



## Hexanuclear zinc(II) carboxylate complexes from the use of pyridine-2,6-dimethanol: Synthetic, structural and photoluminescence studies

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### ABSTRACT

The employment of pyridine-2,6-dimethanol (pdmH<sub>2</sub>) in zinc(II) carboxylate chemistry is reported. The syntheses, crystal structures, and spectroscopic characterization are described for the structurally similar cluster compounds [Zn<sub>6</sub>(OH)<sub>2</sub>(O<sub>2</sub>CR)<sub>8</sub>(pdmH)<sub>2</sub>] (R = Ph (**1**); Bu<sup>t</sup> (**2**)), obtained in very good yields by the reactions between Zn(O<sub>2</sub>CR)<sub>2</sub>·2H<sub>2</sub>O (R = Ph, Bu<sup>t</sup>) and pdmH<sub>2</sub> in a 3:1 molar ratio in MeOH or MeCN solvent media, respectively. The [Zn<sub>6</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OR)<sub>2</sub>]<sup>8+</sup> core of both clusters can be conveniently described as four edge-sharing triangles (RO<sup>-</sup> = pdmH<sup>-</sup>). The three crystallographically unique metal ions in both **1** and **2** are found in three different coordination environments (4-, 5- and 6-coordinate), within the same molecule, a very rare case in hexanuclear Zn(II) cluster chemistry. The benzoate-analogue Zn<sup>II</sup><sub>6</sub> (**1**) displays photoluminescence with a maximum at 404 nm, upon maximum excitation at 337 nm, whereas the pivalate-analogue Zn<sup>II</sup><sub>6</sub> (**2**) shows a non-emissive character; the origin of the photoluminescence is discussed.

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### 1. Introduction

There are no more than two decades or so since the interest in polynuclear 3d-metal complexes (clusters [1]) at moderate oxidation states has provided a new inspiration of many research groups worldwide [2]; it should be mentioned that fascination with such species has existed since the Werner time. The current interest is mainly due to the fact that 3d-metal clusters with primarily O- and/or N-based ligands could provide invaluable opportunities for crossing boundaries both inside and between the fields of chemistry, physics, biology, medicine and materials science. For synthetic inorganic chemists, the current intense interest is mainly focused on (i) the preparation of high-nuclearity 3d-metal complexes with aesthetically pleasing structures and unprecedented metal topologies [3], (ii) the search for various nuclearity oxide-bridged metal clusters to model M<sub>x</sub> sites in biomolecules [4], and (iii) the discovery of compounds with interesting magnetic and

optical properties, such as single-molecule magnetism (SMM) and photoluminescence behaviors, respectively [5].

In contrast to the paramagnetic 3d-metal ions, the chemistry of diamagnetic Zn<sup>II</sup> clusters has been far less developed. Polynuclear Zn<sup>II</sup> complexes are being studied as polymerization catalysts, reagents in organic synthesis, precursors to ZnO-based materials, models of active sites in zinc enzymes and molecular materials with interesting optical properties [6]. The synthetic methodology [7] and the nature of the organic ligands employed [8–13] are undoubtedly key issues for the preparation of such complexes. There are now several empirically established approaches to a variety of clusters with different nuclearities and structural architectures. In the chemistry of most 3d metal ions, for example, alcoholysis has proven to be a very useful method for obtaining oxido-, and hydroxido- or alkoxido-containing complexes [3a,14]. Another fertile approach is the investigation of new reaction systems using appropriate chelating/bridging organic ligands, such as those containing alkoxide [7b] or oximate [8] functionalities since these are excellent bridging groups that can foster formation of polynuclear products. Indeed, alkoxide-based ligands such as pyridyl alcohols [9], diols [10] and triols [11], and oximates such as 2-pyridyl oximes [12], R-substituted salicylaldoximes [5d] and

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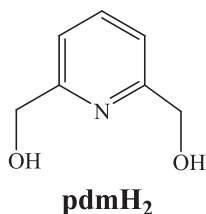


Fig. 1. Structural formula and abbreviation of pyridine-2,6-dimethanol.

dioximes [13], have yielded a number of 3d metal clusters with various structural motifs and interesting physical properties.

A modern synthetic trend is the employment of two or even three ligands in the reaction systems (combination of ligands or “ligand blends”). The loss of a degree of the synthetic control [7] is more than compensated for by the vast diversity of structural types using the combination of ligands. Carboxylates  $\text{RCO}_2^-$  are excellent ancillary terminal or/and bridging groups in 3d-metal chemistry when they are combined with suitable organic ligands (generally denoted as “L”) [15]. The versatility of the  $\text{RCO}_2^-$  ligands is reflected in the variety of metal binding modes they can adopt; up to four transition metal ions have been shown to bind to a single carboxylate ligand. In contrast to the extensive number of studies concerning  $3d^n$ ,  $4d^n$ ,  $5d^n$  ( $n = 1-9$ ) and 4f-metal carboxylate cluster chemistry, normally associated with other organic coligands, relatively little is known about the group 12 metal discrete carboxylate complexes. The current interest in studying new mono-, di- and polynuclear  $\text{Zn}^{\text{II}}$  carboxylate complexes has three main driving forces: (i) the desire to recreate with synthetic models the structure, properties, reactivity and/or function of the mononuclear and dinuclear active sites in  $\text{Zn}^{\text{II}}$  metalloenzymes [4b,16]; (ii) the realization that some  $\text{Zn}^{\text{II}}$  carboxylate complexes based on aromatic ligands are luminescent [17], and; (iii) the fact that some  $\text{Zn}^{\text{II}}$  carboxylates are active catalysts for the coupling of  $\text{CO}_2$  and epoxides [18]. Thus, we have been exploring various such binary (i.e.,  $\text{L}/\text{RCO}_2^-$ ) reaction schemes as potentially new routes to molecular species with unprecedented structural motifs and exciting magnetic and/or optical properties.

As far as the nature of L is concerned, our group and others have had a longstanding interest in the reactivity of pyridyl alcohol ligands for the synthesis of polynuclear 3d-metal complexes [9]. In particular, some of our current efforts are focused on the synthesis, structural and spectroscopic characterization of new polynuclear  $\text{Zn}^{\text{II}}$  carboxylate complexes using the pyridyl alkoxide ligand pyridine-2,6-dimethanol ( $\text{pdmH}_2$ , Fig. 1). Despite its rather extensive use in trivalent 3d-metal cluster chemistry (see Section 3), there has been only very limited use of  $\text{pdmH}_2$  in divalent 3d-metal chemistry, and only a tetranuclear [19] and few mononuclear [19,20]  $\text{Zn}^{\text{II}}$  complexes have been reported so far.

In the present work, we report the synthesis, structural and spectroscopic characterization of two new, structurally similar hexanuclear  $\text{Zn}(\text{II})$  complexes bearing carboxylate (benzoate or pivalate) ligands and the monoanionic form ( $\text{pdmH}^-$ ) of pyridine-2,6-dimethanol. Interestingly, only the benzoate-analogue exhibits photoluminescence behavior as a result of a carboxylate-to-metal charge transfer mechanism introduced by the aromatic phenyl groups.

## 2. Experimental

### 2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.  $\text{Zn}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Zn}(\text{O}_2\text{CBu}^t)_2 \cdot 2\text{H}_2\text{O}$  were prepared as white

microcrystalline solids in high yields by the 1:2 reaction of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and the corresponding  $\text{NaO}_2\text{CR}$  ( $\text{R} = \text{Ph}$  or  $\text{Bu}^t$ ) salt in  $\text{H}_2\text{O}$ . The microcrystalline solids were collected by filtration, washed with cold  $\text{H}_2\text{O}$  ( $2 \times 5$  mL), and dried under vacuum. Typical yields were in the 85–90% range. The metal carboxylate starting materials were characterized by microanalysis, thermogravimetry/differential thermogravimetry (TG/DTG) and IR spectroscopy. In more detail: *Anal. Calc.* for  $\text{Zn}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ : C, 48.93; H, 4.11. Found: C, 49.05; H, 4.23%. *Anal. Calc.* for  $\text{Zn}(\text{O}_2\text{CBu}^t)_2 \cdot 2\text{H}_2\text{O}$ : C, 39.55; H, 7.30. Found: C, 39.45; H, 7.19%.

Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Patras (Greece) using an EA 1108 Carlo Erba analyser. IR spectra ( $4000-400$   $\text{cm}^{-1}$ ) were recorded on a Perkin-Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. Emission and excitation spectra were recorded in the solid state using a Cary Eclipse spectrofluorometer.

### 2.2. Compound preparation

#### 2.2.1. $[\text{Zn}_6(\text{OH})_2(\text{O}_2\text{CPh})_8(\text{pdmH})_2] \cdot 3.05\text{MeOH} \cdot 0.5\text{H}_2\text{O}$ (**1**·3.05MeOH·0.5H<sub>2</sub>O)

To a colorless solution of  $\text{Zn}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$  (0.51 g, 1.50 mmol) in MeOH (20 mL) was slowly added a solution of  $\text{pdmH}_2$  (0.07 g, 0.50 mmol) in the same solvent (10 mL). The resulting colorless solution was kept under stirring at room temperature for about 40 min, filtered, and the filtrate was layered with  $\text{Et}_2\text{O}$  (60 mL). Slow mixing gave after 2 days well-formed, X-ray quality colorless prismatic crystals of **1**·3.05MeOH·0.5H<sub>2</sub>O. The crystals were collected by filtration, washed with cold MeOH ( $2 \times 3$  mL) and  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL), and dried in air. Typical yields were in the 65–70% range. The air-dried solid was analyzed as solvent-free **1**. *Anal. Calc.* for  $\text{C}_{70}\text{H}_{58}\text{Zn}_6\text{N}_2\text{O}_{22}$ : C, 50.30; H, 3.50; N, 1.68. Found: C, 50.42; H, 3.58; N, 1.46%. IR data (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu = 3422\text{mb}$ ,  $3062\text{m}$ ,  $1612\text{vs}$ ,  $1572\text{vs}$ ,  $1538\text{vs}$ ,  $1492\text{m}$ ,  $1446\text{s}$ ,  $1400\text{vs}$ ,  $1361\text{s}$ ,  $1214\text{w}$ ,  $1174\text{m}$ ,  $1160\text{m}$ ,  $1096\text{w}$ ,  $1052\text{s}$ ,  $1026\text{m}$ ,  $1002\text{w}$ ,  $938\text{w}$ ,  $840\text{m}$ ,  $824\text{m}$ ,  $778\text{m}$ ,  $718\text{vs}$ ,  $682\text{s}$ ,  $628\text{m}$ ,  $584\text{w}$ ,  $470\text{m}$ ,  $436\text{m}$ ,  $408\text{m}$ .

#### 2.2.2. $[\text{Zn}_6(\text{OH})_2(\text{O}_2\text{CBu}^t)_8(\text{pdmH})_2] \cdot 4\text{MeCN}$ (**2**·4MeCN)

To a colorless suspension of  $\text{Zn}(\text{O}_2\text{CBu}^t)_2 \cdot 2\text{H}_2\text{O}$  (0.46 g, 1.50 mmol) in MeCN (20 mL) was slowly added a solution of  $\text{pdmH}_2$  (0.07 g, 0.50 mmol) in the same solvent (10 mL). The resulting white slurry was refluxed for 1 h, during which time all solid dissolved and the color of the solution turned to pale yellow. The latter solution was then allowed to slowly concentrate by solvent evaporation at room temperature for a period of 4–5 days. Well-formed colorless polyhedral crystals of **2**·4MeCN appeared that were collected by filtration, washed with cold MeCN ( $2 \times 3$  mL) and  $\text{Et}_2\text{O}$  ( $1 \times 2$  mL), and dried in air. Typical yields were in the 70–75% range. The air-dried solid was analyzed as solvent-free **2**. *Anal. Calc.* for  $\text{C}_{54}\text{H}_{90}\text{Zn}_6\text{N}_2\text{O}_{22}$ : C, 42.91; H, 6.00; N, 1.85. Found: C, 43.05; H, 6.13; N, 1.76%. IR data (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu = 3424\text{mb}$ ,  $2962\text{m}$ ,  $2930\text{m}$ ,  $2870\text{w}$ ,  $1598\text{vs}$ ,  $1562\text{vs}$ ,  $1484\text{vs}$ ,  $1458\text{m}$ ,  $1422\text{vs}$ ,  $1376\text{m}$ ,  $1360\text{s}$ ,  $1228\text{m}$ ,  $1162\text{w}$ ,  $1096\text{w}$ ,  $1054\text{m}$ ,  $896\text{w}$ ,  $792\text{m}$ ,  $614\text{m}$ ,  $566\text{w}$ ,  $500\text{w}$ ,  $430\text{m}$ .

### 2.3. Single-crystal X-ray crystallography

The crystallographic data and structure refinement details for the two complexes are summarized in Table 1. A selected crystal of **1**·3.05MeOH·0.5H<sub>2</sub>O ( $0.20 \times 0.30 \times 0.50$  mm) was mounted in capillary filled with drops of mother liquor, whereas a selected crystal of **2**·4MeCN ( $0.14 \times 0.07 \times 0.05$  mm) was mounted in air. Diffraction measurements for complexes **1**·3.05MeOH·0.5H<sub>2</sub>O and **2**·4MeCN were performed on a Crystal Logic Dual Goniometer diffractometer and an Oxford Diffraction Supernova diffractometer (equipped with a Sapphire CCD area detector), respectively, using

**Table 1**  
Crystallographic data for complexes **1**:3.05MeOH·0.5H<sub>2</sub>O and **2**:4MeCN.

Parameter	1·3.05MeOH·0.5H <sub>2</sub> O	2·4MeCN
Empirical formula <sup>a</sup>	C <sub>73.05</sub> H <sub>71.2</sub> Zn <sub>6</sub> N <sub>2</sub> O <sub>25.55</sub>	C <sub>62</sub> H <sub>102</sub> Zn <sub>6</sub> N <sub>6</sub> O <sub>22</sub>
<i>M</i> (g mol <sup>-1</sup> )	1778.14	1675.81
Crystal system	tetragonal	monoclinic
Space group	<i>I</i> 4 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions		
<i>a</i> (Å)	34.300(10)	12.1860(4)
<i>b</i> (Å)	34.300(10)	21.8055(8)
<i>c</i> (Å)	14.162(6)	14.9588(6)
$\alpha$ (°)	90	90
$\beta$ (°)	90	106.658(4)
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	16661(10)	3808.1(2)
<i>Z</i>	8	2
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.418	1.458
Radiation, $\lambda$ (Å)	Mo K $\alpha$ , 0.71073	Mo K $\alpha$ , 0.71073
<i>T</i> (K)	293(2)	100(2)
2 $\theta_{\text{max}}$ (°)	48.50	50.00
$\mu$ (mm <sup>-1</sup> )	1.772	1.931
<i>F</i> (000)	7263	1736
Total reflections	6586	21831
Unique reflections ( <i>R</i> <sub>int</sub> )	6352 (0.0335)	6696 (0.0389)
Data with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	4694	5349
Parameters refined	487	435
( $\Delta\rho$ ) <sub>max</sub> /( $\Delta\rho$ ) <sub>min</sub> (e Å <sup>-3</sup> )	0.847/−0.582	0.686/−0.317
Goodness-of-fit (GOF) (on <i>F</i> <sup>2</sup> )	1.069	1.013
<i>R</i> <sub>1</sub> , <sup>b</sup> <i>wR</i> <sub>2</sub> <sup>c</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0489, 0.1276	0.0290, 0.0738

<sup>a</sup> Including solvate molecules.

<sup>b</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum(|F_o|)$ .

<sup>c</sup>  $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$ .

graphite-monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11° < 2 $\theta$  < 23°. Intensity data were recorded using a  $\theta$ -2 $\theta$  scan to a maximum 2 $\theta$  value of 48.5° (for **1**:3.05MeOH·0.5H<sub>2</sub>O) and 50° (for **2**:4MeCN). Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and psi-scan absorption (for **1**:3.05MeOH·0.5H<sub>2</sub>O) corrections were applied using Crystal Logic software.

The structure of **1**:3.05MeOH·0.5H<sub>2</sub>O was solved by direct methods using SHELXS-97 [21a] and refined on *F*<sup>2</sup> by full-matrix least squares techniques with SHELXL-97 [21b]. All H atoms were either located by Fourier difference maps and refined isotropically or were introduced at calculated positions as riding on respective bonded atoms. All non-H atoms were refined anisotropically, except of the solvate molecules which were refined isotropically. The structure of **2**:4MeCN was solved by direct methods using SIR92 [22] and refined on *F*<sup>2</sup> by full-matrix least squares techniques with SHELXL-97 [21b]. The non-H atoms were treated anisotropically. All H atoms were placed in calculated, ideal positions and refined as riding on their respective bonded atoms. The programs used for **2**:4MeCN were CRYSLIS CCD [23] for data collection, CRYSLIS RED [23] for cell and data refinement, WINGX [24] for crystallographic calculations, and DIAMOND [25] for molecular graphics.

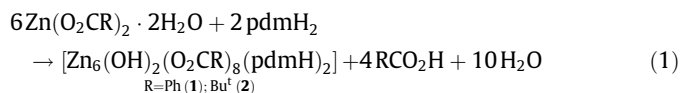
### 3. Results and discussion

#### 3.1. Synthetic comments and IR spectra

Many synthetic procedures [2,7,15] to polynuclear 3d-metal complexes rely on the reactions of metal carboxylate starting materials with a potentially chelating/bridging organic ligand. This route was also known from our previous work to yield structurally interesting Zn<sup>II</sup> complexes using several 2-pyridyl oxime ligands [(py)C(R)NOH; R = various] [26–30]. In the present study, we have instead investigated the reactions between the relatively

unexplored -in divalent transition metal cluster chemistry- pyridine-2,6-dimethanol (pdmH<sub>2</sub>) ligand and simple Zn<sup>II</sup> carboxylate sources.

Various reactions have been systematically explored with differing reagent ratios, reaction solvents, and other conditions. The reaction of Zn(O<sub>2</sub>CPh)<sub>2</sub>·2H<sub>2</sub>O with pdmH<sub>2</sub> in a 3:1 molar ratio in MeOH gave a colorless solution that, upon filtration and layering with Et<sub>2</sub>O, afforded well-formed colorless prismatic crystals of the complex [Zn<sub>6</sub>(OH)<sub>2</sub>(O<sub>2</sub>CPh)<sub>8</sub>(pdmH<sub>2</sub>)<sub>2</sub>].3.05MeOH·0.5H<sub>2</sub>O (**1**:3.05MeOH·0.5H<sub>2</sub>O) in very good yield (~70%). When the same reaction was repeated using Zn(O<sub>2</sub>CBu<sup>t</sup>)<sub>2</sub>·2H<sub>2</sub>O in place of Zn(O<sub>2</sub>CPh)<sub>2</sub>·2H<sub>2</sub>O, and solvent MeCN instead of MeOH, the yield of the corresponding pivalate version of **1**, i.e. the isolated complex [Zn<sub>6</sub>(OH)<sub>2</sub>(O<sub>2</sub>CBu<sup>t</sup>)<sub>8</sub>(pdmH<sub>2</sub>)<sub>2</sub>].4MeCN (**2**:4MeCN), increased slightly to ca. 75%. Note that for the synthesis of **2** were employed higher-temperature conditions (i.e. reflux) in order to enhance the solubility of the Zn(O<sub>2</sub>CBu<sup>t</sup>)<sub>2</sub>·2H<sub>2</sub>O starting material and thus lead the reaction to the product's formation. In case of non-refluxing conditions, complex **2** was also obtained, albeit in the much lower yield of 30–35%. The formation of complexes **1** and **2** is summarized in Eq. (1).



The known basic character of carboxylate ions and their dual role in the reaction mixtures as proton acceptors and versatile bridging groups, was established in both **1** and **2** by the single deprotonation of the pdmH<sup>-</sup> ligand and their bridging and monodentate coordination modes, respectively (*vide infra*). The carboxylate anions are also responsible for the Zn<sup>II</sup>-assisted deprotonation of the H<sub>2</sub>O molecules and the formation of OH<sup>-</sup> ions. Further increase in the Zn(O<sub>2</sub>CR)<sub>2</sub>·2H<sub>2</sub>O/pdmH<sub>2</sub> ratio to 4:1 (or 5:1) still gives complexes **1** and **2**, but in lower yields of 15–20% (depending on the R-group). Given the single-deprotonated form of pdmH<sup>-</sup> in **1** and **2**, we targeted its double deprotonation by reactions of pre-isolated **1** or **2** with 1–3 equivalents of base, either NEt<sub>3</sub> or NaOMe. Such reactions gave insoluble amorphous powders that perhaps were polymeric; these products were not further characterized.

Complexes **1** and **2** were also obtained when the corresponding reactions were performed in EtOH or MeNO<sub>2</sub>, but in much lower yields (~20–25%), whereas no significant reactions were observed when the solvent was CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. Finally, the presence/absence of countercations or anions, and the crystallization method (addition of a precipitation solvent or slow evaporation at room temperature) have no influence on the identity of the products. Thus, despite our efforts we could not obtain anionic or cationic complexes.

A characteristic feature in the IR spectra of dried **1** and **2** is the appearance of a medium to strong band at ~3422–3424 cm<sup>-1</sup> assignable [31] to  $\nu(\text{OH})$  of the hydroxido ligand and the hydroxyl group of pdmH<sup>-</sup>. The broadness and relatively low frequency of these bands are both indicative of strong hydrogen bonding (*vide infra*) [29]. Several bands appear in the ~1600–1360 cm<sup>-1</sup> range in the spectra of both **1** and **2**. These are assigned to contributions from the stretching vibrations of the aromatic rings, which overlap with stretches of the carboxylate bands; they, thus, do not represent pure vibrations and render exact assignments difficult [32]. In the case of the benzoate-analogue **1**, the  $\nu(\text{CO}_2)$  bands are difficult to assign due to the appearance of overlapping carboxylate, phenyl and pyridyl stretching vibrations in the 1600–1400 cm<sup>-1</sup> region, and thus the application of the spectroscopic criterion of Deacon and Phillips [33] is very difficult. In contrast, the strong bands at 1598 and 1422 cm<sup>-1</sup> in the spectrum of **2** can be assigned

to the  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  modes, respectively; the former should also involve a ring stretching character. The difference  $\Delta$  [ $\Delta = \nu_{as}(\text{CO}_2) - \nu_s(\text{CO}_2)$ ] is small ( $176 \text{ cm}^{-1}$ ), as expected for the predominant bidentate bridging mode of carboxylate ligation [33,34]. Note that in **2**, two of the carboxylate groups are monodentate (*vide infra*), expected to contribute to a larger  $\Delta$  value [29,33,34]. However, this was not the case, presumably due to the fact that the carboxylate oxygen atoms not coordinated to  $\text{Zn}^{\text{II}}$  (O6, O6' in Fig. 5, *vide infra*) are each hydrogen bonded to the neutral alkoxide arm of the  $\text{pdmH}^-$  groups, giving what be regarded as a “pseudobridging arrangement” [29,33].

### 3.2. Description of structures

A partially labeled representation and a stereoview of complex **1** are shown in Fig. 2. Selected interatomic distances and angles are listed in Table 2.

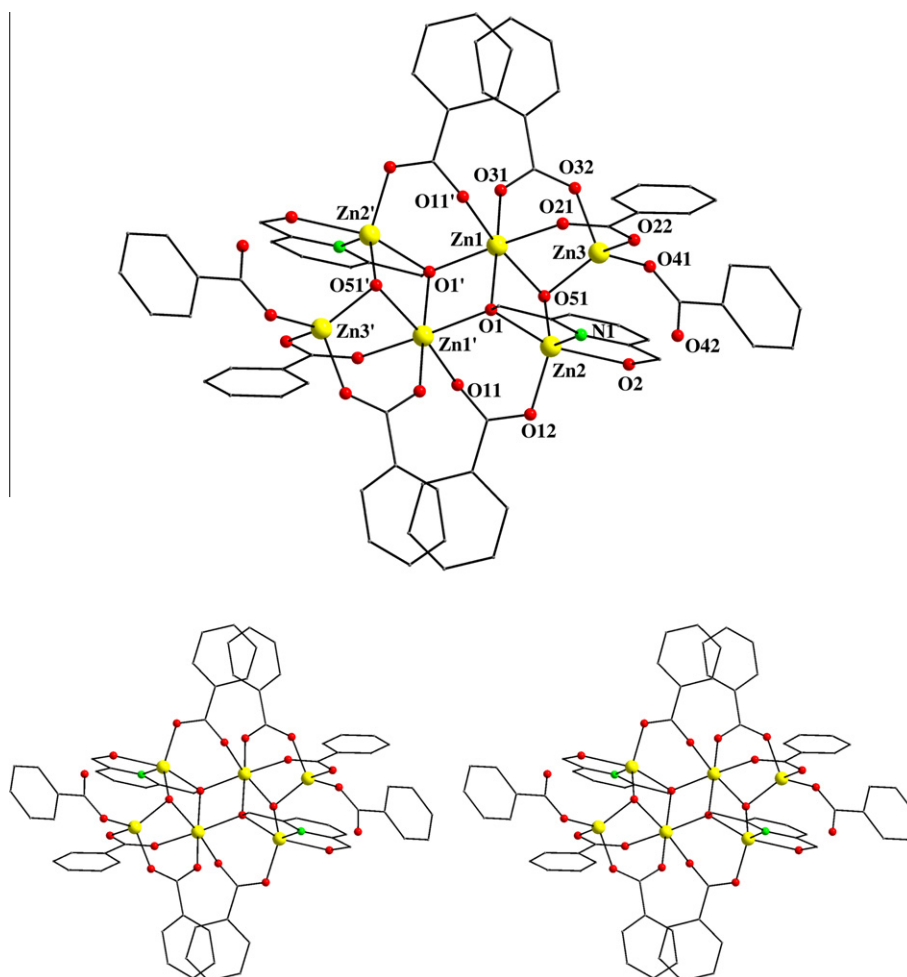
Complex **1**·3.05MeOH·0.5H<sub>2</sub>O crystallizes in the tetragonal space group  $I4_1/a$ ; the hexanuclear molecule possesses a crystallographic inversion center. Its structure consists of hexanuclear  $[\text{Zn}_6(\text{OH})_2(\text{O}_2\text{CPh})_8(\text{pdmH})_2]$  molecules and solvate MeOH and H<sub>2</sub>O molecules; the latter two will not be further discussed. The core of **1** consists of six  $\text{Zn}^{\text{II}}$  atoms arranged as four edge-sharing triangles (Fig. 3, top), the two extrinsic containing a central  $\mu_3\text{-OH}^-$  ion (O51, O51') and the two intrinsic containing a central  $\mu_3\text{-OR}^-$  group (O1, O1') each arising from a  $\text{pdmH}^-$  ligand; the complex thus contains an overall  $[\text{Zn}_6(\mu_3\text{-OH})_2(\mu_3\text{-OR})_2]^{8+}$  core

**Table 2**  
Interatomic distances (Å) and angles (°) for complex **1**·3.05MeOH·0.5H<sub>2</sub>O.<sup>a</sup>

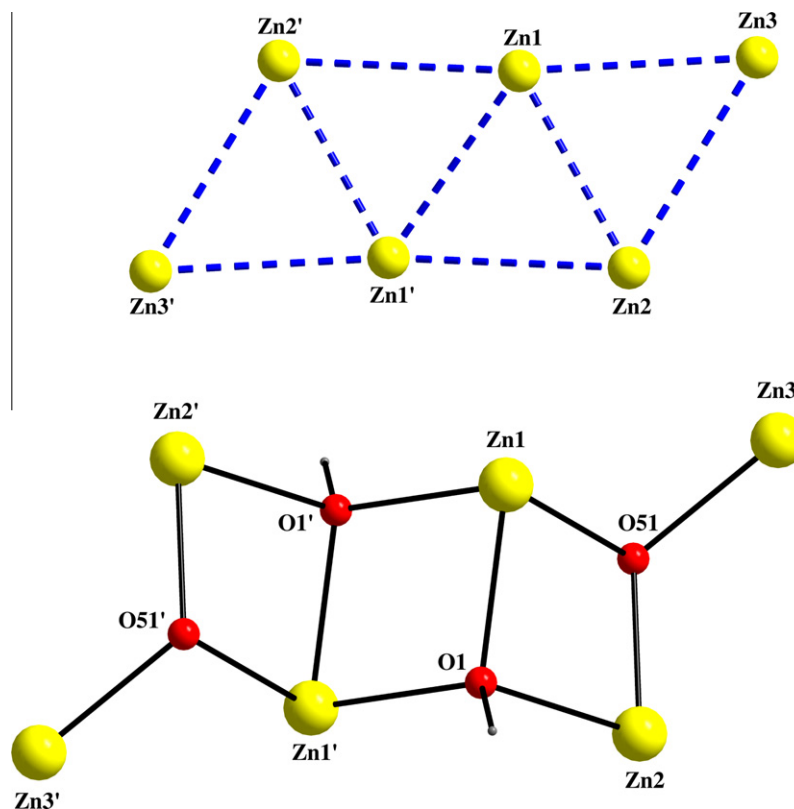
Bond lengths			
Zn(1)–Zn(1')	3.172(1)	Zn(1)–O(21)	2.102(4)
Zn(1)–Zn(2)	3.077(2)	Zn(1)–O(31)	2.038(4)
Zn(1)–Zn(2')	3.448(1)	Zn(1)–O(51)	2.218(4)
Zn(1)–Zn(3)	3.258(1)	Zn(2)–O(1)	2.134(3)
Zn(1)–Zn(3')	5.683(1)	Zn(2)–O(2)	2.172(4)
Zn(2)–Zn(2')	5.715(2)	Zn(2)–O(12)	1.949(4)
Zn(2)–Zn(3)	3.451(1)	Zn(2)–O(51)	1.969(4)
Zn(2)–Zn(3')	6.503(2)	Zn(2)–N(1)	2.015(4)
Zn(3)–Zn(3')	8.703(2)	Zn(3)–O(22)	1.968(4)
Zn(1)–O(1)	2.113(3)	Zn(3)–O(32)	1.959(4)
Zn(1)–O(1')	2.085(3)	Zn(3)–O(41)	1.928(5)
Zn(1)–O(11')	2.100(4)	Zn(3)–O(51)	1.955(4)
Bond angles			
Zn(1)–O(1)–Zn(1')	98.2(1)	O(1)–Zn(2)–O(2)	152.9(2)
Zn(1)–O(1)–Zn(2)	92.9(1)	O(51)–Zn(2)–N(1)	125.5(2)
Zn(1)–O(1')–Zn(2')	109.6(2)	O(22)–Zn(3)–O(32)	106.3(2)
Zn(1)–O(51)–Zn(2)	94.4(2)	O(22)–Zn(3)–O(41)	106.1(2)
Zn(1)–O(51)–Zn(3)	102.5(2)	O(22)–Zn(3)–O(51)	102.9(2)
Zn(2)–O(51)–Zn(3)	123.1(2)	O(32)–Zn(3)–O(41)	100.6(2)
O(1)–Zn(1)–O(31)	171.9(2)	O(32)–Zn(3)–O(51)	111.8(2)
O(1')–Zn(1)–O(21)	172.3(2)	O(41)–Zn(3)–O(51)	127.6(2)
O(11')–Zn(1)–O(51)	170.5(1)		

<sup>a</sup> Symmetry operation to generate equivalent atoms: (')  $1 - x, 1 - y, -z$ .

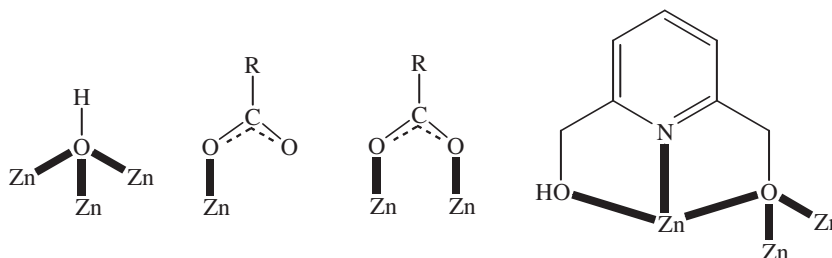
(Fig. 3, bottom). The Zn– $\mu_3\text{-OH}^-$ –Zn angles range from 94.4(2) to 123.1(2)°, thus giving a distorted pyramidal geometry for O1 and O1'. The six  $\text{Zn}^{\text{II}}$  atoms are additionally held together by six



**Fig. 2.** Partially labeled PovRay representation (top) and stereopair (bottom) of complex **1**, with H atoms omitted for clarity. Primes are used for symmetry-related atoms, see the footnote of Table 2. Color scheme: Zn<sup>II</sup>, yellow; O, red; N, green; C, gray. (Color online.)



**Fig. 3.** (top) The  $Zn_6$  topology of **1**, emphasizing the four-edge-sharing triangular description (blue dashed lines). (bottom) PovRay representation of the complete  $[Zn_6(\mu_3-OH)_2(\mu_3-OR)_2]^{8+}$  core of **1**. Color scheme: Color scheme:  $Zn^{II}$ , yellow; O, red; C, gray. (Color online.)



**Fig. 4.** The crystallographically established coordination modes of the inorganic and organic ligands in complexes **1** ( $R = Ph$ ) and **2** ( $R = Bu^t$ ).

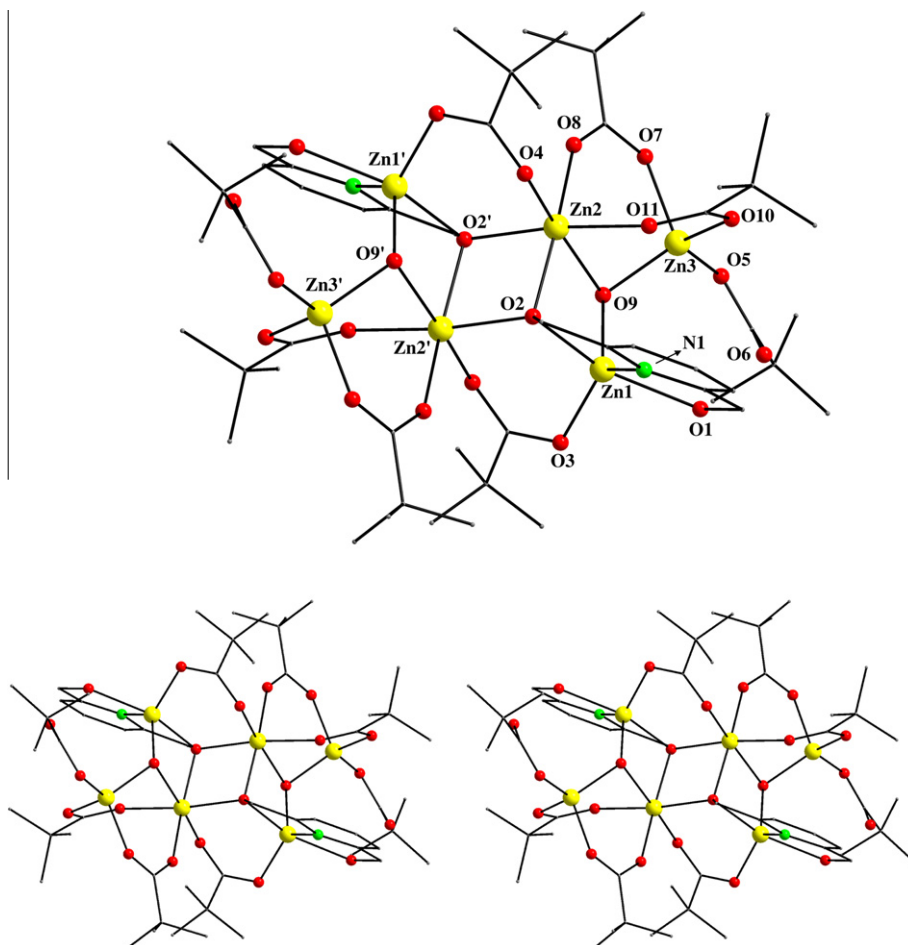
$\eta^1:\eta^1:\mu$   $PhCO_2^-$  groups. The  $pdmH^-$  ligands are  $\eta^1:\eta^1:\eta^3:\mu_3$ . Two monodentate benzoate ligands complete the coordination spheres of  $Zn3$  and  $Zn3'$ . The coordination modes of the three ligands that are present in **1** are depicted in Fig. 4.

$Zn1$  and  $Zn1'$  are six-coordinate with a distorted octahedral geometry, whereas  $Zn2$  and  $Zn2'$  are five-coordinate; analysis of the shape determining angles [35] yields a value for the trigonality index,  $\tau$ , of 0.46, indicating that the geometry about  $Zn2$  and  $Zn2'$  is significantly distorted, intermediate between square pyramidal ( $sp$ ) and trigonal bipyramidal ( $tbp$ ). Finally,  $Zn3$  and  $Zn3'$  are four-coordinate with distorted tetrahedral geometry; the tetrahedrality calculated for these metal atoms gives an average dihedral angle of  $83.8^\circ$  (the tetrahedrality for a four-coordinate complex can be determined from the angle subtended by two planes, each encompassing the metal and two adjacent atoms; for strictly square planar complexes with  $D_{4h}$  symmetry, the tetrahedrality is  $0^\circ$ ; for tetrahedral complexes with  $D_{2d}$  symmetry, the tetrahedrality equals  $90^\circ$ ), supporting a distorted tetrahedral geometry for the  $ZnO_4$  coordination sphere [36]. Additionally, the  $O-Zn3(3')-O$  angles lie in the  $100.6$ – $127.6^\circ$  range, deviating from the  $109.5^\circ$  value of an ideal

tetrahedron. Note that the case of complex **1** (and **2**), where all three crystallographically unique metal ions coexist in three different coordination environments within the same molecular species, is very rare and has been observed only in few hexanuclear coordination clusters [37]. There is a range of  $Zn \dots Zn$  separations, depending on the nature of the bridges between the metal ions; the longest  $Zn \dots Zn$  separation is  $8.703(2) \text{ \AA}$  ( $Zn3 \dots Zn3'$ ).

There are two, symmetry-related, very strong intramolecular H bonds between the neutral  $-OH$  groups ( $O2, O2'$ ) of the  $pdmH^-$  ligands and the uncoordinated benzoate O atoms ( $O42, O42'$ ). The dimensions are:  $O(2) \dots O(42) 2.549(8) \text{ \AA}$ ,  $HO(2) \dots O(42) 1.773(7) \text{ \AA}$ ,  $O(2)-HO(2) \dots O(42) 170.4(7)^\circ$ . There are also two weak H bonds with the hydroxido oxygen ( $O51$  and its symmetry equivalent) as the donor and the lattice MeOH oxygen atom ( $O1M$  and its symmetry equivalent) as the acceptor, the  $O(51) \dots O(1M)$  distance being  $2.777(3) \text{ \AA}$ . The  $Zn_6$  molecules are well separated in the crystal, without evidences of significant intermolecular interactions or contacts.

A partially labeled representation and a stereoview of complex **2** are shown in Fig. 5. Selected interatomic distances and angles are



**Fig. 5.** Partially labeled PovRay representation (top) and stereopair (bottom) of complex **2**, with H atoms omitted for clarity. Primes are used for symmetry-related atoms, see the footnote of Table 3. Color scheme: Zn<sup>II</sup>, yellow; O, red; N, green; C, gray. (Color online.)

listed in Table 3. The structure of complex **2** is very similar to that of **1**, with the main differences being the pivalate vs benzoate identity of the carboxylate employed and the MeCN vs MeOH/H<sub>2</sub>O solvate molecules in the crystal lattice, both differences causing changes in the nature and strength of the hydrogen bonding interactions. Thus, the Zn<sup>II</sup> atoms are again six- (Zn2, Zn2'), five- (Zn1, Zn1') and four-coordinate (Zn3, Zn3') with distorted octahedral, intermediate between *sp* and *tbp* ( $\tau = 0.45$ ) and slightly distorted tetrahedral (the tetrahedrality is equal to 87.4°) geometries, respectively. Peripheral ligation about the central [Zn<sub>6</sub>( $\mu_3$ -OH)<sub>2</sub>( $\mu_3$ -OR)<sub>2</sub>]<sup>8+</sup> core in **2** is provided by a ligand set similar to that found in **1** (Fig. 4). Finally, there are again two, symmetry-related, strong intramolecular H bonds between the –OH groups (O1, O1') of the pdmH<sup>–</sup> ligands and the uncoordinated pivalate O atoms (O6, O6') with the donor-to-acceptor distance being 2.570(2) Å. The weak H bonds between the hydroxido oxygen (O9 and its symmetry equivalent) as the donor, are now including the lattice MeCN nitrogen atom (N3 and its symmetry equivalent) as the acceptor, with the O(9) ... N(3) distance being 3.050(3) Å, significantly larger than the corresponding contact in **1**.

Compounds **1** and **2** join a small family of non-organometallic Zn(II) clusters of nuclearity six with O- and N-based ligands possessing a cage-like metal topology [37,38]. Both complexes are the highest nuclearity Zn(II) species bearing any form (neutral, mono- or dianionic) of the ligand pyridine-2,6-dimethanol, while their [Zn<sub>6</sub>( $\mu_3$ -OH)<sub>2</sub>( $\mu_3$ -OR)<sub>2</sub>]<sup>8+</sup> core has never been reported so far in Zn(II) cluster chemistry. Further, the reported nuclearity is unprecedented in metal/pdmH<sub>2</sub> coordination chemistry, and we

have thus felt it timely to collect all the structurally characterized metal clusters (with nuclearity  $\geq 3$ ) of the pdmH<sub>2</sub>-based ligands in Table 4, together with the coordination modes of the latter groups, for conventional comparison. It is clear that the pdmH<sup>–</sup> and pdm<sup>2–</sup> groups exhibit a variety of bridging coordination modes favoring cluster formation.

**Table 3**  
Selected bond lengths (Å) and angles (°) for complex **2**·4MeCN.<sup>a</sup>

Bond lengths			
Zn(1)–O(1)	2.191(2)	Zn(2)–O(8)	2.029(2)
Zn(1)–O(2)	2.106(2)	Zn(2)–O(9)	2.244(2)
Zn(1)–O(3)	1.947(2)	Zn(2)–O(11)	2.095(2)
Zn(1)–O(9)	2.005(2)	Zn(3)–O(5)	1.946(2)
Zn(1)–N(1)	2.028(2)	Zn(3)–O(7)	1.993(2)
Zn(2)–O(2)	2.110(2)	Zn(3)–O(9)	1.963(2)
Zn(2)–O(2')	2.081(2)	Zn(3)–O(10)	1.949(2)
Zn(2)–O(4)	2.061(2)		
Bond angles			
Zn(1)–O(2)–Zn(2)	93.5 (7)	O(2')–Zn(2)–O(11)	173.6(7)
Zn(1)–O(2)–Zn(2')	109.9(7)	O(4)–Zn(2)–O(9)	168.9(7)
Zn(1)–O(9)–Zn(2)	92.4(6)	O(5)–Zn(3)–O(7)	101.7(7)
Zn(1)–O(9)–Zn(3)	128.5(9)	O(5)–Zn(3)–O(9)	115.1(7)
Zn(2)–O(2)–Zn(2')	97.8(7)	O(5)–Zn(3)–O(10)	117.5(8)
Zn(2)–O(9)–Zn(3)	101.5(7)	O(7)–Zn(3)–O(9)	108.9(8)
O(1)–Zn(1)–O(2)	153.6(6)	O(7)–Zn(3)–O(10)	102.5(8)
O(3)–Zn(1)–N(1)	126.8(8)	O(9)–Zn(3)–O(10)	109.5(7)
O(2)–Zn(2)–O(8)	173.4(7)		

<sup>a</sup> Symmetry operation to generate equivalent atoms: (') 1 – *x*, 2 – *y*, 2 – *z*.

**Table 4**Formulae and organic ligand's coordination modes for structurally characterized metal clusters of pdmH<sub>2</sub>, and its mono- and dianionic forms.

Complex <sup>a,b</sup>	Coordination modes	Refs.
[Mn <sup>II</sup> <sub>2</sub> Mn <sup>III</sup> <sub>2</sub> (O <sub>2</sub> CMe) <sub>2</sub> (pdmH) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	η <sup>1</sup> :η <sup>2</sup> :μ; η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[39]
{[Mn <sup>II</sup> <sub>2</sub> Mn <sup>III</sup> <sub>2</sub> (hmp) <sub>4</sub> (pdmH) <sub>2</sub> (N(CN) <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ] <sub>n</sub>	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[40]
[Mn <sup>II</sup> <sub>2</sub> Mn <sup>III</sup> <sub>2</sub> (N <sub>3</sub> ) <sub>4</sub> (teaH) <sub>2</sub> (pdmH) <sub>2</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[41]
[Mn <sup>II</sup> <sub>7</sub> Mn <sup>III</sup> <sub>2</sub> (O <sub>2</sub> CEt) <sub>12</sub> (pdm)(pdmH) <sub>2</sub> (L) <sub>2</sub> ]	η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub> ; η <sup>2</sup> :η <sup>1</sup> :η <sup>2</sup> :μ <sub>3</sub>	[42]
[Mn <sup>II</sup> <sub>4</sub> Mn <sup>III</sup> <sub>6</sub> O <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> (thme) <sub>4</sub> (pdmH) <sub>4</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[41]
[Mn <sup>II</sup> <sub>4</sub> Mn <sup>III</sup> <sub>7</sub> O <sub>2</sub> (OH) <sub>2</sub> (nmpd)(pdm) <sub>5</sub> (pdmH) <sub>5</sub> Cl <sub>6</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ; η <sup>2</sup> :η <sup>1</sup> :μ; η <sup>2</sup> :η <sup>1</sup> :η <sup>2</sup> :μ <sub>3</sub>	[43]
[Mn <sup>II</sup> <sub>6</sub> Mn <sup>III</sup> <sub>18</sub> Mn <sup>IV</sup> O <sub>18</sub> (OH) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> (pdm) <sub>6</sub> (pdmH) <sub>6</sub> Cl <sub>2</sub> ]	η <sup>3</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>5</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[44]
[Mn <sup>II</sup> <sub>6</sub> Mn <sup>III</sup> <sub>18</sub> Mn <sup>IV</sup> O <sub>18</sub> (OH)(OMe)(hmp) <sub>6</sub> (pdm) <sub>6</sub> (pdmH) <sub>6</sub> (N <sub>3</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>6</sub> ]	η <sup>3</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>5</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[45]
[Fe <sup>III</sup> <sub>8</sub> O <sub>3</sub> (OMe)(pdm) <sub>4</sub> (pdmH) <sub>4</sub> (MeOH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>5</sub>	η <sup>1</sup> :η <sup>3</sup> :η <sup>1</sup> :μ <sub>3</sub> ; η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[46]
[Fe <sup>III</sup> <sub>9</sub> O <sub>4</sub> (OH) <sub>2</sub> (O <sub>2</sub> CMe) <sub>10</sub> (pdm)(pdmH) <sub>4</sub> ](NO <sub>3</sub> ) <sub>4</sub>	η <sup>1</sup> :η <sup>2</sup> :μ; η <sup>2</sup> :η <sup>1</sup> :η <sup>2</sup> :μ <sub>3</sub>	[47]
[Fe <sup>III</sup> <sub>18</sub> O <sub>6</sub> (OH) <sub>8</sub> (pdm) <sub>10</sub> (pdmH) <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>10</sub>	η <sup>2</sup> :η <sup>1</sup> :η <sup>2</sup> :μ <sub>3</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[47]
[Fe <sup>III</sup> <sub>2</sub> Y <sub>2</sub> (pdmH) <sub>6</sub> Cl <sub>4</sub> Cl <sub>2</sub> ]	η <sup>1</sup> :η <sup>2</sup> :μ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[48]
[Fe <sup>III</sup> <sub>2</sub> Ho <sub>2</sub> (pdmH) <sub>6</sub> Cl <sub>4</sub> Cl <sub>2</sub> ]	η <sup>1</sup> :η <sup>2</sup> :μ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[48]
[Co <sup>II</sup> <sub>2</sub> Ln <sup>III</sup> <sub>2</sub> (O <sub>2</sub> CBu <sup>t</sup> ) <sub>6</sub> (pdmH) <sub>4</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub> ; η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[49]
[Ni <sup>II</sup> <sub>4</sub> (O <sub>2</sub> CMe) <sub>4</sub> (pdmH) <sub>4</sub> ]	η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[50]
[Ni <sup>II</sup> <sub>4</sub> (O <sub>2</sub> CMe) <sub>6</sub> (pdmH) <sub>2</sub> (EtOH) <sub>2</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[50]
[Cu <sup>II</sup> <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> (pdmH) <sub>4</sub> (H <sub>2</sub> O)(MeOH)](NO <sub>3</sub> ) <sub>2</sub>	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[32b]
[Cu <sup>II</sup> <sub>4</sub> (O <sub>2</sub> CMe) <sub>2</sub> (pdmH) <sub>4</sub> ](O <sub>2</sub> CMe) <sub>2</sub>	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[51]
[Cu <sup>II</sup> <sub>5</sub> (O <sub>2</sub> CMe) <sub>6</sub> (pdm) <sub>2</sub> ] <sub>n</sub>	η <sup>2</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>4</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[51]
{[Cu <sup>II</sup> <sub>3</sub> (O <sub>2</sub> CMe) <sub>2</sub> (pdm) <sub>2</sub> (MeOH) <sub>2</sub> ][Cu <sup>II</sup> <sub>4</sub> (O <sub>2</sub> CMe) <sub>2</sub> (pdmH) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub> ; η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[51]
[Zn <sup>II</sup> <sub>3</sub> (salphen) <sub>2</sub> (pdmH) <sub>2</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[52]
[Zn <sup>II</sup> <sub>4</sub> (O <sub>2</sub> CMe) <sub>4</sub> (pdmH) <sub>4</sub> ]	η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	[19]
[Zn <sup>II</sup> <sub>6</sub> (OH) <sub>2</sub> (O <sub>2</sub> CPh) <sub>8</sub> (pdmH) <sub>2</sub> ] ( <b>1</b> )	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	This work
[Zn <sup>II</sup> <sub>6</sub> (OH) <sub>2</sub> (O <sub>2</sub> CBu <sup>t</sup> ) <sub>8</sub> (pdmH) <sub>2</sub> ] ( <b>2</b> )	η <sup>1</sup> :η <sup>1</sup> :η <sup>3</sup> :μ <sub>3</sub>	This work
[Hg <sup>II</sup> <sub>3</sub> Cl <sub>5</sub> (pdmH)(pdmH <sub>2</sub> ) <sub>2</sub> ]	tridentate chelating	[53]
[Dy <sup>III</sup> <sub>4</sub> (O <sub>2</sub> CPh) <sub>2</sub> (pdm) <sub>4</sub> (pdmH) <sub>2</sub> (HO <sub>2</sub> CPh) <sub>4</sub> ]	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ	[54]
[Ln <sup>III</sup> <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> (pdmH) <sub>6</sub> (pdmH <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>4</sub>	η <sup>1</sup> :η <sup>1</sup> :η <sup>2</sup> :μ; tridentate chelating	[55]

<sup>a</sup> Solvate molecules have been omitted.<sup>b</sup> Abbreviations: hmpH = 2-(hydroxymethyl)pyridine; teaH<sub>3</sub> = triethanolamine; LH<sub>2</sub> = (6-hydroxymethylpyridin-2-yl)-(6-hydroxymethylpyridin-2-ylmethoxy)-methanol; thmeH<sub>3</sub> = 1,1,1-tris(hydroxymethyl)ethane; nmpdH<sub>2</sub> = 2-nitro-2-methyl-1,3-propanediol; Ln = Y, Gd, Tb, Ho, Dy; salphenH<sub>2</sub> = N,N'-disalicylidene-1,2-phenylenediamine.

### 3.3. Photoluminescence studies

The photoluminescence properties of solid complexes **1** and **2** were studied at room temperature. Work in the area of luminescent d<sup>10</sup> polynuclear metal complexes has been developing rapidly and gaining a lot of attention [56]. The free ligand pdmH<sub>2</sub> does not emit in the solid state or in solution. The Zn(O<sub>2</sub>CBu<sup>t</sup>)<sub>2</sub>·2H<sub>2</sub>O starting material is non-luminescent, whereas Zn(O<sub>2</sub>CPh)<sub>2</sub>·2H<sub>2</sub>O displays a weak emission with a maximum at 385 nm upon maximum excitation at 317 nm [27,29,30].

Upon maximum excitation at 337 nm, a solid sample of **1** displays room temperature photoluminescence with a maximum at 404 nm (Fig. 6). It is known that PhCO<sub>2</sub><sup>-</sup> displays a weak emission with a maximum at ~312 nm (close to the excitation wavelength of compound **1**) [29]. Thus, it seems that benzoates contribute significantly in the excitation of **1** with an energy transfer mechanism to the complex (antenna effect). The emission at 404 nm very likely arises from PhCO<sub>2</sub><sup>-</sup>-to-metal charge transfer [27,29,30,57,58]. Alternatively, the luminescence shown in **1** may generally result from ligand-based interactions, that are assisted by the presence of the Zn(II) ions. It is possible that the phenyl groups may interact in the excited states to become an “excimer” [59], or, more likely, phenyl and Zn(II)-bound pyridyl form an emissive “exciplex” [59] upon excitation, where a charge transfer occurs from the excited benzoate group to the LUMO of Zn(II)-bound pyridyl. “Excimer”-based sensors have often been used to probe host-guest interactions with anions and/or cations in organic solvent media [60]. A fluorescent chemosensor may exhibit “excimer” emission by two different mechanisms [61]. One results from π-π stacking of the aromatic rings from two different molecules resulting in a characteristic decrease of the “excimer” emission intensity with a concomitant increase of monomer emission intensity. The other mechanism is based on the interaction of an excited unit with a ground state unit. It appears that this is not the case for the isostructural, pivalate-rich/benzoate-free complex **2**, which does not

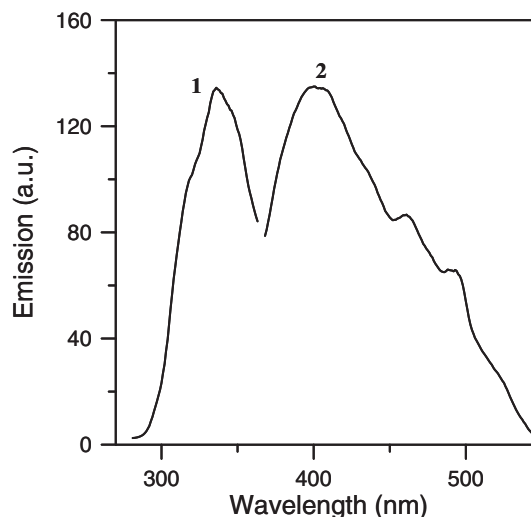


Fig. 6. Excitation (1) and emission (2) spectra of solid complex **1** at room temperature.

exhibit any fluorescence at room temperature. We tried to excite this compound in the whole region between 220 and 380 nm but no emission was detected. The absence of PhCO<sub>2</sub><sup>-</sup> ligands in **2** seems to be the dominant factor for the non-emissive character of the compound, and instead the key factor for the strong emission of **1**.

### 4. Conclusions and perspectives

The present work extends the body of results that emphasize the ability of pdmH<sub>2</sub> to form interesting structural

types in 3d-metal cluster chemistry. In addition to the recently reported  $[Zn_4(O_2CMe)_4(pdmH)_4]$  carboxylate-based complex [19], the  $Zn/RCO_2^-/pdmH_2$  ( $R = Ph, Bu^+$ ) reaction system has provided further access to the new hexanuclear compounds **1** and **2**, bearing the monoanionic  $pdmH^-$  ligand. The reported compounds clearly support the pronounced ability of the  $pdmH^-$  anion to stabilize high nuclearity molecular species when combined with various bulky (i.e. benzoates) or versatile (i.e. pivalates) carboxylate groups. The structurally similar  $Zn^II_6$  clusters **1** and **2** are novel in multiple ways, as described, but also provide (in case of **1**) a rare example of a photoluminescent  $Zn^II$  cluster. The detailed discussion let us believe that the presence of aromatic carboxylate ligands in  $Zn^II$  coordination chemistry is crucial, if not necessary, for the observation of photoluminescence, especially in complexes where the organic chelating/bridging ligand is unable to add to the observed emission.

We have no reason to believe that this research area is exhausted of new results. Indeed, ongoing studies are producing additional products with interesting structures and physical properties, and our belief is that we have scratched only the surface of  $Zn^II$  carboxylate cluster chemistry based on the anion(s) of pyridyl-2,6-dimethanol ligand. As far as future perspectives are concerned, it is currently not established whether the preparation and stability of such  $Zn^II_6$  clusters are dependent on the particular nature of the R-substituent on the carboxylate group, and we are currently investigating such reactions. Further, substitution of the benzoate groups in **1** by bulkier/aromatic carboxylates is also unexplored and we are pursuing this substitution in an effort to obtain deeper insights into the photoluminescence properties of **1** and related clusters. Finally, there are also magnetic implications of this work, even though  $Zn(II)$  is diamagnetic: extension to structurally similar  $M^II_6$  clusters for paramagnetic metals, such as  $Co(II)$ , might provide molecular species with relevance to the field of molecular magnetism.

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## Appendix A. Supplementary data

CCDC 886472 and 886473 contain the supplementary crystallographic data for **1**·3.05MeOH·0.5H<sub>2</sub>O and **2**·4MeCN, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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