

# A photochromic dinuclear compound: aquatetrakis( $\mu$ -2,3-diphenylprop-2-enoato)bis(2,3-diphenylprop-2-enoato)-ethanolbis(1,10-phenanthroline)-dilanthanum(III)

Yunyun Yang,<sup>a</sup> Wenxiang Chai,<sup>a\*</sup> Li Song<sup>b</sup> and Jian Lin<sup>a</sup>

<sup>a</sup>College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, People's Republic of China, and <sup>b</sup>Department of Chemistry, Key Laboratory of Advanced Textile Materials and, Manufacturing Technology of Education Ministry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China  
Correspondence e-mail: wxchai\_cm@yahoo.com.cn

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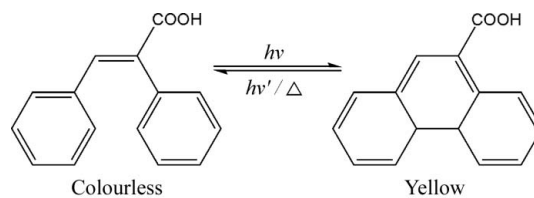
The title dinuclear complex, (aqua-1 $\kappa$ O)tetrakis( $\mu$ -2,3-diphenylprop-2-enoato-1:2 $\kappa^2$ O:O')bis(2,3-diphenylprop-2-enoato)-1 $\kappa$ O;2 $\kappa$ O-(ethanol-2 $\kappa$ O)bis(1,10-phenanthroline)-1 $\kappa^2$ N,N';2 $\kappa^2$ N,N'-dilanthanum(III), [La<sub>2</sub>(C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>)<sub>6</sub>(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>OH)(H<sub>2</sub>O)], contains two similar La<sup>III</sup> centres with distorted [LaO<sub>6</sub>N<sub>2</sub>] bicapped trigonal–prismatic coordination polyhedra formed by six phenylcinnamate (PCA<sup>−</sup> or 2,3-diphenylprop-2-enoate) ligands, two 1,10-phenanthroline (phen) ligands, a coordinating ethanol molecule and a coordinating water molecule. The two metal centres are bridged by four  $\mu$ -PCA<sup>−</sup> ligands, with the remaining two PCA<sup>−</sup> ligands coordinated in a monodentate fashion. The noncoordinated carboxylate O atoms on the terminal PCA<sup>−</sup> ligands form O–H...O hydrogen bonds with the coordinated solvent molecules. Each La centre is also coordinated by a bidentate phen ligand. The PCA<sup>−</sup> ligands all adopt *syn–syn* orientations, with the two phenyl rings presenting dihedral angles of about 70°. The compound displays photochromic behaviour both in solution and in the solid state.

## Comment

Photochromism, a photoinduced reversible transformation between two chemical forms having different absorption spectra, *i.e.* different colours, is both of great basic interest and of high application potential (Dürr & Bouas-Laurent, 2003). Among all the photochromic families, diarylethenes are some of the most efficient compounds used for photoswitching applications because of their thermal irreversibility, high fatigue resistance, and good photoconversion yield between an open form and a closed form (Irie, 2002). For these reasons, numerous recent advances focused on diarylethene photochemistry have been reported (Tsuboi *et al.*, 2009). Organic–

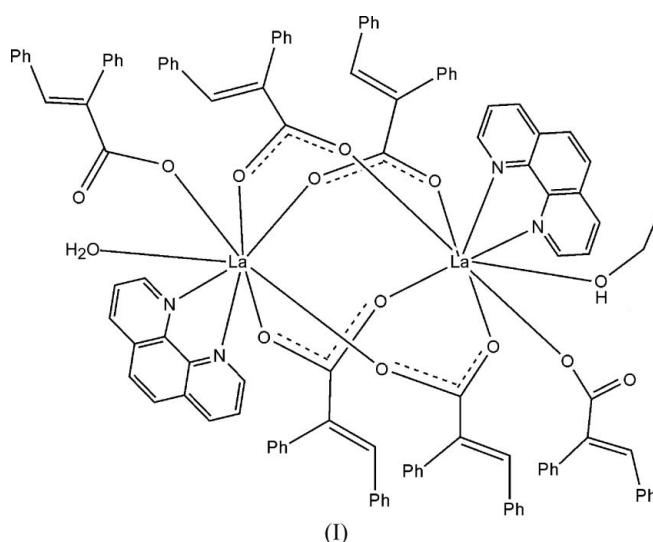
inorganic hybrids based on diarylethene moieties have attracted particular interest for their varied structures, novel photophysical and/or photochemical phenomena and fascinating properties (Wenger *et al.*, 2004; Busby *et al.*, 2005; Yam *et al.*, 2004; Ko *et al.*, 2006).

In our recent work, we have become interested in preparing self-assembled organic–inorganic hybrid materials by dint of either coordinate bonds or Coulombic interactions based on organic templates (Chai *et al.*, 2007*a,b*, 2009, 2010). With the aim of constructing organic–inorganic hybrids in the field of coordinate chemistry, carboxylate ligands are versatile candidates which can adopt several chelating bidentate and/or different carboxylate-bridging coordinate modes. Additionally, a carboxylate group in a bridging mode provides an efficient pathway that couples magnetic or luminescent metal centres for ferromagnetic interaction or energy transfer (Oldham *et al.*, 1987; Faulkner & Pope, 2003). Phenylcinnamic acid (PCA) is a monocarboxylic acid in which two arene rings are connected by  $\pi$ -conjugated ethylene, and the diarylethene unit could show a typical photochromic transformation (see Scheme 1 below) (Dürr & Bouas-Laurent, 2003). Previously,

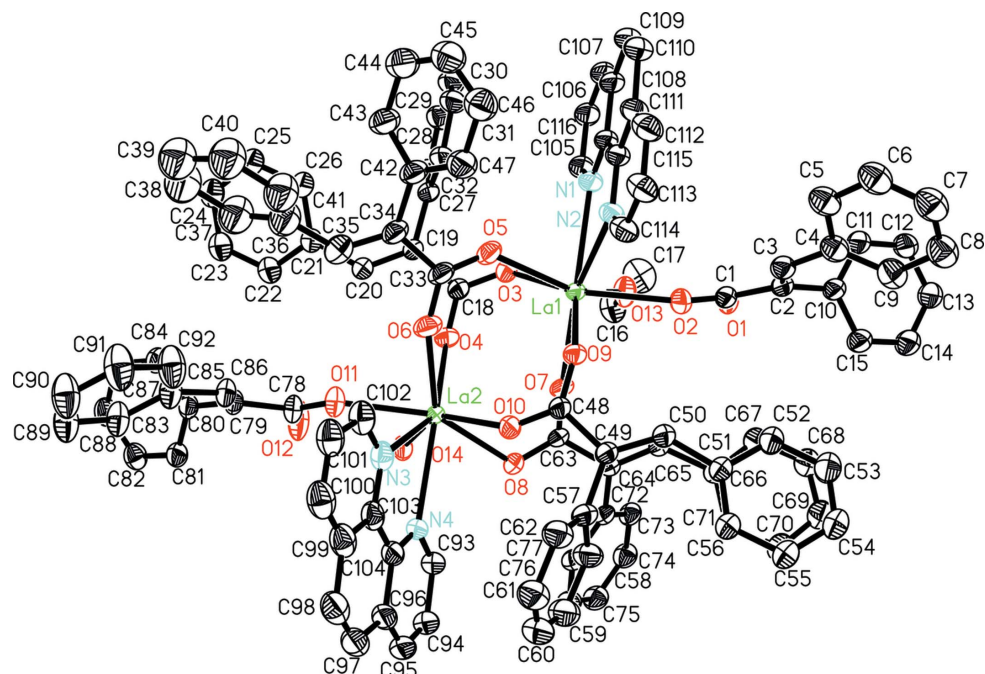


Scheme 1

Kumagai and co-workers synthesized and characterized some transition metal complexes using PCA<sup>−</sup> as a ligand, but neither photochromic nor luminescent properties were reported (Kumagai *et al.*, 2003, 2005; Oka & Inoue, 2004). In this study, we have focused on the construction of novel



organic–inorganic complexes by utilizing PCA<sup>−</sup> as a ligand and rare earth ions as metal centres, and the title novel photochromic dinuclear compound, (I), has been successfully synthesized. Considering the photochromism derived from the PCA<sup>−</sup> ligand and the photoluminescence displayed by rare

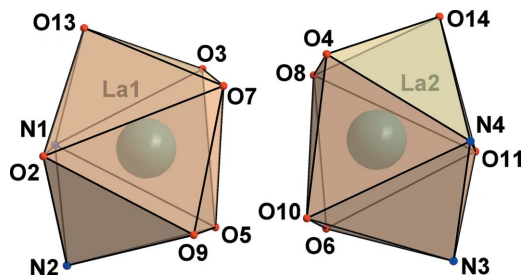

**Figure 1**

The molecular structure and atom-labelling scheme of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

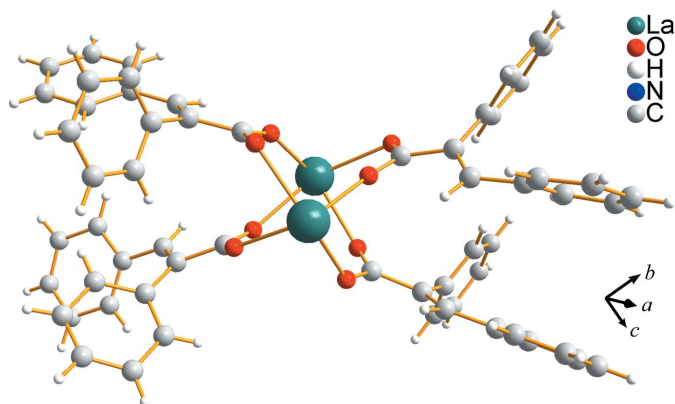
earth ions, this novel hybrid may be endowed with new functions, such as luminescence modulation by photochromic switching.

The structure of (I) has been characterized as a dinuclear cluster (Fig. 1), consisting of two  $\text{La}^{\text{III}}$  cations, six  $\text{PCA}^-$  anions, two 1,10-phenanthroline (phen) ligands, one ethanol molecule and one water molecule. Each crystallographically independent  $\text{La}^{\text{III}}$  cation adopts a distorted  $[\text{LaO}_6\text{N}_2]$  bicapped trigonal-prismatic coordination geometry, with one capping site occupied by a coordinating solvent (*i.e.* by O13 from water or O14 from ethanol) and the other occupied by N2 and N3 from phen ligands (Fig. 2). The La–O [2.398 (5)–2.620 (5) Å] and La–N [2.722 (7)–2.772 (7) Å] bond lengths are similar to previously reported values (Khanjani *et al.*, 2010; Li *et al.*, 2007; Gao, 2009; Zhu *et al.*, 2005; Liu *et al.*, 2008). The two La centres are connected by four bridging  $\text{PCA}^-$  ligands to form the dinuclear cluster. Each La coordination polyhedron is completed by one monodentate  $\text{PCA}^-$  ligand, one bidentate phen ligand and one coordinated solvent molecule (ethanol or water). Previous reports (Kumagai *et al.*, 2003, 2005; Oka & Inoue, 2004) have described two coordination modes for the  $\text{PCA}^-$  ligand, *viz.* bridging and tricoordinated. In the dinuclear metal–carboxylate cluster of (I), the tricoordinated mode means that one of the carboxylate O atoms is coordinated to a single metal centre while the other is within coordinating distance of both metal centres. The terminal  $\text{PCA}^-$  ligands observed in (I) thus appear to be relatively rare in this type of complex. The configurations of the  $\text{PCA}^-$  ligands in the complex are almost the same. All six atoms in and around the C=C bonds are essentially coplanar, while the two phenyl rings are in a *syn–syn* mode with a dihedral angle of about  $70^\circ$ .

Previously, some dinuclear La cluster compounds have been synthesized from carboxylate and neutral ligands. Focusing on the structural features of the cluster core, there are two modes that have been observed to construct such clusters. In the first mode, also seen in a dinuclear Nd cluster we reported recently (Chai *et al.*, 2009), two carboxylate groups bridge the La centres to form a dinuclear  $\text{La}_2$  cluster (Li *et al.*, 2007; Gao, 2009) and the remaining coordination sites are occupied by other anionic and neutral ligands. In the second mode, four carboxylate groups bridge the La centres to form a dinuclear unit, with two groups adopting a  $\mu_2$ -bridged arrangement and the other two adopting a tricoordinated mode (Lu *et al.*, 1996; Shi *et al.*, 2001; Zheng & Jin, 2003; Lu *et al.*, 2001; Fu *et al.*, 2004; Zhu *et al.*, 2005; Liu *et al.*, 2008). Here, the structure of the cluster core is notably different from the reported examples. The difference may be due to the large size of the  $\text{PCA}^-$  ligand and the steric crowding it creates around the cluster core. Viewed along the  $\text{La1}\cdots\text{La2}$  axis, this  $\text{La}_2(\text{PCA})_4$  unit


**Figure 2**

The two distorted bicapped trigonal-prismatic  $[\text{LaO}_6\text{N}_2]$  polyhedra in the dinuclear cluster. The capping atoms are O13 or O14 from the coordinated solvent and N2 or N3 from the phen ligand.



**Figure 3**  
The windmill-like structure of the  $\text{La}_2(\text{PCA})_4$  cluster core unit.

looks like a windmill (Fig. 3). The two remaining  $\text{PCA}^-$  ligands adopt a monocoordinated mode, with a phen ligand and a coordinating solvent molecule completing the remaining coordination sites on each side of the windmill-like unit.  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonding links the noncoordinated carboxylate O atom of the monodentate  $\text{PCA}^-$  ligand to the solvent molecule coordinated to each La centre [ $\text{O}13 \cdots \text{O}1 = 2.600$  (8) Å and  $\text{O}14 \cdots \text{O}12 = 2.653$  (8) Å].

As the  $\text{PCA}^-$  ligand contains a feature of a potentially photochromic molecule (Dürr & Bouas-Laurent, 2003), the photochromism of (I) has been observed roughly. When a colourless ethanolic solution of (I) is irradiated with UV light for some minutes, a gradual colour change to yellow occurs. Similar behaviour is shown by a powder sample of (I), though the transformation is slower than that in solution. The corresponding  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  samples have also been synthesized due to their expected luminescent properties. Detailed analyses of their spectroscopic properties are ongoing.

## Experimental

A mixture of  $\text{La}(\text{NO}_3)_3$  (0.086 g, 0.2 mmol), PCA (0.137 mg, 0.6 mmol), phen (40 mg, 0.2 mmol), NaOH (0.240 g, 0.5 M) and  $\text{EtOH}/\text{H}_2\text{O}$  (10 ml, 4:1 v/v) was heated at 453 K for 50 h in a sealed 25 ml Teflon-lined stainless steel vessel under autogenous pressure. The reaction mixture was then cooled slowly to room temperature, whereupon colourless platelet-shaped single crystals of (I) were obtained in a yield of 55%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3609 (*ms*), 3427 (*m*), 3077 (*m*), 3055 (*m*), 3020 (*m*), 2925 (*m*), 1953 (*w*), 1885 (*w*), 1808 (*w*), 1757 (*w*), 1635 (*s*), 1587 (*sh*), 1543 (*sh*), 1517 (*s*), 1490 (*s*), 1394 (*sh*), 1349 (*s*), 846 (*m*), 709 (*s*), 693 (*s*), 630 (*m*).

### Crystal data

$[\text{La}_2(\text{C}_{15}\text{H}_{11}\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{C}_2\text{H}_6\text{O})(\text{H}_2\text{O})]$	$\beta = 89.01$ (3)°
$M_r = 2041.74$	$\gamma = 77.94$ (3)°
Triclinic, $P\bar{1}$	$V = 4887.9$ (17) Å <sup>3</sup>
$a = 13.464$ (3) Å	$Z = 2$
$b = 18.572$ (4) Å	Mo $K\alpha$ radiation
$c = 20.490$ (4) Å	$\mu = 0.93$ mm <sup>-1</sup>
$\alpha = 77.42$ (3)°	$T = 293$ K
	$0.38 \times 0.27 \times 0.10$ mm

### Data collection

Rigaku R-Axis RAPID diffractometer	38229 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	17208 independent reflections
$T_{\min} = 0.719$ , $T_{\max} = 0.913$	11202 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.056$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	960 restraints
$wR(F^2) = 0.169$	H-atom parameters constrained
$S = 1.16$	$\Delta\rho_{\max} = 1.36$ e Å <sup>-3</sup>
17208 reflections	$\Delta\rho_{\min} = -1.22$ e Å <sup>-3</sup>
1226 parameters	

All H atoms bonded to C atoms were added at calculated positions and refined using a riding model, with  $\text{C}-\text{H} = 0.93$  Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The O-bound H atoms of the coordinated water and ethanol molecules could not be located reliably from the difference Fourier map; they have therefore been omitted from the refinement model but are included in the chemical formula and in all values derived from it. The displacement parameters indicated the presence of disorder, but a split-site model combined with restraints to the anisotropic displacement parameters (ADPs) did not improve the model. We therefore adopted a dynamic disorder model with extremely strong restraints applied to the ADPs (ISOR and SIMU parameters of 0.004 Å<sup>2</sup>; Sheldrick, 2008).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3293). Services for accessing these data are described at the back of the journal.

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