

Short communication

Synthesis, crystal structure and antibacterial activity of a novel phenolato- and peroxy-bridged dinuclear cerium(IV) complex with tripodal Schiff bases



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ABSTRACT

A novel phenolato- and peroxy-bridged dinuclear cerium(IV) complex, $[\text{Ce}_2\text{L}^1\text{L}^2(\mu^2\text{-O}_2)](\text{O}_3\text{SCF}_3)_3$, where L^1 and L^2 are the deprotonated form of tris(2-((4-bromosalicylidene)amino)ethyl)amine and bis(2-((4-bromosalicylidene)aminoethyl))(2-aminoethyl)amine, respectively, was prepared and characterized. The asymmetric unit of the complex contains a dinuclear cerium(IV) complex cation and a trifluoromethanesulfonate anion. The complex has effective activities against the bacteria *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas fluorescens*.

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Cerium is a member of lanthanide group of elements and the most abundant of them. It is found in monazite, ceric bastnaesite and silicate rocks. It has many industrial applications in the areas of lighting and television, metallurgy, glass and ceramics. Thus, there is growing need to study the environmental, medical and biological effects of cerium [1–4]. Cerium can form versatile metal complexes with coordination numbers from 4 to 13. Cerium complexes with various ligands have been found to possess interesting properties, such as catalytic property for oxidation of benzoin to benzil [5,6], antitumor and antimicrobial activities [7–12]. Schelter and coworkers reported that a cerium(IV) hydroxamate complex has implications for the beneficiation of light rare earth ores [13]. Schelter and coworkers reviewed the electrochemical behavior of cerium(III/IV) complexes, including their thermodynamics, kinetics and applications in synthesis [14]. Thus, study on cerium complexes is very interesting in coordination with chemistry and material sciences.

Schiff bases are readily synthesized by the condensation reaction of carbonyl compounds with primary amines, which have been found to be among the most convenient and attractive ligands for the preparation of various complexes with metal ions [15,16]. To date, a great deal of Schiff base complexes has been reported, however, cerium complexes with Schiff bases are much rare. Schiff bases derived from tris(2-aminoethyl)amine with salicylaldehyde and its derivatives are called 'tripodal ligands', which have attracted much attention due to their

coordination chemistry [17–19]. Most of the compounds show versatile biological properties. It was reported that the compounds bearing one or more halo-atoms on the aromatic ring have improved antibacterial and antifungal activities [20]. In 2011, Sui and coworkers reported that cerium complexes with Schiff bases have interesting antimicrobial activity [21]. As to further study the biological effects of Schiff base cerium complexes, in the present work, we report the synthesis and structure of a novel phenolato- and peroxy-bridged dinuclear cerium(IV) complex, $[\text{Ce}_2\text{L}^1\text{L}^2(\mu^2\text{-O}_2)](\text{O}_3\text{SCF}_3)_3$, where L^1 and L^2 are the deprotonated form of tris(2-((4-bromosalicylidene)amino)ethyl)amine and bis(2-((4-bromosalicylidene)aminoethyl))(2-aminoethyl)amine, respectively. To our knowledge, there are only five cerium complexes with peroxy bridges that have been reported so far [22,23]. The antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas fluorescens* was evaluated for the complex.

The complex was prepared by the reaction of 4-bromosalicylaldehyde, tris(2-aminoethyl)amine, and cerium(III) trifluoromethanesulfonate in methanol [24]. Antibacterial activities of the tripodal Schiff base H_3L^1 and the complex were tested *in vitro* against *B. subtilis*, *S. aureus*, *E. coli*, and *P. fluorescens* using MH medium (Mueller–Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL) in triplicate [25]. The observed MICs are presented in Table 1.

The cerium(IV) complex was readily prepared by the reaction of 3:2:2 M ratio of 4-bromosalicylaldehyde, tris(2-aminoethyl)amine and cerium(III) trifluoromethanesulfonate in methanol (Scheme 2). It is interesting that during the *in situ* reaction, two tripodal Schiff base ligands were formed, viz. tris(2-((4-bromosalicylidene)amino)ethyl)amine

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Table 1
Antibacterial results (MIC ($\mu\text{g mL}^{-1}$)).

	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Pseudomonas fluorescens</i>	<i>Staphylococcus aureus</i>
H_3L^1	25	>100	50	12.5
The complex	3.12	12.5	6.25	1.56
Cerium(III) trifluoromethanesulfonate	12.5	>100	25	6.25
Penicillin	1.3	>100	>100	2.1

(H_3L^1) and bis-(2-((4-bromosalicylidene)aminoethyl))(2-aminoethyl)amine (H_3L^2). The formation of H_3L^2 instead of pure H_3L^1 may be due to the formation of hydrogen bonds of the NH_2 groups of H_3L^2 in the complex. In fact, we have tried to prepare the complex by the reaction of H_3L^1 with cerium(III) trifluoromethanesulfonate, or by the reaction of 4-bromosalicylaldehyde, tris(2-aminoethyl)amine and cerium nitrate or cerium acetate, but no single crystals can obtain. As usually observed for the preparation of cerium(IV) complexes, Ce^{III} underwent aerial oxidation to Ce^{IV} in the synthetic route. The peroxide ligand of the complex may come from air, because we did not use any peroxides during the synthesis and crystallization. From the NMR signals, the prepared $\text{Ce}(\text{IV})$ complex exists in the solution. See Scheme 1

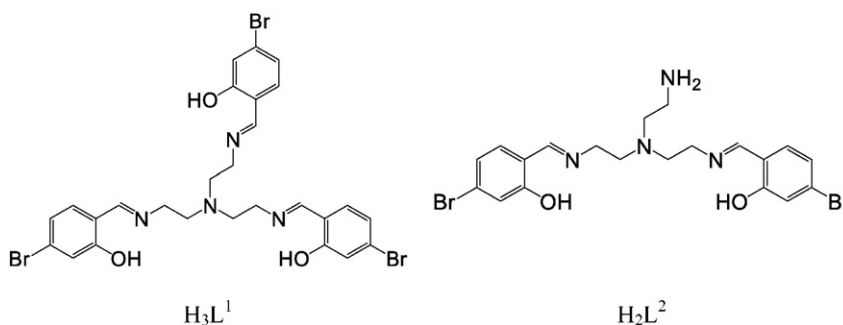
X-ray crystallography [26] reveals that the asymmetric unit of the complex contains a phenolato- and peroxy-bridged dinuclear cerium(IV) complex cation (Fig. 1) and a disordered trifluoromethanesulfonate anion. In the cationic part, the ligands L^1 and L^2 coordinate to the Ce atoms through all the phenolate oxygen, imino nitrogen and amino nitrogen atoms. The two Ce atoms in the complex are bridged by one phenolate oxygen atom from L^1 , and two peroxy oxygen atoms. The distance between the two oxygen atoms of peroxy group is 1.408(10) Å, which is within the values observed in peroxide bridged cerium complexes [22,23]. The Ce– N_{amino} bond lengths of 2.71–2.75 Å and the Ce–O bond lengths of 2.21–2.39 Å are shorter than those observed in a Ce(III) complex with tris(2-(salicylideneamino)ethyl)amine [27], while the Ce– N_{imino} bond lengths of 2.57–2.65 Å are comparable to that observed in the complex. As for similar Ce(IV) complexes with tris(2-((3,5-di-*tert*-butylsalicylidene)amino)ethyl)amine [28–31], the Ce– N_{imino} , Ce– N_{amino} and Ce–O bond lengths are comparable to those in the present complex. The Ce– O_{peroxy} distance is a little shorter than those observed in the peroxide bridged cerium complex with similar tripodal Schiff base ligands

[22]. As expected, the bond lengths between the Ce atom and the central N atoms of the tripodal Schiff bases are longer than the remaining Ce–N bonds. In ligand L^1 , the dihedral angles among the three benzene rings are 34.7(5)°, 1.7(5)°, and 35.9(5)°. In ligand L^2 , the dihedral angle between the two benzene rings is 13.9(5)°. See Fig. 2

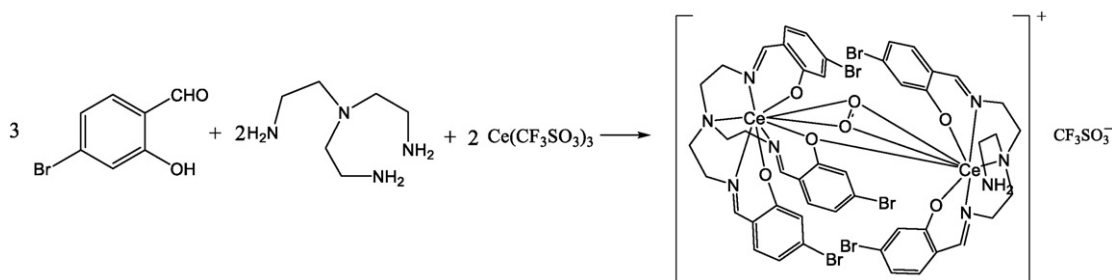
In the crystal structure of the complex, the dinuclear cerium complex cations are linked through intermolecular N–H \cdots O hydrogen bonds [N8–H8A \cdots O5ⁱ: N8–H8A = 0.90 Å, H8A \cdots O5ⁱ = 2.34 Å, N8 \cdots O5ⁱ = 3.131(10) Å, N8–H8A \cdots O5ⁱ = 147.0(3)°; N8–H8B \cdots O4ⁱ: N8–H8B = 0.90 Å, H8B \cdots O4ⁱ = 2.50 Å, N8 \cdots O4ⁱ = 3.233(11) Å, N8–H8B \cdots O4ⁱ = 138.5(3)°; symmetry code for i: 1–x, 1–y, 1–z] to form a dimer. The trifluoromethanesulfonate anions are located among the cations.

In the spectrum of the complex, the strong characteristic absorption of the $\nu(\text{C}=\text{N})$ vibration is located at 1621 cm^{-1} [32]. The bands indicative of the trifluoromethanesulfonate anion are observed at 1145, 1063, 1032 and 602 cm^{-1} . The S–O stretching vibration is observed at 1063 and 1032 cm^{-1} . The weak band at 3279 cm^{-1} can be assigned to $\nu(\text{N}-\text{H})$, and the medium band at 1271 cm^{-1} can be assigned to $\nu(\text{C}-\text{O})$ [33]. The UV–Vis spectrum of the complex is shown in Fig. 3, which was recorded in acetonitrile. The typical absorptions at 235, 266 and 320 nm are attributed to the $\pi-\pi^*$ transition of the aromatic ring and azomethine chromophores [34]. The IR and UV–Vis spectra are in accordance with the results determined by single crystal X-ray diffraction.

Thermal gravimetric (TG) and differential thermal analyses (DTA) were conducted to examine the stability of the complex (Fig. 4). The first step started at 220 °C and completed at 377 °C, corresponding to the loss of the trifluoromethanesulfonate anion. The observed weight loss of 9.0% is in accordance with the calculated value. The second



Scheme 1. The Schiff base ligands.



Scheme 2. Synthetic procedure of the complex.

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