium complex with a semirigid macrocycle

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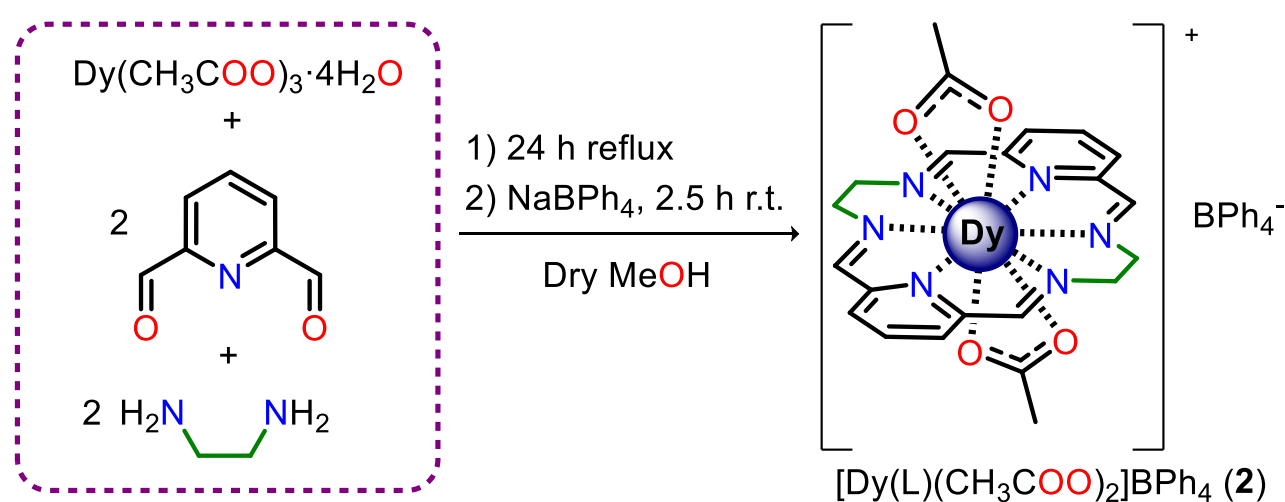
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## INTRODUCTION

We have shown that  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$  (**1**) can behave as a single-molecule magnet under an optimal field of 2000 Oe, as well as a secondary luminescent thermometer.<sup>1</sup> Hence, we would like to know how changing the counterion could influence these interesting properties. Thus, we will firstly study the novel complex  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]\text{BPh}_4$  (**2**), and the differences between these two crystal structures.

## SYNTHESIS

$[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]\text{BPh}_4$  was obtained by a template method, as shown in the scheme below.



Scheme 1. Reaction scheme to obtain **2**.

The crystal structure of **2** comprises  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]^+$  cations, in two slightly different conformations, and  $\text{BPh}_4^-$  anions. Figure 1 shows the superimposition of the cations and single X-ray diffraction.

## STRUCTURAL CHARACTERIZATION

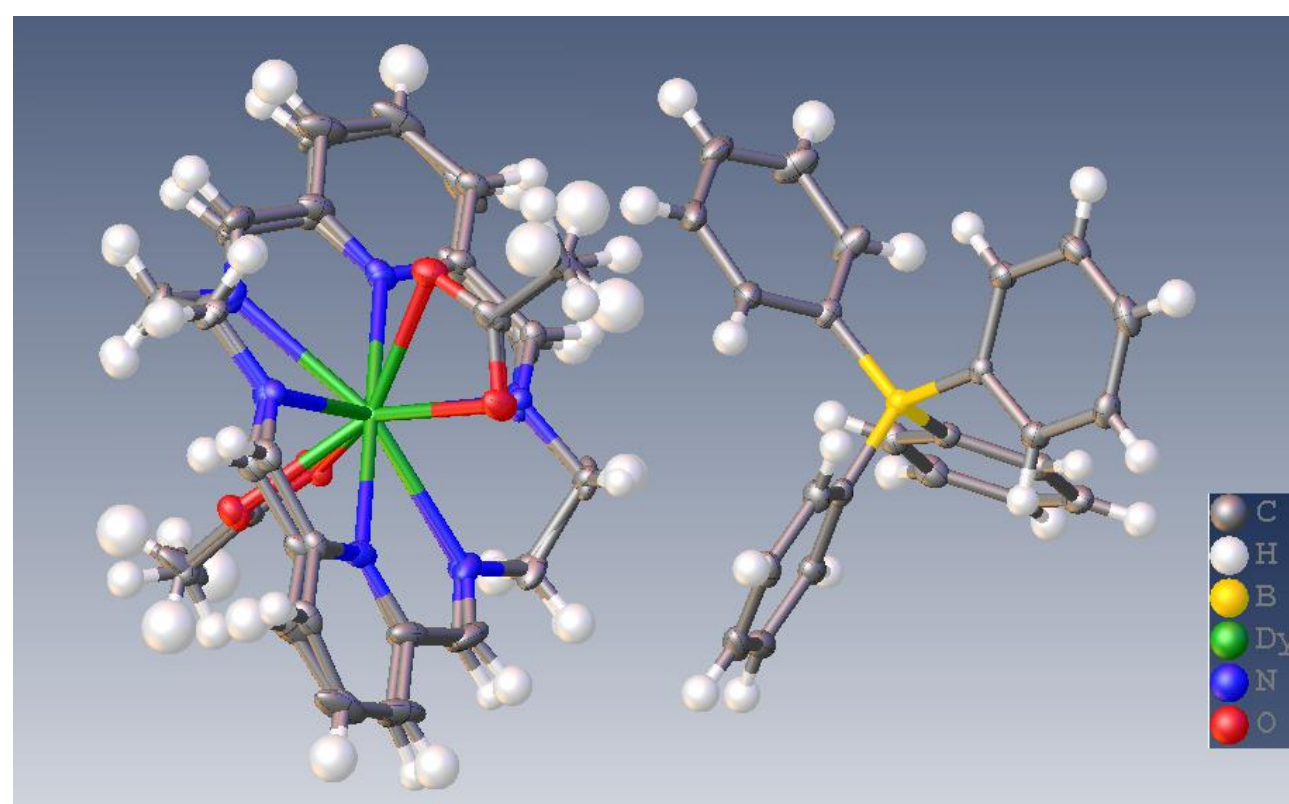


Figure 1. Ellipsoid view of two superimposed units of  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]^+$  and a  $\text{BPh}_4^-$  in their vicinity, as occurring in the unit cell of **2**.

## COMPARISON WITH ANOTHER SPECIES

The conformation found for both  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]^+$  units of **2** are also closely similar to that present in the crystal structure of **1**, as Figure 2 shows. In all these cations, their  $\text{N}_6\text{O}_4$  coordination polyhedra can be described by a distorted tetradecahedron geometry, according to calculations made with SHAPE.<sup>2</sup> Hirshfeld surfaces shown in Figure 3 illustrate the differences between the crystal packings of **1** and **2**.

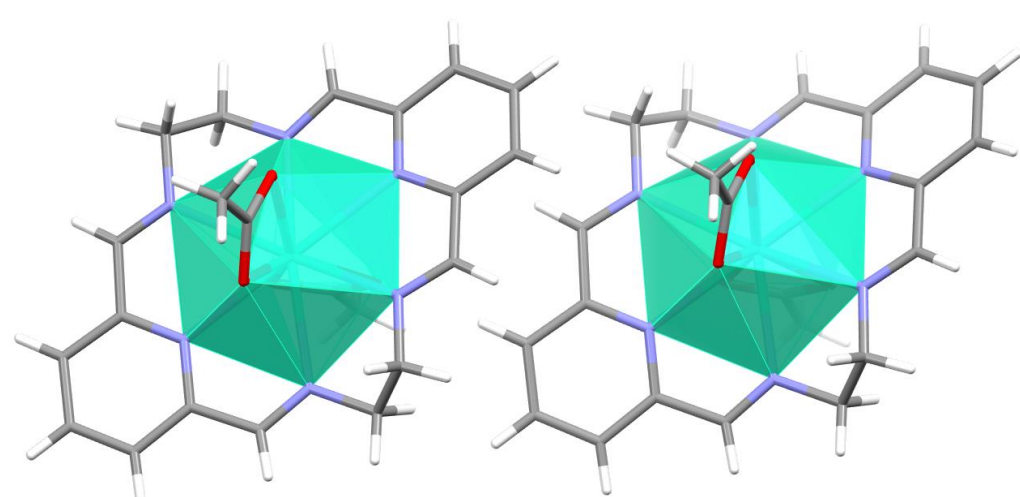


Figure 2. Different cationic units found in **2** showing their coordination polyhedra.

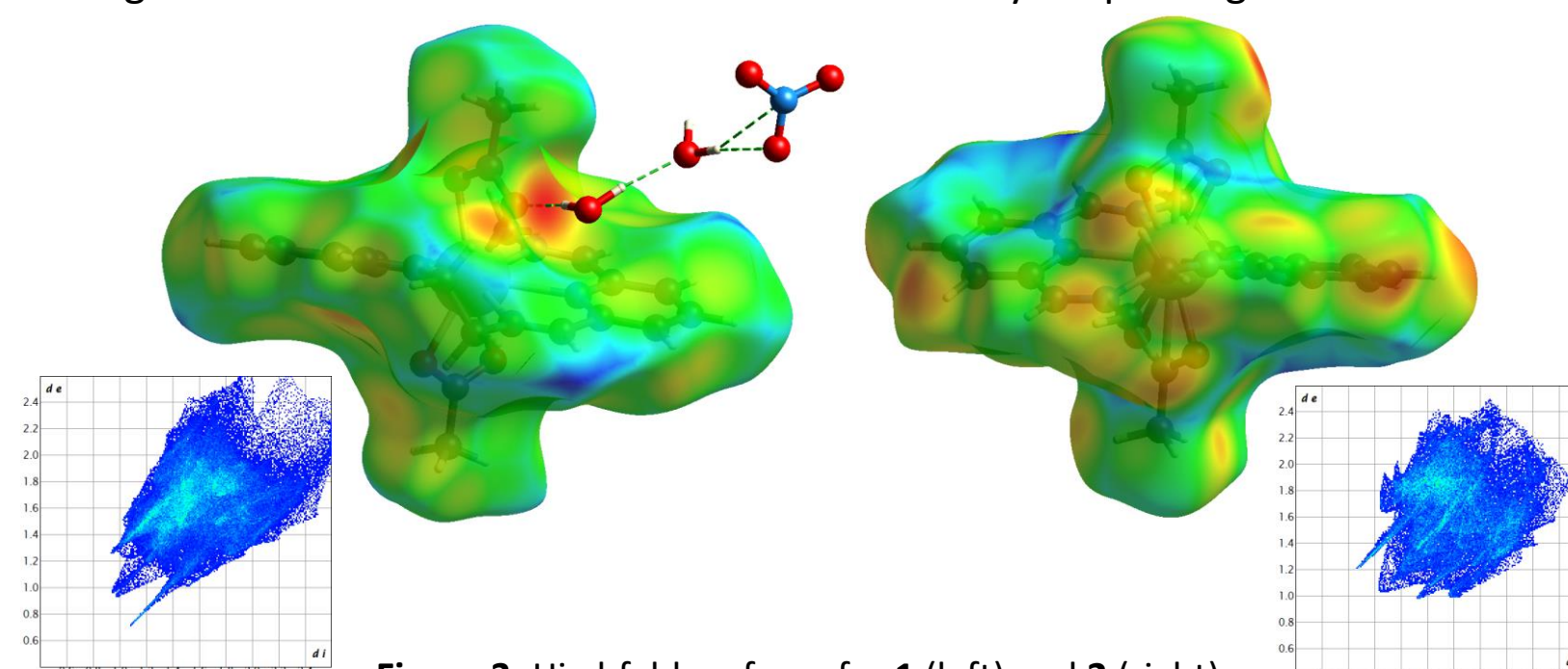


Figure 3. Hirshfeld surfaces for **1** (left) and **2** (right).

## CONCLUSION

The presence of such a polar counterion as nitrate in **1** allows the connection of one of its acetate ligand by classic H bonds through two neighboring water molecules. In contrast, the hydrophobic counterion of **2** is contacting with the cationic complex  $[\text{Dy}(\text{L})(\text{CH}_3\text{COO})_2]^+$  by means of C-H $\cdots\pi$  interactions.

## REFERENCES

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- 2 M. Llunell, D. Casanova, J. Cirera, J. M. Bofill, P. Alemany, S. Álvarez, M. Pinsky, D. D. Avnir, SHAPE v1.1b, Barcelona, 2005.