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Adjustment of the structures and biological activities by the ratio of NiL to RE for two sets of Schiff Base complexes $[(NiL)_n RE]$ (n = 1 or 2; RE = La or Ce)

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ABSTRACT

Two sets of 3d–4f complexes $[(NiL)_nRE]$ (n=1, 2; RE=La and Ce; H₂L=N,N'-bis(3-ethoxysalicylidene) ethylenediamine) were obtained by reacting NiL with RE(NO₃)₃ in the ratios of 1/1 and 2/1, respectively. With the NiL/RE ratio changing from 1/1 to 2/1, not only the crystal structures were changed from discrete dinuclear complexes [(NiL)RE] to sandwich-like trinuclear complexes $[(NiL)_2RE]$, but also the biological activities were greatly influenced. The trinuclear complexes $[(NiL)_2RE]$ exhibited higher antimicrobial activities than the corresponding dinuclear counterpart [(NiL)RE].

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For the past few decades, the biological activities of rare earth and transition metal complexes containing Schiff base ligands have been widely studied, but the adjustment of structures and activities is still a challenging subject [1-4]. Much effort has been devoted to the design and synthesis of different kinds of Schiff bases and their metal complexes [5]. Salen-type Schiff base (H_2 salen = N, N'-bis (salicylidene) ethylenediamine) is of great interest and importance for its structural flexibility, special chelating property and easy preparation. Its alkoxy derivatives contain an inner site with N- and O-donor chelating centers suitable for the linkage to d-block ions. The outer coordination site with its O-donor atoms is greater than the inner one and can act as a type of crown ether ligands to incorporate larger ions, such as rare earth ions [6]. More interestingly, these compartmental ligands can form not only the classical 3d-4f dinuclear complexes but also the trinuclear ones between two set of Schiff base oxygen [7]. As far as 3d-4f complexes were concerned, the main research focus was centered on their magnetic and electric properties [8], and the antimicrobial activities had been rarely studied [9].

In this paper, N, N'-bis(3-ethoxysalicylidene)ethylenediamine (H₂L) was used to coordinate with nickel and rare earth ions (RE = La and Ce) to construct 3d–4f heteronuclear complexes (Scheme 1). It was the first time that trinuclear (NiL)₂RE complexes and dinuclear [(NiL)RE] complexes (RE = La and Ce) could be obtained, respectively, when the ratios of NiL to RE were 2:1 and 1:1, and their antimicrobial activities were also greatly influenced with the changes of their structures. The

trinuclear [(NiL)₂RE] complexes had higher antimicrobial activities than the corresponding dinuclear counterpart [(NiL)RE].

N, N'-bis(3-ethoxysalicylidene)ethylenediamine (H₂L) was prepared by the 2:1 condensation of 3-ethoxysalicylaldehyde and ethylenediamine in methanol solution. Both trinuclear complexes [(NiL)₂RE] (**1a** and **1b**) and dinuclear complexes [(NiL)RE] (**2a** and **2b**) could be prepared directly from solutions by controlling the stoichiometric ratio of NiL/RE to 2/1 and 1/1, respectively. It was worthy to note that complex **2a** could also be obtained from **1a**, if complex **1a** was redissolved in the methanol solution containing lanthanum(III) nitrate hexahydrate and slowly evaporated for several days. A reverse process from **2a** to **1a** could also be realized by dissolving **2a** in the methanol solution containing NiL and after several days of evaporation. Similar results were found for the transformation between **1b** and **2b**. It was not unreasonable to think that these reversible transformations should be related with the exchange equilibrium of complexes in solutions [10,11].

Complexes **1a** and **1b** are isostructure, so only **1a** is given and discussed here (Fig. 1). Complex **1a** crystallizes in the space group $P2_1/n$ with the lanthanum wrapped up by two NiL entities and two NO_3^- anions to form a sandwich-like structure. Lanthanum is linked to unusual 12 oxygen atoms, four coming from the phenolato atoms, four from the ethoxy oxygen atoms and four from NO_3^- anions. Three kinds of La–O bond distances are significantly different in **1a**, the longest being the La–O (ethoxy) separations and the shortest being the La–O (phenolate). The coordination of two nickel (II) can be considered as square planar, which is defined by two nitrogen atoms (N1 and N2) and two oxygen atoms (O1 and O2) from one ligand. The nickel atom is situated in the mean N_2O_2 coordination plane. The separation of Ni1...La1 is 3.532(4) Å which is slightly shorter than

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Scheme 1. Synthesis routine of the complexes.

that of Ni2...La1 (3.564(4) Å). The intramolecular distance of Ni1... Ni2 is 3.958(3) Å.

Complex **2a** is isostructural with **2b** which has been reported by others [12]. For **2a**, the central region of the dinuclear entity is occupied by Ni(II) and La(III) that are doubly bridged one to the other by two phenolato oxygen atoms from the ligand. The nickel lanthanum separation is 3.452(4) Å which is shorter than that of **1a**.



Fig. 1. ORTEP diagram of complex 1a. Thermal ellipsoids are at the 30% probability level.

The nickel ion adopts a square planar coordination mode. The donor centers are alternatively above and below the mean N_2O_2 plane, with an average deviation from the plane of 0.0841(3) Å, while Ni1 is 0.0062(3) Å above this square plane. The dihedral angles between the planes 01–Ni1–O2 and 01–La1–O2 are equal to 5.9(2) Å, suggesting that the bridging group is almost coplanar. The lanthanum(III) center in **2a** has a decacoordination environment of O atoms. In addition to the two phenolate O atoms, the lanthanum(III) achieves its environment with two ethoxy oxygen atoms from L and six oxygen atoms coming from three bidentate nitrato ions. The three kinds of La–O bond distances are significantly different, the shortest being the La–O (phenolate) and longest being the La–O (ethoxy) separations (Fig. 2).

The anti-microbial activities of NiL, the trinuclear complexes (1a and **1b**) and dinuclear complexes (**2a** and **2b**) against bacteria (*E. coli* and S. aureus) and fungi (CA) were tested and the results were summarized in Table 1. The results indicated that there was no obvious activity observed by NiL against S. aureus and CA, except for the weak inhibition to E. coli, whereas complexes 1a, 2a, 1b and 2b had an obvious inhibition on the culture of E. coli, S. aureus and CA. The activities of anti-E. coli and anti-CA of 1a were higher than those of other complexes, with inhibition zones of 20 mm and 8 mm, respectively. The anti-S. aureus activity of 1a was similar with that of 1b, but on the whole, the trinuclear complexes (whether 1a or 1b) had a better inhibition property than the dinuclear complexes (2a or 2b). Compared with these synthesized 3d-4f heteronuclear complexes, pure $RE(NO_3)_3$ (RE = La or Ce) showed lower anti-microbial activities than the trinuclear complexes (1a and 1b), even lower than the dinuclear complexes (2a and 2b). These results indicated that the anti-microbial activities of rare earth ions could be improved when coordinated with NiL ligand, although NiL has no obvious activities in itself. The reason that the anti-microbial activities of the trinuclear complexes (1a and 1b) are advantageous over those of the dinuclear complexes (2a and 2b) may also be attributed to the function of NiL



Fig. 2. ORTEP diagram of complex 2a. Thermal ellipsoids are at the 30% probability level.

ligand which can improve the anti-microbial activities of rare earth ions. These biological activity results may provide us a new way to adjust the antimicrobial activities of rare earth ions by coordinating them with different ratios of NiL ligand.

In conclusion, two sets of 3d–4f complexes $[(NiL)_nRE]$ (n = 1, 2; RE = La and Ce) containing Salen-type Schiff base ligand were prepared by adjusting the ratio of NiL/RE in 1/1 and 2/1, respectively. The trinuclear complexes $[(NiL)_2RE]$ exhibited higher antimicrobial activities than the dinuclear counterpart [(NiL)RE]. The results indicated that the antimicrobial activities of rare earth ions could be adjusted by coordinating with adequate ratio of metal complex ligands. It may be a promising way to explore new types of adjustable antimicrobial reagents.

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Appendix A. Supplementary material

CCDC 750887, 750888 and 750889 contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 1	
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Zone of inhibition of the compounds.

Compounds	E. coli	S. aureus	CA
NiL	2	-	-
1a	20	10	8
2a	11	6	5
1b	15	11	6
2b	9	7	4
$La(NO_3)_3$	4	3	2
$Ce(NO_3)_3$	3	3	3
DMSO	-	-	-
Standard drugs	Penicillin 37	Gentamicin 17	Nistatin 26

"-", indicates that the bacteria are resistant to the compounds. Zones of inhibition are reported for diameters in mm. Disks were inoculated with 6 mg of the compounds dissolved in DMSO.

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. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.12.010.

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