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Hydrothermal syntheses, structures and properties of three cyclic tetranuclear complexes and one 1D chain complex with 3,5-dinitrosalicylate

De-Cai Wen [a,b], Shi-Xiong Liu [a,*], Joan Ribas [c]

[a] Department of Chemistry, Fuzhou University, Fuzhou 350002, PR China
[b] Department of Chemistry, Longyan University, Longyan 364000, PR China
[c] Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain

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Abstract

The hydrothermal reactions of $Co(OAc)_2 \cdot 4H_2O$, 3,5-dinitrosalicylate (3,5-$(NO_2)_2$sal) and 2,2′-bipyridine (2,2′-bipy) with different reaction periods give metallamacrocycles **1** and **2** with the same chemical formula Co_4(2,2′-bipy)$_4${3,5-$(NO_2)_2$sal}$_4$. Replacing $Co(OAc)_2 \cdot 4H_2O$ with $Zn(NO_3)_2 \cdot 6H_2O$, using the same synthetic procedures, results in the formation of compound [Zn(2,2′-bipy){3,5-$(NO_2)_2$sal}]$_n$ (**3**) with a 1D chain structure and the metallamacrocycle compound Zn_4(2,2′-bipy)$_4${3,5-$(NO_2)_2$sal}$_4$ (**4**). Compounds **1** and **2** crystallize as two different polymorphs of cyclic tetranuclear compounds. Compounds **3** and **4** are polymorphic too. The compounds **1** and **4** are isomorphous. The weak coordination interactions have significant influence on the spacial orientations of the 3,5-$(NO_2)_2$sal ligand, and may affect the crystallization processes. There are antiferromagnetic interactions in the cyclic tetranuclear cobalt(II) compounds **1** and **2**. Compound **3** exhibits weak fluorescent emission in the solid state at room temperature.

Keywords: Metallamacrocycle; Supramolecular isomerism; Hydrothermal synthesis; Cobalt complex; Zinc complex

1. Introduction

Self-assembly in metallamacrocycles is a growing area at the forefront of modern supramolecular chemistry. Many diverse metallamacrocycles, such as molecular triangles, squares, rectangles, pentagons and hexagons, have been synthesized [1,2]. Pd(II) and Pt(II) units and N-donor ligands are the most favorite building blocks, and these species are highly charged. Except for 4,4′-bipy derivatives and imidazolate derivatives, most of the ligands used in the formation of metallamacrocycles are easily broken during hydrothermal reactions. Therefore, most of the syntheses of metallamacrocycles are solution reactions. Formation of metallamacrocycles by hydrothermal reactions is quite rare. On the other hand, considerable research effort has been focused on the study of polymorphs and isomorphous compounds in supramolecular chemistry [3,4].

Many carboxylate ligands have been shown to be good building blocks in the preparation of polynuclear complexes with desired topologies owing to their rich coordination modes [5]. Although a lot of carboxylate complexes have been studied, reports on the syntheses and magnetic properties of pentacoordinated cobalt(II) carboxylate complexes are far less in number.

We found that the choice of ligand plays an important role in preparing new metallamacrocycles. The self-assembly of decanuclear metallacrowns based on 3d-series metals M(III) with *N*-acyl salicylhydrazides was reported in our group [6a]. As shown in Scheme 1, the fully deprotonated salicylate(sal^{2-}) can act in two coordination modes: monochelating-bridging (I*a*) and bichelating (I*b*). Acting as mode I*b*, sal^{2-} may be a good linker to generate neutral metallamacrocycles with M(II), sal^{2-} in this case is similar

* Corresponding author. Tel./fax: +86 591 83729860.
E-mail address: shixiongliu@yahoo.com (S.-X. Liu).

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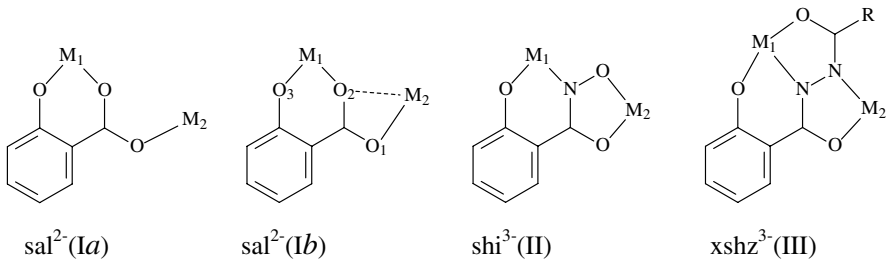
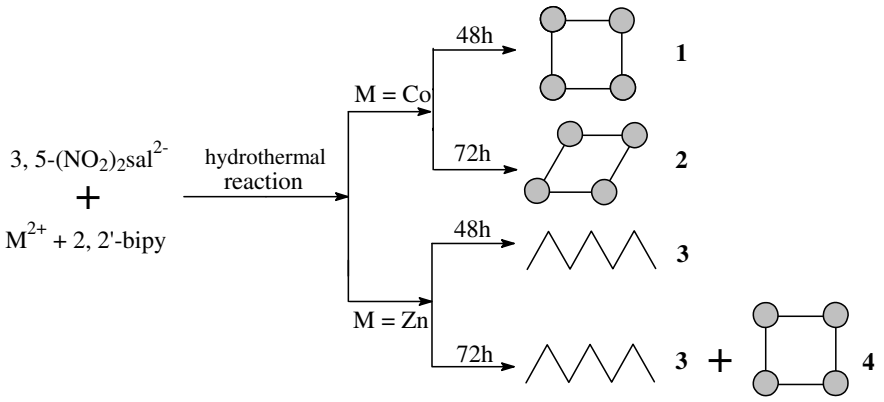


Scheme 1. Binding models of sal^{2-} in complexes **1**–**4** and binding mode of shi^{3-} and $xshz^{3-}$ ligands.



Scheme 2. Formation pathways of complexes **1**–**4**.

to $xshz^{3-}$ (*N*-substituted salicylhydrazidate, H_3xshz) or shi^{3-} (substituted salicylhydroxamic acid, H_3shi) [1a,6,7]. There is a weak coordination between M2 and O2 in model I*b*. The alternation between the existence and the non-existence of weak coordination may lead to polymorphs.

As a continuation of our effort in the formation of metallamacrocycles, we attempted to explore the assembly of metallamacrocycles by hydrothermal reactions, using 3d-series metals M(II), 3,5-dinitrosalicylate (3,5-$(NO_2)_2$sal) and 2,2′-bipyridine (2,2′-bipy). Herein, we report the syntheses, crystal structures and properties of four Co/Zn 3,5-$(NO_2)_2$sal complexes. Among the four title compounds, the cyclic tetranuclear cobalt compounds **1** and **2** are polymorphic, and the zinc compounds **3** and **4** are polymorphic too. Complex **3** has a 1D chain structure while the complex **4** has a cyclic tetranuclear structure. Compounds **1** and **4** form an isomorphous pair. The title complexes **1**, **2** and **4** are the first examples of a 3,5-$(NO_2)_2$sal complex with a metallamacrocyclic structure. The formation pathway of the title compounds **1**–**4** is shown in Scheme 2. This research represents an interesting fact that different isomeric complexes can be obtained by a simple change of the reaction time.

2. Experimental

2.1. Materials and general procedures

All of the chemicals were obtained from commercial sources and were used without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN elemental analyzer. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants. Fluorescence spectroscopy was performed on a Perkin-Elmer LS 55 luminescence spectrometer.

2.2. Synthesis of complexes

2.2.1. Synthesis of $Co_4(2,2'\text{-bipy})_4\{3,5\text{-}(NO_2)_2sal\}_4$ (*1*)

A mixture of $Co(OAc)_2 \cdot 4H_2O$ (0.1 mmol), 2,2′-bipy (0.1 mmol), 3,5-dinitrosalicylic acid (0.2 mmol) and distilled water (10 ml), with the pH value adjusted to 7 by addition of 1 M NaOH solution, was put into a Teflon-lined autoclave (20 mL) and then heated at 180 °C for 48 h. Deep brown block-like crystals of **1** in 93% yield based on Co were obtained. *Anal.* Calc. for $C_{68}H_{40}N_{16}O_{28}Co_4$: C, 46.27; H, 2.2; N, 12.70. Found: C, 46.22; H, 2.25; N, 12.75%.

2.2.2. Synthesis of $Co_4(2,2'\text{-bipy})_4\{3,5\text{-}(NO_2)_2sal\}_4$ (*2*)

The same mixture as that for **1** was used, with the reaction at 180 °C for 72 h, resulting in deep brown block-like crystal of **2** in 92% yield based on Co. *Anal.* Calc. for $C_{68}H_{40}N_{16}O_{28}Co_4$: C, 46.27; H, 2.2; N, 12.70. Found: C, 46.19; H, 2.23; N, 12.76%.