

# Synthesis, structure and properties of $(V^{IV}O)_2M^{II}$ ( $M = Cu, Zn$ ) trinuclear complexes derived from a new macrocyclic oxamido vanadium (IV)-oxo ligand

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## HIGHLIGHTS

- ▶ A novel macrocyclic oxamidato-bridged vanadium (IV)-oxo mononuclear ligand has been prepared.
- ▶ Two new trinuclear complexes have been synthesized using VOL as a precursor.
- ▶ TGA showed thermal stability of the two trinuclear complexes is higher than the mononuclear.
- ▶ EPR spectra indicated the three oxo-vanadium samples remained in the active +4 oxidation state.

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## ABSTRACT

A novel macrocyclic oxamidato-bridged vanadium (IV)-oxo mononuclear ligand VOL (VOL = vanadium (IV)-oxo  $H_2L = 2,3$ -dioxo-5,6:13,14-dibenzo-7,10,12-trimethyl-1,4,8,11-tetraazacyclo-tetradeca-7,12-diene) (**1**) has been synthesized by solvent-thermal in situ reaction and characterized by electron paramagnetic resonance (EPR). Subsequently, using VOL as a precursor, its derivative trinuclear complexes  $[(VOL)_2Cu(CH_3OH)_2](ClO_4)_2 \cdot 2CH_3OH$  (**2**) and  $[(VOL)_2Zn(CH_3OH)_2](ClO_4)_2 \cdot 2CH_3OH$  (**3**) have been prepared and the crystal structures of the two complexes have been identified by the same method with **1**. Thermal stabilities of compounds **1**, **2** and **3** were studied and the results revealed that **1**, **2** and **3** could be stable up to 205 °C, 234 °C and 250 °C, respectively. Moreover, the simulation of the EPR spectra of **1**, **2** and **3** indicated the three oxo-vanadium samples were not oxidized and all of them remained in the active +4 oxidation state.

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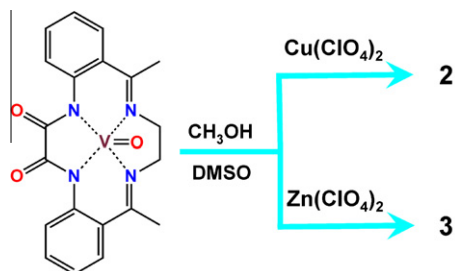
## 1. Introduction

The significant research efforts in the design and preparation of macrocyclic heterometallic complexes are stimulated by their applications in the fields of chemistry, physics, biology, and magnetic materials [1–5]. In order to construct such polynuclear complexes rationally, one of the best strategies is the ‘complex as ligand’ approach, i.e., utilizing a metal complex as a ligand to coordinate with an appropriate additional metal ion [6–9]. Moreover, as one of the well-known bridges, oxamido-bridged ligands, which contain potential donor groups towards another metal ion and can act as a bidentate ligand through its two exo-cis carbonyl oxygen atoms, have gained a great deal of attentions [10–13]. As far as we are aware, many macrocyclic polynuclear complexes based on copper and nickel oxamido complex ligands [14] as well as very few examples of the cobalt oxamido complex ligands [15–17] have been reported. However, examples of vanadium templated by macrocyclic complexes, especially with oxamido-bridge, are still rare [18].

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On the other hand, one of the most outstanding characteristics of the vanadium atom is the wide variety of coordination polyhedra due to the high nuclear charge (5+, 4+, and 3+): tetrahedral ( $V^{5+}$ ), square pyramids and distorted octahedra ( $V^{5+}$ ,  $V^{4+}$ ), trigonal bipyramid ( $V^{4+}$ ), and regular octahedra ( $V^{3+}$ ) [19]. Owing to the character of the vanadium atom above, some inorganic–organic hybrid vanadium phosphates and selenates systems with zero-dimensional, 1D chain, 2D layer and 3D network structures have been prepared successfully in recent years [27–31], as well as some vanadium oxides templated by organic amines and other bridging ligands [32]. In addition, as for tetravalent vanadyl species ( $V^{4+}$ ), EPR spectroscopy is a powerful characterization method and a great deal of EPR studies have addressed the presence and coordination geometry of the paramagnetic  $V^{4+}$  ions on vanadium oxide nanotubes in recent years [33–35]. Taking all the above facts into account and in continuation of our interest in macrocyclic polynuclear complexes, we introduce vanadium into this system and report here a new mononuclear precursor VOL (VO = vanadium (IV)-oxo and  $H_2L = 2,3$ -dioxo-5,6:13,14-dibenzo-7,10,12-trimethyl-1,4,8,11-tetraazacyclo-tetradeca-7,12-diene) and two novel trinuclear complexes  $[(VOL)_2Cu(CH_3OH)_2](ClO_4)_2 \cdot 2CH_3OH$  (**2**) and  $[(VOL)_2Zn(CH_3OH)_2](ClO_4)_2 \cdot 2CH_3OH$  (**3**).



**Scheme 1.** Formation of oxamido-bridged copper (II) and zinc (II) complexes.

$2\text{CH}_3\text{OH}$  (**3**) derived from the new VOL precursor (Scheme 1). The obtained compounds were characterized by single-crystal X-ray diffraction, IR spectra, elemental analyses and electron paramagnetic resonance (EPR). Furthermore, their thermal stabilities were also investigated.

## 2. Experimental

### 2.1. General materials and physical measurements

All chemicals and solvents were commercially available reagents of analytical grade and used as received without further purification. The ligand  $\text{H}_2\text{L}$  ( $\text{H}_2\text{L} = 2,3$ -dioxo-5,6:13,14-dibenzo-7,10,12-trimethyl-1,4,8,11-tetraazacyclo-tetradeca-7,12-diene) were prepared as described previously in the literature [20]. Elemental analyses for C, H, and N were carried out on a Perkin–Elmer 240 analyzer. Sample powders dispersed on KBr disks were run on the FT-IR spectrometer in the  $4000$ – $400\text{ cm}^{-1}$  range. X-band EPR spectra of a crystalline sample were recorded on a Bruker EMX-6/1 D-SPC spectrometer at room temperature. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG–DTA analyzer with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  from ambient temperature to  $800\text{ }^\circ\text{C}$ .

### 2.2. Synthesis

#### 2.2.1. VOL precursor (**1**)

In order to prevent the oxidation of V(IV) to V(V), solvent-thermal synthesis route was adopted for the precursor mononuclear complex

**1**, which is different from the traditional templated solvent routes for other CuL and NiL complexes [21]. A mixture of  $\text{VOSO}_4\cdot\text{H}_2\text{O}$  (0.178 g, 1 mmol),  $\text{H}_2\text{L}$  (0.326 g, 1 mmol), ethylenediamine (1.2 mL, 2 mmol) and methanol (15 mL) was sealed in a 18 mL Teflon-lined reactor at  $120\text{ }^\circ\text{C}$  under autogenous pressure for 72 h. After slowly cooling to room temperature, good-quality dark red crystals were obtained in a yield of 60.9%, washed with distilled water, methanol and dried in air. Elemental Anal. Calc. for  $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_3\text{V}$ : C, 58.11; H, 4.36; N, 13.56%. Found: C, 57.96; H, 4.31; N, 13.49%.

#### 2.2.2. $[(\text{VOL})_2\text{Cu}(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2\cdot 2\text{CH}_3\text{OH}$ (**2**)

To a methanol (20 mL) solution of VOL (0.2 mmol, 0.083 g) was added a solution of  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.036 g) in methanol (10 mL), followed by the addition of DMSO (dimethyl sulfoxide) solution (2 mL). The mixture was stirred under reflux for 6 h, the resulting red solution was cooled and filtered. Red single crystals suitable for X-ray analysis were collected with a yield of 75% by slow evaporation of the filtrate in the open air at room temperature three weeks later. Elemental Anal. Calc. for  $\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{CuN}_8\text{O}_{18}\text{V}_2$ : C, 43.51; H, 4.36; N, 9.35%. Found: C, 43.42; H, 4.27; N, 9.26%.

#### 2.2.3. $[(\text{VOL})_2\text{Zn}(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2\cdot 2\text{CH}_3\text{OH}$ (**3**)

The synthesis method of **3** was similar with **2**,  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  was substituted by  $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.037 g) and the same VOL yielded the complex **3** (70%). Elemental Anal. Calc. for  $\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{ZnN}_8\text{O}_{18}\text{V}_2$ : C, 43.49; H, 4.34; N, 9.21%. Found: C, 43.56; H, 4.29; N, 9.24%.

### 2.3. X-ray crystallography

Diffraction intensity data for single crystals of complexes **1–3** were mounted on room temperature on a Bruker Smart 1000 CCD area detector equipped with a graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct method SHELXS-97 and refined by the full-matrix least-squares method on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms [25,26]. Crystal data and details of structural determination refinement are summarized in Table 1.

**Table 1**  
Crystal data and structure refinements for complexes **1–3**.

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Formula	$\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_3\text{V}$	$\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{CuN}_8\text{O}_{18}\text{V}_2$	$\text{C}_{44}\text{H}_{50}\text{Cl}_2\text{N}_8\text{O}_{18}\text{V}_2\text{Zn}$
Formula weight	413.32	1217.26	1217.09
Space group	P2(1)/n	P2(1)/c	P2(1)/c
Crystal system	Monoclinic	Monoclinic	Monoclinic
$a$ (Å)	9.2072(17)	10.478(2)	10.454(2)
$b$ (Å)	19.091(3)	15.658(3)	15.830(3)
$c$ (Å)	10.5796(19)	15.269(3)	15.524(3)
$\alpha$ (°)	90	90	90
$\beta$ (°)	109.636(3)	90.26	91.09
$\gamma$ (°)	90	90	90
$V$ (Å <sup>3</sup> )	1751.5(5)	2505.0(9)	2568.6(9)
$Z$	4	2	2
$T$ (K)	294(2)	113(2)	293(2)
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.567	1.614	1.574
Crystal size (mm)	$0.22 \times 0.20 \times 0.16$	$0.20 \times 0.18 \times 0.16$	$0.20 \times 0.20 \times 0.20$
Completeness to $\theta = 25.02^\circ$	99.9%	99.8%	98.4
$\mu$ (Mo $\text{K}\alpha$ ) (mm <sup>-1</sup> )	0.598	0.975	1.004
Goodness- $F^2$	1.015	1.149	1.087
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0371, 0.0885	0.0631, 0.1618	0.0792, 0.1479
$R_1, wR_2$ (all data)	0.0644, 0.1019	0.0873, 0.1736	0.1307, 0.1682

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