



New salen-type dysprosium(III) double-decker and triple-decker complexes



Yu-Ling Chien^a, Ming-Wen Chang^a, Yuan-Che Tsai^a, Gene-Hsian Lee^b, Wen-Shyan Sheu^{a,*}, En-Che Yang^{a,*}

^a Department of Chemistry, Fu Jen Catholic University, Hsinchuang, New Taipei City 24205, Taiwan, Republic of China

^b Instrumentation Centre, College of Science, National Taiwan University, Taipei 106, Taiwan, Republic of China

ARTICLE INFO

Article history:

Received 28 April 2015

Accepted 20 July 2015

Available online 26 July 2015

Keywords:

Dysprosium

Magnetic property

Slow magnetization relaxation

Double-decker

Triple-decker

ABSTRACT

We report on the synthesis of two dysprosium(III) containing complexes with double-decker and triple-decker sandwich structures. These two complexes have formulae $(\text{NMe}_4)[\text{Dy}(\text{dsp})_2]$ (**1**) and $[\text{Dy}_2(\text{dsp})_3(\text{EtOH})]$ (**2**), where H_2dsp is a salen type ligand. Both compounds were characterized by X-ray structural analysis, UV–Vis, IR spectral and magnetic studies. Complex **1** crystallized in the space group $Pna2_1$. This X-ray structural data provides the first example of the structure of $[\text{Ln}(\text{dsp})_2]^-$. Compound **2** crystallized in a triclinic space group $P\bar{1}$. In both cases, two similar but symmetry-independent molecules are present. The UV–Vis spectra of the complexes indicate that they are ligand-based $\pi-\pi^*$ transitions, which was further supported by DFT calculations. Both compounds display field-induced out-of-phase signals. In particular, step-wise slow magnetization relaxation processes are observed in the case of complex **2**. This indicates that compound **1** and **2** undergo slow magnetization relaxation when a small dc magnetic field is applied.

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1. Introduction

In the past two decades, the research dealing with molecules that show slow magnetization relaxation characteristics have become of great interesting because they possess the potential to be a single-molecule magnet (SMM). Owing to the fact that their size is at the molecule level, SMMs represent good candidates for observations of various physical phenomena and form the basis of many potential scientific applications, such as quantum computing [1–7] and spintronics [8–12]. Although research on SMMs started in the early 1990's [13,14], lanthanide containing SMMs were not discovered until 2003 [15–20]. Ishikawa and coworkers reported on the first sandwich form of a mononuclear complex with two phthalocyaninato groups acting as double-decker ligands. Among such complexes, a terbium compound showed out-of-phase signals at around 40 K. Since then, many efforts have been made to prepare double-decker or triple-decker phthalocyaninato sandwich complexes of lanthanides [21–24]. These complexes soon became subject of great interest in the field of SMMs. In exploring relevant double-decker and triple-decker

complexes, the salen-type ligand H_2dsp , attracted our eyes as well. The synthesis of complexes $[\text{Ln}_2(\text{dsp})_3(\text{Sol})]$ (Sol is the coordinate solvent molecule) can be traced back to the year 1968 [25]. Both $[\text{Ln}(\text{dsp})_2]^-$ and $[\text{Ln}_2(\text{dsp})_3(\text{Sol})]$ were spectrally characterized in 1994 [26]. However, the X-ray crystallographic data for $[\text{Ln}_2(\text{dsp})_3(\text{EtOH})]$ as well as other analogues did not appear until 2012 [27]. In the meantime, in a survey of the literature, no X-ray data was found to be available for $[\text{Ln}(\text{dsp})_2]^-$. Herein, we wish to report on the structure of $[\text{Dy}(\text{dsp})_2]^-$. In the interim time, Magadur and co-workers first combined three-decker complexes $[\text{Ln}_2(\text{dsp})_3(\text{EtOH})]$ with single walled carbon nanotubes (SWNT) [27–31] to produce Carbon Nanotube Field Effect Transistors (CNFET) [27,32–35]. This work demonstrated that $[\text{Ln}_2(\text{dsp})_3(\text{EtOH})]$ possesses the potential for applications to molecular electronic devices. In addition, the H_2dsp ligand was recently used to incorporate Dy^{III} ions to form a trinuclear triple-decker structure [36], or to combine $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{P}(\text{O})(\text{OEt})_3)]^-$ and TTF (tetra-thiafulvalene) fragments all in one mono-nuclear Dy^{III} complex [37]. Both of these molecules exhibit slow magnetization relaxation. Although with such a long history and so much progress, there continue to be many new opportunities for studies of $[\text{Ln}_2(\text{dsp})_3(\text{EtOH})]$ and $[\text{Ln}(\text{dsp})_2]^-$. It is noteworthy that structural data for $[\text{Ln}(\text{dsp})_2]^-$ is still not available and that no structural information regarding $[\text{Dy}_2(\text{dsp})_3(\text{EtOH})]$ is currently available.

* Corresponding authors.

E-mail addresses: 034793@mail.fju.edu.tw (W.-S. Sheu), 071549@mail.fju.edu.tw (E.-C. Yang).

Second, the complexes $[\text{Ln}_2(\text{dsp})_3(\text{Sol})]$ and $[\text{Ln}(\text{dsp})_2]^-$ have no slow magnetization relaxation phenomenon been reported. Thirdly, based on UV–Vis spectra for both compounds, they were assigned as ligand-based, but no MO calculations have appeared in support of the peak assignments. In the current paper, we report on the synthesis, X-ray structural data, UV–Vis with DFT calculations on the free ligand, and the magnetic properties of $[\text{Dy}_2(\text{dsp})_3(\text{EtOH})]$ and $[\text{Dy}(\text{dsp})_2]^-$.

In the current paper, we report X-ray structural data for both double-decker and triple-decker complexes, in which compound **1** represents the first reports of a double decker $[\text{Ln}(\text{dsp})_2]^-$. IR spectra for compounds **1**, **2** and the ligand confirmed the structural assignment. We also characterizes the UV–Vis spectra by DFT calculations. Finally, although applications of some analogous complexes have been reported for use in molecular electronic devices, the studies of their magnetic properties are still quite scarce. We also conducted measurements of both the d.c. and a.c. magnetic properties of compounds **1** and **2**, which led additional possible applications for these molecules.

2. Results and discussion

2.1. Synthesis and structures

As of this writing, no X-ray structural data has been reported for any $[\text{Ln}(\text{dsp})_2]^-$ complex. To facilitate the crystallization, we switched the counter ions from alkali metal ions to the tetramethylammonium ion, which leads to the formation of yellow crystals of $(\text{NMe}_4)[\text{Dy}(\text{dsp})_2]$ (**1**). Crystallographic parameters for compounds **1** are given in Table 1. Compound **1** crystallized in an orthorhombic space group $Pna2_1$. There are two crystallographically independent $(\text{NMe}_4)[\text{Dy}(\text{dsp})_2]$ units in the lattice. Since the differences between these two molecules are quite limited, we arbitrarily choose one to discuss here for purposes of illustration. The ORTEP plot for complex **1** is given in Fig. 1 which shows a double decker mononuclear sandwich structure. The charge on the dysprosium unit is +3. The two phenol groups on each ligand were deprotonated so that each carried a charge of -2 . The central

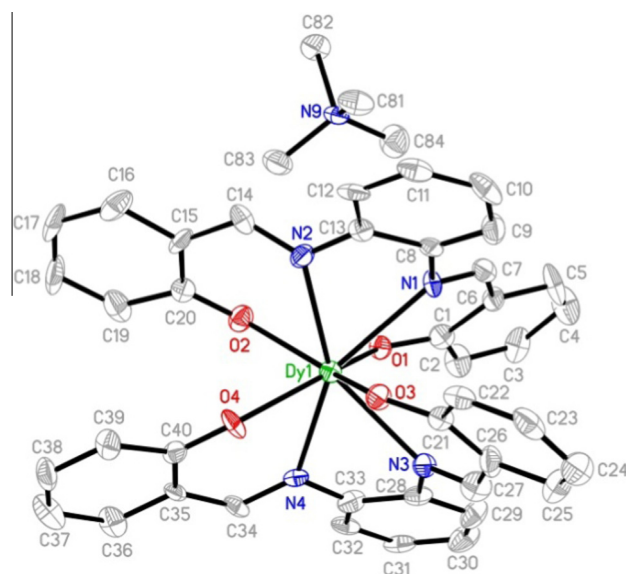


Fig. 1. ORTEP plot showing complex **1** $(\text{NMe}_4)[\text{Dy}(\text{dsp})_2]$. Hydrogen atoms are omitted for clarity. Dy, green; O, red; N, blue; C, gray. (Colour online.)

Dy^{3+} ion is eight-coordinated and is bound to two N_2O_2 units from the two ligands under and above the Dy^{3+} center. The Dy–O bond distances are in the range of 2.239–2.282 Å and for Dy–N, they are about 2.542–2.576 Å. More detailed information on the metal–ligand bond lengths and angles are given in Table 2. Although the dsp^{2-} ligands are quite distorted, the N_2O_2 units from each ligand are arranged quite close to a square plane. The four edges of each of the N_2O_2 units are in the range of 2.67–2.93 Å and the deviations of the N or O atoms from the least-square average plane are all below 0.074 Å. As shown in Fig. 2(a), the two N_2O_2 unit squares are twisted by 44.7° away from each other, which is quite close to the ideal value of 45°. Therefore, it is quite reasonable to roughly describe the geometry of the metal core as square-antiprismatic [38]. The two dsp^{2-} ligands are distorted away from a planar geometry in different ways. In the one on the top, the two phenol planes are tilted away from the central diimine plane with angles of 7.7° and 22.4°. The angles for the bottom unit are 17.8° and 23.4°. A detailed plot that shows dsp^{2-} ligands distortion can be found in Fig. 1S.

Since there were no X-ray structural data available for double-decker $[\text{Ln}(\text{dsp})_2]^-$ complex, chemists have used $[\text{Ce}(\text{dsp})_2]$ as a

Table 1
Crystallographic parameters for compounds **1** and **2**.

	1	2
Formula	$\text{C}_{88}\text{H}_{80}\text{Dy}_2\text{N}_{10}\text{O}_8$	$\text{C}_{136}\text{H}_{120}\text{Dy}_4\text{N}_{12}\text{O}_{17}$
Formula weight	1730.62	2844.44
<i>T</i> (K)	150(2)	150(2)
Crystal system	orthorhombic	triclinic
Space group	$Pna2_1$	$P\bar{1}$
<i>a</i> (Å)	18.0725(3)	13.6346(3)
<i>b</i> (Å)	17.2140(3)	19.0288(5)
<i>c</i> (Å)	24.0488(4)	25.2585(5)
<i>a</i> (°)	90	68.6099(12)
<i>b</i> (°)	90	77.9763(15)
<i>g</i> (°)	90	72.4353(10)
<i>V</i> (Å ³)	7481.6(2)	5781.7(2)
<i>Z</i>	4	2
ρ (g cm ⁻³)	1.536	1.634
μ (mm ⁻¹)	2.049	2.63
<i>F</i> (000)	3496	2840
Reflections collected	39112	50426
Independent reflections R_{int}	16905 (0.0922)	20194 (0.1059)
Maximum and minimum transmission	0.926 and 0.776	0.925 and 0.836
Data/restraints/parameters	16905/13/981	20194/61/1498
Goodness-of-fit (GOF) on F^2	1.01	1.028
Final <i>R</i> indices	$R_1 = 0.0563$	$R_1 = 0.0561$
$[I > 2\sigma(I)]$	$wR_2 = 0.1186$	$wR_2 = 0.1039$
<i>R</i> indices (all data)	$R_1 = 0.1326$	$R_1 = 0.1569$
	$wR_2 = 0.1533$	$wR_2 = 0.1479$

Table 2
Selected metal–ligand bond lengths and metal centered bond angles for compound **1**.

Dy(1)–O(3)	2.282(8)	Dy(1)–N(4)	2.542(10)
Dy(1)–O(2)	2.239(7)	Dy(1)–N(3)	2.552(10)
Dy(1)–O(1)	2.255(9)	Dy(1)–N(2)	2.573(10)
Dy(1)–O(4)	2.280(8)	Dy(1)–N(1)	2.576(10)
O(3)–Dy(1)–O(2)	143.4(3)	N(4)Dy(1)–N(3)	63.5(3)
O(3)–Dy(1)–O(1)	131.2(3)	O(3)–Dy(1)–N(2)	78.6(3)
O(2)–Dy(1)–O(1)	80.7(3)	O(2)–Dy(1)–N(2)	71.9(3)
O(3)–Dy(1)–O(4)	80.4(3)	O(1)–Dy(1)–N(2)	110.9(3)
O(2)–Dy(1)–O(4)	77.7(3)	O(4)–Dy(1)–N(2)	88.5(3)
O(1)–Dy(1)–O(4)	144.6(3)	N(4)–Dy(1)–N(2)	153.0(3)
O(3)–Dy(1)–N(4)	114.0(3)	N(3)–Dy(1)–N(2)	142.3(3)
O(2)–Dy(1)–N(4)	86.1(3)	O(3)–Dy(1)–N(1)	73.4(3)
O(1)–Dy(1)–N(4)	79.7(3)	O(2)–Dy(1)–N(1)	109.9(3)
O(4)–Dy(1)–N(4)	71.3(3)	O(1)–Dy(1)–N(1)	70.4(3)
O(3)–Dy(1)–N(3)	71.6(3)	O(4)–Dy(1)–N(1)	143.9(3)
O(2)–Dy(1)–N(3)	143.6(3)	N(4)–Dy(1)–N(1)	142.5(3)
O(1)–Dy(1)–N(3)	74.8(3)	N(3)–Dy(1)–N(1)	86.8(3)
O(4)–Dy(1)–N(3)	108.1(3)	N(2)–Dy(1)–N(1)	62.5(3)

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