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Partially cyclopentadienyl-substituted tetranuclear lanthanide Schiff base complexes

Yue-Peng Cai [a], Huai-Zhu Ma [b], Bei-Sheng Kang [a,*1], Cheng-Yong Su [a,*2], Wu Zhang [b], Jie Sun [c], Yan-Ling Xiong [b]

[a] *School of Chemistry and Chemical Engineering, Zhongshan University, 135 West Xingang Road, Guangzhou 510275, People's Republic of China*

[b] *Institute of Organic Chemistry, Anhui Normal University, Wuhu 241000, People's Republic of China*

[c] *State Key Laboratory of Organometallic Chemistry, Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

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Abstract

Treatment of Cp_3Ln (Ln = Pr, Nd) with an equimolar amount of the Schiff base bis(acetylacetone)ethylenediamine (H_2acacen) half hydrate ($H_2L^1 \cdot 1/2H_2O$) or bis(salicylidene)trimethylenediamine (H_2saltn) half hydrate ($H_2L^2 \cdot 1/2H_2O$) in THF affords three novel μ-hydroxo-bridged tetranuclear organolanthanide complexes $[\eta^5\text{-CpLn}_2L_2(\mu\text{-OH})]_2 \cdot n$THF, $L = L^1$, $n = 4$, Ln = Pr (**1**), Nd (**2**); $L = L^2$, $n = 2$, Ln = Nd (**3**). A reaction scheme was proposed in which the cyclopentadienyl lanthanide coordination motif [CpLnL] (**A**) and the hydroxyl lanthanide motif [LnL(OH)] (**B**) cross-reacted and then dimerized through the μ-hydroxo bridges to give the tetranuclear Ln complexes containing an Ln_4O_8 skeleton with two reciprocally oriented face-sharing defect cubanes. In each monomeric species $[CpLn_2L_2(OH)]$ (**C**) the Ln atoms are 8- or 9-coordinated. All complexes have been characterized by EA, IR and Mass spectroscopy.

Keywords: Tetranuclear lanthanide cluster complex; Cyclopentadienyl lanthanide complex; Nd- and Pr-complexes; Schiff base; Face-sharing defect dicubic Ln_4O_8 core; Crystal structures

1. Introduction

Organolanthanide complexes have attracted much attention of both organic and inorganic chemists since the 1960s [1] for their catalytic activities and application as reagents in organic syntheses [2]. Among these, cyclopentadiene containing complexes are the most thoroughly studied and numerous mono-, bi-, tri-, tetra-, penta-, and even hexanuclear [2–8] complexes have been reported, just to cite a few. To our knowledge however, complexes with only part of the lanthanide atoms substituted by cyclopentadienyl ligand have not been reported previously. As inorganic chemists, we have been working on Ln complexes with the metal atoms encapsulated within multidentate tripodal amino ligands, which were found to have interesting luminescent properties [9]. In the meantime, we have extended our interest to the structural chemistry of lanthanide cluster complexes containing cyclopentadienyl groups by employing the simple Schiff bases as auxilary ligands.

Although lanthanide complexes coordinated by H_2salen (bis(salicylidene)ethylenediamine) have been studied before [10], the syntheses and molecular structures of organolanthanide Schiff base complexes containing cyclopentadienyl ligands are still underdeveloped. Until now only a few such complexes have been reported in the literature [11–18], where all are either mono- or dinuclear. On the other hand, polynuclear lanthanocene complexes have been well established in which the coordinating cores are usually generated by some simple bridging units containing oxygen [19], halogen [20], hydrogen [21], cyanogen [13], or alkyne [22], or even via bridging of the cyclopentadienyl ligand itself [23].

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[1] *Corresponding author. Fax: +86-20-84110318; email: ceslhq@zsu.edu.cn

[2] *Corresponding author.

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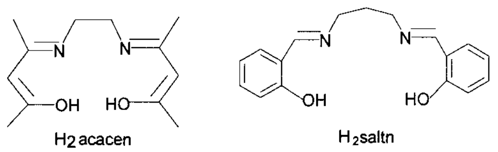
Herein we report a series of tetranuclear cluster complexes formed by the construction of lanthanide Schiff base 'building blocks' which provide different coordination environments for the Ln atoms in the same molecule. To the best of our knowledge, lanthanocene Schiff base complexes assembled via hydroxo-bridging interactions have not been reported before.

2. Results and discussion

2.1. Synthesis

The ligands bis(acetylacetone)ethylenediamine (H_2acacen) H_2L^1 and bis(salicylidene)trimethylenediamine (H_2saltn) H_2L^2 used in this work are shown below:



H_2acacen H_2L^1 H_2saltn H_2L^2

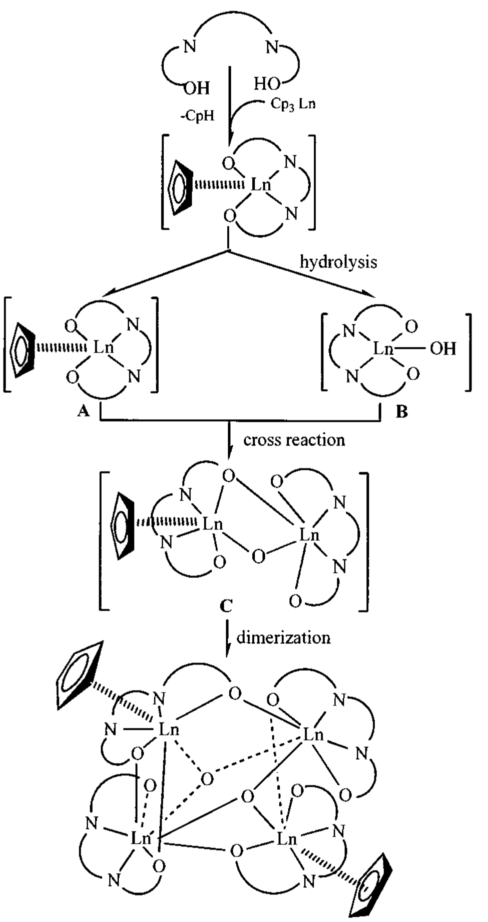
H_2L^1 [24] and H_2L^2 [25] have been reported previously and were synthesized here by a slightly modified method by adding glacial acetic acid to adjust the pH value to 6 after the initial reaction of ketone or aldehyde with diamine under inert atmosphere.

In the reaction process, the ligand dianion $[L]^{2-}$ chelates first to the tricyclo-pentadienyllanthanide Cp_3Ln by the replacement reaction of two of the three Cp^{1-} substituents to give the Cp-substituted lanthanide species [CpLnL] (**A**), which then partially hydrolyzes to the non-Cp-substituted species [LnL(OH)] (**B**), as shown in Scheme 1. Liberation of Cp^{1-} from Cp_3Ln by the action of protonic acids stronger than HCp has been well documented [26]. Complexes with molecular formula [CpLnL] as that of (**A**) have been characterized previously [27] by spectroscopic methods, indicating that the mononuclear organolanthanide species could exist but was unstable and would be partially hydrolyzed into the hydroxo-substituted motif [LnL(OH)] (**B**) in the presence of H_2O (from the ligands). For this reason, the handling of single crystals of **A** for X-ray analysis was difficult [27]. The occurrence of **B** is thus also understandable, as hydrolysis is easy and being the most common method to prepare organometallic oxo complexes [4,28,29] and numerous HO-bridged lanthanide complexes have been reported [30,31]. **A** and **B** on formation then quickly cross-react and form the dinuclear intermediate **C** which finally dimerizes to give the air sensitive tetranuclear clusters. The driving force of the self-assembly process is thus the bridging coordination of the oxo-atoms of the ligands and the hydroxy groups to satisfy the most stable coordination environment of 8 or 9 for the Ln^{3+} ions. The result showed that the presence of half a molecule of water in the ligand is just the right amount for the formation of the cluster complexes which need two hydroxo groups as a little excess of moisture would completely destroy the skeleton.

The complexes **1**–**3** thus are all extremely air and moisture sensitive and decompose at 230°C and turn into light blue (**1** and **2**) or change into a yellow powder (**3**) in ca. 10 min when exposed to air (30°C, relative humidity 60–70% in Southern China).

2.2. Physical and chemical properties

Complexes **1**–**3** all showed a strong bathochromically shifted $\nu_{C=N}$ absorption at 1609–1610 cm^{-1} as compared to the free ligand H_2acacen (1622 cm^{-1}) or H_2saltn (1623 cm^{-1}), showing that chelation apparently weakens the C=N double bonds. The hydroxyl protons were confirmed by the broad bands in range



	Ln	L
1	Pr	L^1 (acacen)
2	Nd	L^1 (acacen)
3	Nd	L^2 (saltn)

Scheme 1.

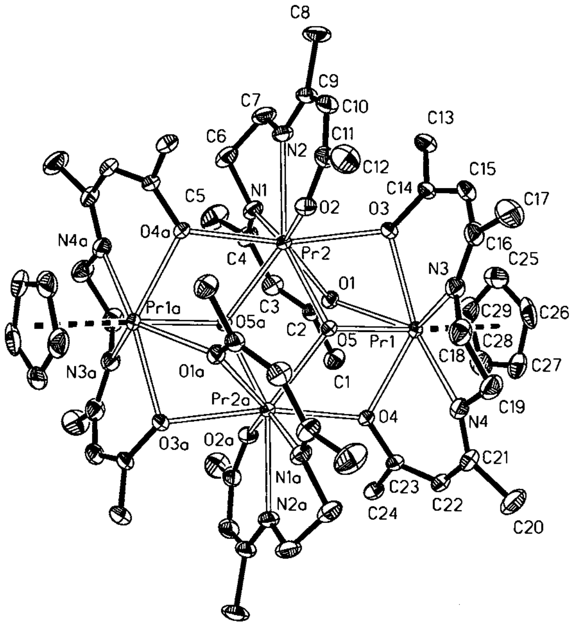


Fig. 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Pr_2(L^1)_2(\mu\text{-}OH)]_2 \cdot 4THF$ (**1**) with atomic numberings without the solvent molecules (hydrogen atoms have been omitted for clarity).

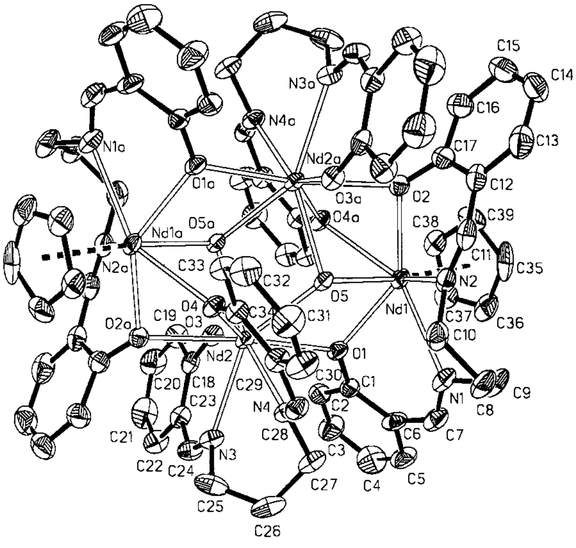


Fig. 2. Molecular structure of $[(\eta^5\text{-}C_5H_5)Nd_2(L^2)_2(\mu\text{-}OH)]_2 \cdot 2THF$ (**3**) with atomic numberings without the solvent molecules (hydrogen atoms have been omitted for clarity).

3250–3350 cm^{-1}, and also by stoichiometric balance of charges in the molecules.

The fast atom bombardment mass spectrum (FABMS) of complex **3** shows the presence of fragments $[CpNdL^2(OH)L^2Nd]^+$ (*m*/*z* 931), $[CpNdL^2]^+$ (490), and $[NdL^2(OH)]^+$ (442), demonstrating that both building blocks $[CpNdL^2]^+$ and $[NdL^2(OH)]^+$ are present, and the dinuclear motif is also found in the spectrum, a further evidence for the proposed reaction process shown in Scheme 1. Mass spectral studies (EIMS) were also performed for the complexes **1** and **2**, and the results (see Section 2) are also indicative of the presence of similar reaction species and will not be discussed further.

2.3. Structural characterization

Figs. 1 and 2 depict the molecular structures of complexes $[(\eta^5\text{-}Cp)Pr_2(L^1)_2(\mu\text{-}OH)]_2 \cdot 4THF$ (**1**) and $[(\eta^5\text{-}Cp)Nd_2(L^2)_2(\mu\text{-}OH)]_2 \cdot 2THF$ (**3**), respectively, without the solvate molecules. Complex $[(\eta^5\text{-}Cp)Nd_2(L^1)_2(\mu\text{-}OH)]_2 \cdot 4THF$ (**2**) is isomorphous to **1** and will not be discussed. Selected atomic distances and bond angles of all three complexes are listed in Tables 1 and 2, respectively. The structures of the tetranuclear **1** and **3** are quite similar with the crystallographic center of symmetry located at the center of the Ln_4O_8 core which may be described as two reversely oriented face-sharing defect cubanes as shown in Fig. 3, but with one additional μ_2-oxo bridge connecting two of the Ln atoms in each cube. The molecule can be considered as a dimer of the dinuclear motif $[CpLn_2L_2(OH)]$ in which the two Ln atoms show different coordination geometries: one is 9-coordinated by one Cp (cyclopentadienyl) anion (occupying three of the coordinating sites) [32] and O_2N_2 from one ligand and one O from another ligand, while the remaining site is occupied by an μ-OH group. The other Ln ion is 8-coordinated, also by O_2N_2 from one ligand, but further by two O atoms from two other ligands in *trans*-positions with the *trans*-O–Ln–O angles in the range of 157.9–160.41°. The remaining two coordination sites are occupied by the two symmetry-related μ-bridging OH groups so that these second Ln atoms act as bridges between the two Cp substituted Ln moieties of the molecule, forming an $Ln_2(OH)_2$ rhomb.

Besides being similarly chelated tetradentately to an Ln atom — each ligand forming two six- and one five-membered chelate rings in **1** and **2**, and three six-membered rings in **3**, the two Schiff bases within a dinuclear moiety $[CpLn_2L_2(OH)]$ however, behave differently: the one chelating to the Cp-ligated lanthanide atom links further to two other Ln atoms via the two μ_2-O-bridges, while the other chelating to the non-Cp-ligated lanthanide atom offers only one μ_2-bridging oxo-atom, with the other oxo-atom only terminally ligated to Ln. As a result, there are six μ_2-O-bridges within the tetranuclear molecule aside from the two μ-OH bridges capping the Ln_3 triangles.

The chelate angles Ln–N–C are the smallest in the five-membered $\overline{\text{LnNCCN}}$ rings, while the Ln–O–C angle containing the terminal oxygen atom is the largest and that containing the singly bridging μ_2-O the smallest. It is also observed that whether in six- or five-membered rings, the chelate angles Ln–X–C (X = O or N) are all quite close to the sp^2 hybrid angle for the X atom and there is significant delocalization over all the chelate environment of each rare earth atom. However, the bite angles O–Ln–N are all acute in range 69.9–70.7°, with very small deviations, due to the high coordination number of the metal ions. The bridging angles Ln–O–Ln′ are more acute between the doubly μ_2-O bridged atoms than the singly bridged ones.

On examining the Ln–O bonds, it is observed that the distance inside a chelate ring is always shorter than that outside, by -0.1 Å, which is common to most multidentate chelating ligands [33]. The Ln–O distances can be divided into three types: (i) terminally ligated to Ln with distances in the range of 2.29–2.33 Å, the shortest; (ii) singly or doubly bridging two Ln atoms (μ_2-bridge) with average value in the range of 2.49–2.53 Å, the longest; (iii) the μ-bridging Ln–OH bonds which have an average value of 2.43–2.46 Å, with lengths in between the terminal and the μ_2-bridging bonds. The average Ln–N distances in complexes **1**–**3** are in range of 2.55–2.63 Å, with that in **3** the longest.

The Ln···Ln distances (3.7–4.0 Å) in an Ln$_3$ triangle bridged by μ-OH show similar trends for all three complexes: the ones with double μ_2-O bridges have the shortest distance (3.69–3.77 Å) and the one with single μ_2-O bridge the longest (4.03–4.05 Å), while the one without μ_2-O bridge (passing through the crystallographic symmetry center) has distances (3.95–3.98 Å) in between. The much shorter Nd(1)–Nd(2a) distance (3.6887 (9) Å) in **3** as compared to that in **2** may have been caused by weak intramolecular π···π interaction of the two adjacent phenyl rings of the two Schiff base ligands L^2 coordinated to the two μ-OH bridged Nd atoms, with centroid-to-centroid distance of 3.95 Å and dihedral angle of 15.9°. The Ln–C distances of the Cp to metal atom are slightly longer than those in other Cp-substituted complexes [34], probably caused by steric congestion of the three chelate rings of the Schiff base.

Table 1
Selected atomic distances (Å) for complexes **1**–**3** [a]

1		**2**		**3**	
Ln–Ln					
Pr(1)–Pr(2)	3.7713(9)	Nd(1)–Nd(2a′)	3.7438(12)	Nd(1)–Nd(2a)	3.6887(9)
Pr(2)–Pr(2a)	3.9848(9)	Nd(1)–Nd(1a′)	3.9526(12)	Nd(2)–Nd(2a)	3.9694(13)
Pr(1)–Pr(2a)	4.0496(16)	Nd(1)–Nd(2)	4.0252(9)	Nd(1)–Nd(2)	4.0542(13)
Ln–O Terminal					
Pr(2)–O(2)	2.327(3)	Nd(1)–O(1)	2.321(4)	Nd(2)–O(3)	2.285(5)
μ_2-Bridging					
Pr(1)–O(1)	2.625(3)	Nd(2)–O(2a′)	2.605(4)	Nd(1)–O(4a)	2.559(5)
Pr(1)–O(3)	2.449(3)	Nd(2)–O(4)	2.430(4)	Nd(1)–O(2)	2.381(5)
Pr(1)–O(4)	2.447(3)	Nd(2)–O(3)	2.429(4)	Nd(1)–O(1)	2.411(5)
Pr(2)–O(1)	2.530(3)	Nd(1)–O(2)	2.511(4)	Nd(2)–O(4)	2.492(5)
Pr(2)–O(3)	2.539(3)	Nd(1)–O(4a′)	2.514(4)	Nd(2)–O(2a)	2.536(5)
Pr(2)–O(4a)	2.571(3)	Nd(1)–O(3)	2.552(4)	Nd(2)–O(1)	2.566(5)
Mean	2.527		2.507		2.491
μ_3-Bridging					
Pr(1)–O(5)	2.419(3)	Nd(2)–O(5)	2.406(4)	Nd(1)–O(5)	2.404(4)
Pr(2)–O(5)	2.476(3)	Nd(1)–O(5)	2.455(4)	Nd(2)–O(5a)	2.416(4)
Pr(2)–O(5a)	2.476(3)	Nd(1)–O(5a′)	2.458(4)	Nd(2)–O(5)	2.481(5)
Mean	2.457		2.440		2.434
Ln–N					
Pr(1)–N(3)	2.580(4)	Nd(2)–N(4)	2.564(6)	Nd(1)–N(2)	2.642(7)
Pr(1)–N(4)	2.604(4)	Nd(2)–N(3)	2.590(6)	Nd(1)–N(1)	2.688(7)
Pr(2)–N(1)	2.530(4)	Nd(1)–N(2)	2.517(6)	Nd(2)–N(4)	2.548(6)
Pr(2)–N(2)	2.595(4)	Nd(1)–N(1)	2.564(5)	Nd(2)–N(3)	2.629(7)
Mean	2.577	2.559	2.627		
Cp–Ln					
Pr(1)–C(25)	2.799(10)	Nd(2)–C(25)	2.803(8)	Nd(1)–C(35)	2.827(9)
Pr(1)–C(26)	2.843(7)	Nd(2)–C(26)	2.822(8)	Nd(1)–C(36)	2.813(9)
Pr(1)–C(27)	2.850(8)	Nd(2)–C(27)	2.843(7)	Nd(1)–C(37)	2.810(8)
Pr(1)–C(28)	2.838(9)	Nd(2)–C(28)	2.821(8)	Nd(1)–C(38)	2.804(8)
Pr(1)–C(29)	2.818(8)	Nd(2)–C(29)	2.788(7)	Nd(1)–C(39)	2.812(8)
Mean	2.830		2.815		2.813

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, -y, -z$; (a′) $-x+1, -y, -z$.

Table 2
Selected bond angles (°) for complexes **1**–**3** [a]

1		**2**		**3**	
Chelate angle					
Pr(1)–O(3)–C(14)	121.9(3)	Nd(2)–O(4)–C(23)	121.5(4)	Nd(1a)–O(1)–C(1)	127.8(5)
Pr(1)–O(4)–C(23)	119.6(3)	Nd(2)–O(3)–C(14)	119.5(4)	Nd(1)–O(2)–C(17)	125.4(5)
Pr(1)–N(3)–C(16)	126.9(4)	Nd(2)–N(4)–C(20)	126.7(5)	Nd(1)–N(1)–C(7)	122.2(7)
Pr(1)–N(3)–C(18)	112.6(3)	Nd(2)–N(4)–C(19)	112.6(4)	Nd(1)–N(1)–C(8)	116.4(6)
Pr(1)–N(4)–C(19)	114.6(3)	Nd(2)–N(3)–C(18)	114.8(4)	Nd(1)–N(2)–C(10)	114.3(6)
Pr(1)–N(4)–C(21)	123.9(4)	Nd(2)–N(3)–C(16)	123.7(5)	Nd(1)–N(2)–C(11)	126.0(6)
Pr(2)–O(2)–C(11)	137.4(4)	Nd(1)–O(1)–C(2)	136.7(5)	Nd(2)–O(3)–C(18)	143.3(5)
Pr(2)–O(1)–C(2)	128.0(3)	Nd(1)–O(2)–C(11)	127.3(4)	Nd(2)–O(4)–C(34)	133.3(4)
Pr(2)–N(2)–C(9)	127.7(4)	Nd(1)–N(1)–C(4)	127.9(5)	Nd(2)–N(3)–C(24)	127.1(6)
Pr(2)–N(2)–C(7)	113.1(3)	Nd(1)–N(1)–C(6)	113.2(4)	Nd(2)–N(3)–C(25)	114.2(5)
Pr(2)–N(1)–C(6)	108.7(3)	Nd(1)–N(2)–C(7)	109.2(5)	Nd(2)–N(4)–C(27)	112.1(5)
Pr(2)–N(1)–C(4)	129.2(4)	Nd(1)–N(2)–C(9)	129.3(5)	Nd(2)–N(4)–C(28)	129.8(5)
Bridging angle					
Pr(1)–O(3)–Pr(2)	98.21(10)	Nd(2)–O(4)–Nd(1a′)	98.42(14)	Nd(1a)–O(2a)–Nd(2)	97.17(19)
Pr(1)–O(1)–Pr(2)	94.02(10)	Nd(2)–O(2a)–Nd(1a′)	94.07(14)	Nd(2)–O(4)–Nd(1a)	93.81(16)
Pr(1)–O(4)–Pr(2a)	107.58(11)	Nd(2)–O(3)–Nd(1)	107.80(14)	Nd(1)–O(1)–Nd(2)	109.01(18)
Pr(1)–O(5)–Pr(2a)	111.66(11)	Nd(2)–O(5)–Nd(1a′)	100.74(14)	Nd(1)–O(5)–Nd(2)	112.15(17)
Pr(1)–O(5)–Pr(2)	100.78(10)	Nd(2)–O(5)–Nd(1)	111.69(15)	Nd(1)–O(5)–Nd(2a)	99.86(16)
Pr(2)–O(5)–Pr(2a)	107.16(11)	Nd(1)–O(5)–Nd(1a′)	107.15(14)	Nd(2)–O(5)–Nd(2a)	108.28(16)
Bite angle					
O(3)–Pr(1)–N(3)	70.79(13)	O(4)–Nd(2)–N(4)	70.98(17)	O(1)–Nd(1)–N(1)	68.9(2)
N(3)–Pr(1)–N(4)	66.33(14)	N(4)–Nd(2)–N(3)	66.47(19)	N(1)–Nd(1)–N(2)	69.3(2)
N(4)–Pr(1)–O(4)	69.59(12)	N(3)–Nd(2)–O(3)	69.95(16)	N(2)–Nd(1)–O(2)	69.9(2)
O(2)–Pr(2)–N(2)	72.37(14)	O(1)–Nd(1)–N(1)	72.59(18)	O(3)–Nd(2)–N(3)	71.7(2)
N(2)–Pr(2)–N(1)	68.31(15)	N(1)–Nd(1)–N(2)	68.7(2)	N(3)–Nd(2)–N(4)	72.1(2)
N(1)–Pr(2)–O(1)	72.08(12)	N(2)–Nd(1)–O(2)	72.69(16)	N(4)–Nd(2)–O(4)	72.18(18)
Mean	69.91		70.23		70.68

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x$, $-y$, $-z$; (a′) $-x+1$, $-y$, $-z$.

3. Experimental

All experiments were performed under an atmosphere of dry dinitrogen gas using standard Schlenk-type techniques. Toluene, *n*-hexane, diethyl ether and THF were all freshly distilled from sodium benzophenone ketyl immediately prior to use in the syntheses of complexes. The solvents and reagents used in the syntheses of ligands were of reagent grade and used as received. Cp_3Ln (Ln = Nd, Pr) was prepared according to the literature method [35]. Propylenediamine was purchased from Aldrich and used as received. The C, H and N elemental analyses were performed on a Perkin–Elmer elemental analyzer. Lanthanide metal analyses were carried out by complexometric titration. IR spectra were recorded on a Nicolet 5DX FTIR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. FABMS and EIMS were recorded on VG ZAB-HS and Hewlett–Packard 5989A spectrometer, respectively.

3.1. H_2acacen (H_2L^1)·1/2H_2O

The Schiff base H_2acacen was prepared by the method described previously [24] with some modifications. To a clear solution of acetylacetone (4.1 ml, 40 mmol) in a mixed solvent of toluene and diethyl ether (20 ml, 3:1 in volume) was added a solution of ethylenediamine (1.7 ml, 20 mmol) in THF (15 ml) dropwise with stirring at room temperature (r.t.). The resulting light yellow solution was refluxed for 3 h, then acidified with glacial acetic acid to pH 6. After 15 min the mixture was cooled, the precipitate produced was separated by filtration and washed several times with diethyl ether to give the crude product which was purified by recrystallization from hot toluene to afford a white

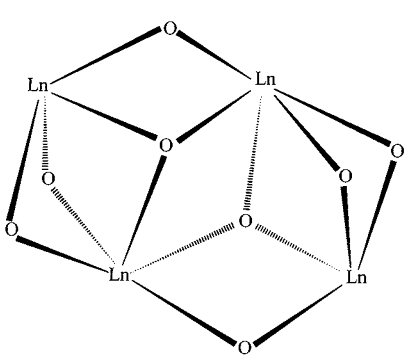


Fig. 3. The reciprocally oriented face-sharing defect dicubane structure of the Ln_4O_8 skeleton in complexes **1**–**3**.

crystalline solid (4.25 g, 95%). M.p. (sealed): 110°C. EIMS; *m*/*z* (abundance): 225 ($M^+ + 1$) (100%), 224 (M^+) (78%). IR (KBr pellet, cm^{-1}): ν 3083(m), 3065(m), 2982(m), 2859(m), 1622(s), 1610(s), 1598(s), 1557(s), 1520(vs), 1339(s), 1252(s). Anal. Found: C, 63.01; H, 8.85; N, 12.35. Calc. for $C_{12}H_{21}N_2O_{2.5}$: C, 61.80; H, 9.01; N, 12.02%.

3.2. H_2saltn (H_2L^2)·1/2H_2O

The Schiff base H_2saltn was prepared according to the method reported in the literature [25] with some modifications. To a clear solution of salicylaldehyde (4.2 ml, 40 mmol) in MeOH (15 ml) was added a solution of 1,3-diaminopropane (1.7 ml, 20 mmol) in toluene (10 ml) dropwise with stirring at r.t. The resulting yellow solution was refluxed for 3 h, then acidified with glacial acetic acid to pH 6 and set aside for cooling. The precipitate formed was filtered and washed with diethyl ether (3 × 10 ml) to give the crude product which was recrystallized from hot mixed solvent of toluene and diethyl ether (15 ml, 2:1 in volume) to afford a pale yellow crystalline solid (25 g, 90%). M.p. (sealed): 136°C. EIMS; *m*/*z* (abundance): 284 ($M^+ + 2$) (64%), 283 ($M^+ + 1$) (100%), 282 (M^+) (52%), 281 ($M^+ - 1$) (45%). IR (KBr pellet, cm^{-1}): ν 3086(w), 2982(m), 2940(m), 2567(s), 1654(s), 1623(s), 1578(s), 1520(m), 1374(m), 1314(m), 1256(s), 1194(m). Anal. Found: C, 69.70; H, 6.33; N, 10.01. Calc. for $C_{17}H_{19}N_2O_{2.5}$: C, 70.10; H, 6.53; N, 9.62%.

3.3. $[(\eta^5\text{-}C_5H_5)Pr_2(L^1)_2(\mu\text{-}OH)]_2\cdot 4THF$ (**1**)

To the THF solution of Cp_3Pr (15 ml, 2.0 mmol) was slowly added the THF (15 ml) solution of $H_2L^1\cdot 1/2H_2O$ (0.45 g, 2 mmol) at r.t. while the color of the solution changed immediately from yellow to pale yellow. The reaction mixture was then stirred at r.t. overnight and the solvent was removed under reduced pressure affording an oily residue, to which was added 15 ml of *n*-hexane. The suspension was heated and filtered and the resulting orange–yellow solid was extracted with a mixed solvent of THF and *n*-hexane (3 × 10 ml, 5:1 in volume). The extracts were combined and centrifuged, the supernatant was concentrated to about 10 ml, from which light yellow crystals were obtained upon standing at −20°C for several weeks (0.12 g, 21%). M.p. (sealed): 228°C (dec.). FABMS; *m*/*z* (abundance): 1617 ($M^+ - 4THF$) (28%), 810 ($CpPrL^1(OH)PrL^1$) (48%), 430 ($CpPrL^1$) (70%), 382 ($PrL^1(OH)$) (63%). IR (KBr pellet, cm^{-1}): ν 3348(m), 3087(m), 3025(m), 2962(m), 2832(m), 1610(s), 1439(m), 1387(s), 1331(m), 1010(s), 778(m), 564(m), 448(m). Anal. Found: C, 46.52; H, 5.93; N, 6.01; Pr, 29.81. Calc. for $C_{74}H_{116}N_8O_{14}Pr_4$: C, 46.60; H, 6.09; N, 5.88; Pr, 29.44%.

3.4. $[(\eta^5\text{-}C_5H_5)Nd_2(L^1)_2(\mu\text{-}OH)]_2\cdot 4THF$ (**2**)

The reaction procedure was the same as for compound **1** except that Cp_3Nd was used instead of Cp_3Pr. Pale blue crystals were obtained upon standing the final solution at −20°C for several weeks (0.09 g, 18%). M.p. (sealed): 225°C (dec.). FABMS; *m*/*z* (abundance): 1634 ($M^+ - 4THF$) (32%), 817 ($CpNdL^1(OH)NdL^1$) (62%), 433 ($CpNdL^1$) (68%), 385 ($NdL^1(OH)$) (59%). IR (KBr pellet, cm^{-1}): ν 3250(m), 3087(m), 3025(m), 2962(m), 2832(m), 1608(s), 1438(m), 1382(m), 1015(s), 780(m), 558(m), 453(m). Anal. Found: C, 46.23; H, 6.11; N, 5.96; Nd, 30.48. Calc. for $C_{74}H_{116}N_8O_{14}Nd_4$: C, 46.32; H, 6.05; N, 5.84; Nd, 30.10%.

3.5. $[(\eta^5\text{-}C_5H_5)Nd_2(L^2)_2(\mu\text{-}OH)]_2\cdot 2THF$ (**3**)

To the THF solution of Cp_3Nd (20 ml, 3.0 mmol) was added the THF (15 ml) solution of $H_2L^2\cdot\frac{1}{2}H_2O$ (0.85 g, 3.0 mmol) dropwise, and the reaction mixture was stirred at r.t. for 28 h. The color of the solution changed from deep blue to pale purple blue and finally to pale blue during the course of the reaction. The solvent was evaporated under vacuum, leaving an oily residue which was washed with 15 ml of *n*-hexane to afford a light blue solid that was washed twice with hot *n*-hexane (2 × 10 ml). The resulting solid was extracted with a mixed solvent of THF and *n*-hexane (3 × 10 ml, 5:1 in volume) at reflux temperature. The extracts were concentrated to about 10 ml, from which pale blue crystals were obtained upon standing the solution at −10°C for several days (0.11 g, 26%). M.p. (sealed): 231°C (dec.). FABMS; *m*/*z* (abundance): 1862 ($M^+ - 2THF$) (38%), 931 ($CpNdL^2(OH)NdL^2$) (58%), 490 ($CpNdL^2$) (47%), 442 ($L^2Nd(OH)$) (75%). IR (KBr pellet, cm^{-1}): ν 3278(m), 3086(m), 3035(m), 2972(m), 2852(m), 1640(s), 1608(s), 1560(s), 1440(m), 1388(s), 1332(m), 12 759(w), 1240(s), 1185(w), 1160(w), 1010(w), 782(w), 560(m), 451(m). Anal. Found: C, 51.28; H, 4.43; N, 5.81; Nd, 29.01. Calc. for $C_{86}H_{92}N_8O_{12}Nd_4$: C, 51.50; H, 4.60; N, 5.59; Nd, 28.78%.

3.6. Crystal structure determination

All single crystals with suitable sizes were sealed under N_2 in thin-walled glass capillaries for X-ray structure analysis. Diffraction data were collected at 293 K on an Rigaku AFC7R diffractometer for **1** and **2** and Siemens CCD diffractometer for **3** using graphite monochromated Mo–K_α ($\lambda = 0.71073$ Å) radiation. During the course of the collection of the intensity data no significant decays were observed. Data were corrected for Lorentz and polarization effects, and, for **1** and **2** an empirical absorption correction based on psi-scans of several reflections was applied, while for **3** absorption correction was performed using SADABS

Table 3
Crystallographic data for complexes **1**–**3**

	1	**2**	**3**
Formula	$C_{74}H_{116}N_8O_{14}Pr_4$	$C_{74}H_{116}N_8O_{14}Nd_4$	$C_{86}H_{92}N_8O_{12}Nd_4$
Mw	1905.39	1918.71	2006.64
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	13.286(2)	13.231(3)	14.709(4)
b (Å)	13.121(2)	13.168(3)	17.340(5)
c (Å)	23.950(10)	23.796(5)	18.325(6)
β (°)	93.50(2)	93.50(3)	106.012(5)
U (Å^3)	4167(2)	4138.1(16)	4493(2)
Z	2	2	2
D_{calc} (Mg m^{-3})	1.518	1.540	1.483
2θ range (°)	4.60–50.02	4.62–49.98	7.70–60.32
h, k, l Ranges	$0,0,-28$ to15,15,28	$0,0,-28$ to 14,15,28	$-20,-21,-25$ to 20,24,20
μ (mm^{-1})	2.358	2.529	2.332
F(000)	1928	1936	2000
Crystal size (mm)	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.10 × 0.07 × 0.06
Reflections observed [$I > 2\sigma(I)$]	7342	5583	13 101
No. of variables	401	401	471
Max/min transmission	1.088, 0.858	1.000, 0.847	1.000, 0.749
R_1 [a]	0.0320	0.0334	0.0473
wR_2 [b]	0.0921	0.0930	0.1195
Goodness-of-fit on F^2	0.965	1.018	0.969
Residual extreme (e Å^{-3})	0.586 and -0.663	0.661 and -0.939	0.825 and -0.926

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0532P)^2 + 5.325P]^{-1}$ **1** and **2**; $w = [\sigma^2(F_o^2) + (0.0606P)^2 + 0.000P]^{-1}$ **3**; $P = ((F_o^2) + 2F_c^2)/3$.

program [36]. A summary of crystallographic data is given in Table 3.

The crystal structures were solved by heavy-atom methods, and refinements against F^2 were carried out by full-matrix least-squares analysis. Anisotropic temperature parameters were used in the last cycles of refinements for most of the non-hydrogen atoms except those of solvent THF molecules. Hydrogen atoms were included in calculated positions and refined riding on their respective parent atoms with the isotropic thermal parameters related to the bonded atoms. All calculations were carried out using the SHELTXL-PC program package [37].

4. Summary

Two tetradentate Schiff base ligands with similar backbone have been utilized to assemble a family of tetranuclear lanthanocene complexes which provide a new strategy for synthesis of polynuclear organolanthanide species. A construction scheme was proposed indicating that the building blocks are spontaneously self-assembled due to the strong oxophilicity of Ln^{3+} ions [30] to give a centro-symmetry related dimer containing Ln_4O_8 skeleton with two reciprocally oriented face-sharing defect cubanes. The bridging interactions of μ_2-O and μ_3-O atoms with lanthanide ions contribute greatly to the assembly. It is believed that by proper selection of reaction conditions including the solvent, the organic ligand, and the substituents on the Schiff base, designed synthesis of multinuclear rare earth cluster complexes can be realized [38]. It will be interesting to obtain heteronuclear complexes by using building blocks of different rare earth metals, such as mixing light and heavy lanthanides, or rare earth metals and transition metals [39], and characteristic properties can be expected from newly synthesized complexes. This work is now underway.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 155138 for compound **1**, 155139 for compound **2**, and 155140 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] F. Calderazzo, Organomet. Chem. Rev. B 4 (1968) 131 (and references therein).

[2] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865 (and references therein).

[3] A.B. Erofeev, J. Organomet. Chem. 335 (1987) 189.

[4] W.J. Evans, Inorg. Chem. 27 (1988) 1990.

[5] (a) W.J. Evans, Inorg. Chem. 31 (1992) 2495. (b) W.J. Evans, J. Am. Chem. Soc. 110 (1988) 439.

[6] Z.S. Jin, Jiegou Huaxue 9 (1990) 140.

[7] W.J. Evans, J. Am. Chem. Soc. 108 (1986) 6095.

[8] (a) W.J. Evans, Organometallics 7 (1988) 797. (b) W. Lamberts, Inorg. Chim. Acta 121 (1986) 81.

[9] C.Y. Su, B.S. Kang, H.Q. Liu, Q.G. Wang, Z.N. Chen, Z.L. Lu, Y.X. Tong, T.C.W. Mak, Inorg. Chem. 38 (1999) 1374.

[10] (a) O. Runte, T. Priermeier, R. Anwander, Chem. Commun. (1996) 1385. (b) L. Huang, C.H. Huang, G.X. Xu, Y. Han, G.P. Li, Jiegou Huaxue 8 (1989) 1. (c) L. Huang, C.H. Huang, G.X. Xu, Y. Han, G.P. Li, Jiegou Huaxue 9 (1990) 100.

[11] W.J. Evans, D.K. Drummond, J. Am. Chem. Soc. 111 (1989) 3329.

[12] K.H. Thiele, A. Schloz, J. Schloz, U. Bohme, R. Kempe, J. Sieler, Z. Naturforsch. B 48 (1993) 1753.

[13] Y. Obora, T. Ohta, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 119 (1997) 3745.

[14] A.S.C. Chan, Q.C. Liu, J.L. Huang, Polyhedron 18 (1999) 2345.

[15] M. Yousaf, Q. Liu, J.L. Huang, Y.L. Qian, Inorg. Chem. Commun. 3 (2000) 105.

[16] Q.C. Liu, M.X. Ding, J. Organomet. Chem. 553 (1998) 179.

[17] Q.C. Liu, M.X. Ding, Y.H. Lin, Y. Xing, Polyhedron 17 (1997) 2327.

[18] A. Rechnagel, M. Noltemeyer, F.T. Edelmann, J. Organomet. Chem. 410 (1991) 53.

[19] W.J. Evans, M.S. Sollberger, T.P. Hanusa, J. Am. Chem. Soc. 110 (1988) 1840.

[20] (a) W.P. Kretschmer, J.H. Teuben, S.I. Troyanov, Angew. Chem. Intl. Ed. Engl. 37 (1998) 88. (b) S.P. Constantine, G.M. De Lima, P.B. Hitchcoco, J.M. Keates, G.A. Lawless, J. Chem. Soc. Chem. Commun. (1996) 2421. (c) H. Schumann, M.R. Keitsch, J. Winterfeld, J. Demtschuk, J. Organomet. Chem. 525 (1996) 279.

[21] K.G. Wang, E.D. Stevens, S.P. Nolan, Organometallics 11 (1992) 1011.

[22] (a) J.M. Boncella, T.D. Tilley, R.A. Anderson, J. Chem. Soc. Chem. Commun. (1984) 710. (b) D.M.L. Goodgame, D.J. Williams, R.E.P. Winpenny, J. Chem. Soc. Dalton Trans. (1989) 1439.

[23] (a) Z.W. Xie, F.E. Hahn, C.T. Qian, J. Organomet. Chem. 414 (1991) C12. (b) S.D. Stults, R.A. Anderson, A. Zalkin, Organometallics 9 (1990) 115.

[24] P.J. McCarthy, R.J. Hovey, K. Veno, A.E. Martell, J. Am. Chem. Soc. 77 (1955) 5820.

[25] J.R. Zamian, E.R. Dockal, G. Casetallano, G. Oliva, Polyhedron 14 (1995) 2411.

[26] (a) C.G. Pernin, J.A. Ibers, Inorg. Chem. 39 (2000) 1216. (b) Z.Z. Wu, X.G. Zhou, W. Zhang, Z. Xu, X.Z. You, Z.S. Jin, J. Chem. Soc. Chem. Commun. (1994) 813, and references therein. (b) S.D. Stults, R.A. Anderson, A. Zalkin, Organometallics 9 (1990) 1623.

[27] Y.P. Cai, Doctor of Science Thesis, Anhue Normal University, 1999.

[28] F.G.A. Stone, R. West, Adv. Organomet. Chem. 28 (1988) 339.

[29] Q. Zhao, H.S. Sun, W.Z. Chen, Y.J. Liu, X.Z. You, J. Organomet. Chem. 556 (1998) 159.

[30] I.P. Beletskaya, A.Z. Voskoboynikov, E.B. Chuklanova, N.I. Kirillova, A.K. Shestakova, I.N. Parshina, A.I. Gusev, G.K.-I. Magomedov, J. Am. Chem. Soc. 115 (1993) 3156.

[31] (a) H. Schumann, J. Loebel, J. Pickardt, C.T. Qian, Z.W. Xie, Organometallics 10 (1991) 215. (b) M.R. Beurgstein, P.W. Roesky, Angew. Chem. Int. Ed. Engl. 39 (2000) 549.

[32] W.W. Ma, Z.Z. Wu, R.F. Cai, Z.E. Huang, J. Sun, Polyhedron 16 (1997) 3726.

[33] (a) J.R. Nicholson, G. Christou, J.C. Huffman, D.K. Folting, Polyhedron 6 (1987) 863. (b) Y.J. Xu, B.S. Kang, Z.T. Chen, Y.B. Cai, Y.H. Hu, J.X. Lu, J. Cluster Sci. 3 (1992) 167.

[34] F.R. Shen, W.H. Zhang, J.P. Hu, S.W. Wang, X.Y. Huang, J. Organomet. Chem. 523 (1996) 121.

[35] G. Wilkinson, J.M. Birmingham, J. Am. Chem. Soc. 76 (1954) 6210.

[36] G.M. Sheldrick, SADABS. Program for Scaling and Correction of Area Detector Data, University of Göttingen, 1996.

[37] SHELXTL Program Package, Version 5.10, Bruker AXS, Inc., Madison, WI, 1998.

[38] I.A. Setyawati, S. Liu, S.J. Rettig, C. Orvig, Inorg. Chem. 39 (2000) 496.

[39] Z.Q. Xu, P.W. Read, D.E. Hibbs, M.B. Hursthouse, K.M. Abdul Malik, B.O. Patrick, S.J. Rettig, M. Seid, D.A. Summers, M. Pink, R.C. Thompson, C. Orvig, Inorg. Chem. 39 (2000) 508.