

Targeted Synthesis of Heterobimetallic Compounds Containing a Discrete Vanadium(V)– $\mu$ -Oxygen–Iron(III) CoreKisholoy Bhattacharya,<sup>†</sup> Manoranjan Maity,<sup>†</sup> Dhruvajyoti Mondal,<sup>†</sup> Akira Endo,<sup>‡</sup> and Muktimoy Chaudhury<sup>\*,†</sup><sup>†</sup>Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700032, India<sup>‡</sup>Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

## S Supporting Information

**ABSTRACT:** Heterobimetallic compounds  $[L^1OV^V=O \rightarrow Fe(\text{metsalophen})(H_2O)]$  (**1**) and  $[L^2OV^V=O \rightarrow Fe(\text{metsalophen})(H_2O)]CH_3CN$  (**2**), where  $H_2L^1$  and  $H_2L^2$  are tridentate dithiocarbazate-based Schiff base ligands, containing a discrete  $V^V-\mu-O-Fe^{III}$  angular core have been synthesized for the first time through a targeted synthesis route: confirmation in favor of such a heterobimetallic core structure has come from single-crystal X-ray diffraction analysis and electrospray ionization mass spectrometry.

Heterobimetallic compounds containing the  $M-O-M'$  framework are a topic of enormous interest in contemporary coordination chemistry research because of their interesting properties arising out of two dissimilar metal ions placed together in close proximity.<sup>1</sup> Nature has used combinations of different metal ions in the active sites of many metalloenzymes to catalyze some of the fundamental reactions of biology. Cytochrome C oxidase and superoxide dismutase are the two enzymes belonging to this category.<sup>2</sup> This information has motivated chemists to develop protocols for the synthesis of oxo-bridged heterobimetallic compounds with the prospect of their use as catalysts for many chemical reactions of industrial importance.<sup>1a,3</sup>

It is well-known that vanadium in higher oxidation states (IV and V) is oxophilic. It forms  $\mu$ -oxidodivanadium compounds involving  $(V_2O_3)^{n+}$  ( $n = 4, 3,$  and  $2$ ) cores almost spontaneously, and a large number of such compounds were crystallographically characterized.<sup>4–6</sup> On the contrary, only a few heterobimetallic compounds, authenticated by X-ray crystallography, with a discrete  $V-O-M$  core were reported in the literature.<sup>7</sup>

As a part of our ongoing project on the coordination chemistry of vanadium,<sup>8</sup> we recently developed a methodology for the synthesis of  $\mu$ -oxidodivanadium(V) compounds with an asymmetry in the metal coordination environments in the form of both octahedral and square-pyramidal  $V^V$  centers.<sup>8b,c</sup> In order to achieve that, we chose  $[V^{IV}O(\text{salen})]^+$  as the precursor for the octahedral  $V^V$  center. This compound, in solution when exposed aeri ally in the presence of an added anion, was reported<sup>9</sup> to be oxidized to  $[V^VO(\text{salen})]^+$ . The  $V^V$  center in this cationic compound achieves an octahedral geometry by accepting the incoming anion in its vacant coordination site, trans to the terminal oxido group. To gain access to a square-

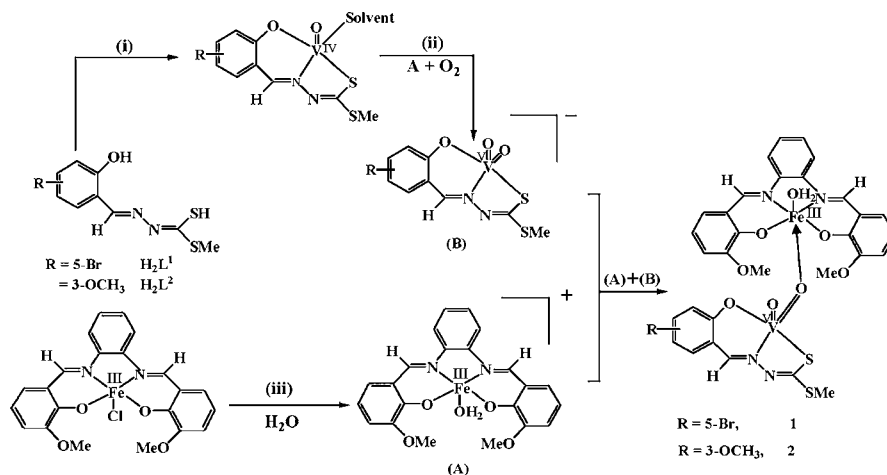
pyramidal  $V^V$  center, a dithiocarbazate-based tridentate biprotic ligand ( $H_2L$ ) was chosen. This ligand can generate an anionic *cis*-dioxidovanadium(V) center  $[LV^VO_2]^-$  when  $[V^{IV}O(\text{acac})_2]$  in acetonitrile is oxidized aeri ally by refluxing with  $H_2L$  in the presence of an added cation.<sup>10</sup> Thus, when  $[V^VO(\text{salen})]^+$  is the chosen cation, the generated *cis*-dioxido anion  $[LV^VO_2]^-$  is accommodated in the vacant coordination site of  $V^V$  in the cation to generate the desired  $\mu$ -oxidodivanadium(V) compound with coordination asymmetry.<sup>8b,c</sup>

We modified the above methodology, as displayed in Scheme 1, for the synthesis of the targeted molecules  $[L^1OV^V-O-Fe(\text{metsalophen})(H_2O)]$  (**1**) and  $[L^2OV^V-O-Fe(\text{metsalophen})(H_2O)]CH_3CN$  (**2**) with a discrete  $V^V-O-Fe^{III}$  core. For this to happen, we chose  $[Fe^{III}(\text{metsalophen})Cl]$  [ $H_2\text{metsalophen} = N,N'$ -bis(3-methoxysalicylidine)-1,2-diaminobenzene] as a replacement for  $[V^{IV}O(\text{salen})]^+$  in our original synthesis protocol.<sup>8b,c</sup> This precursor compound, upon being treated with  $AgNO_3$  in acetonitrile, generates a cationic species  $[Fe^{III}(\text{metsalophen})(H_2O)]^+$  that actually initiates the aeri ally oxidation of the putative  $[LV^VO(\text{solvent})]$  compound<sup>10</sup> [ $H_2L = S$ -methyl-3-(*S*-bromo-2-hydroxyphenyl)methylene-dithiocarbazate ( $H_2L^1$ ) and *S*-methyl-3-(3-methoxy-2-hydroxyphenyl)methylenedithiocarbazate ( $H_2L^2$ )] to generate the anionic *cis*-dioxido species  $[LV^VO_2]^-$ , which ultimately is accommodated into the vacant coordination site of  $[Fe^{III}(\text{metsalophen})(H_2O)]^+$  to get the desired heterobimetallic compound as the only isolable product. In practice,  $[V^{IV}O(\text{acac})_2]$  and  $H_2L$  were taken (1:1 mole ratio) in acetonitrile and refluxed to generate  $[LV^VO(\text{solvent})]$  species. To this was then added 1 equiv of the cationic species generated in situ in acetonitrile by the reaction of  $[Fe^{III}(\text{metsalophen})Cl]$  and  $AgNO_3$ , and the combined solution was stirred in the air to get the desired compounds as brown crystalline solids in moderate yields (details are available in the Supporting Information).

The IR spectrum of compound **1** shows a strong signature band at  $968\text{ cm}^{-1}$  (appearing at  $974\text{ cm}^{-1}$  in **2**) due to terminal  $V=O$  stretching. Of particular interest is the appearance of a moderately strong band at  $854\text{ cm}^{-1}$  ( $833\text{ cm}^{-1}$ ), which indicates the presence of a stretched  $V=O$  bond,<sup>11</sup> possibly as a part of the  $V=O \rightarrow Fe$  bridging moiety (see later). Electrospray ionization mass spectrometry (ESI-MS) spectra (in positive-ion mode) for the compounds have been recorded

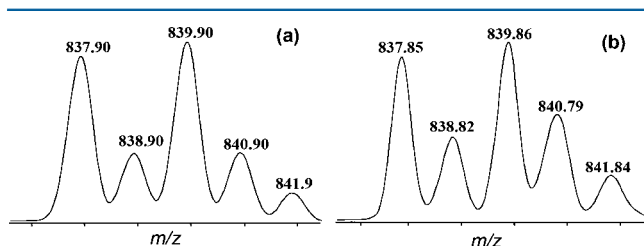
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Scheme 1. Protocol Followed for the Synthesis of Compounds 1 and 2<sup>a</sup>

<sup>a</sup>Conditions: (i) VO(acac)<sub>2</sub>/CH<sub>3</sub>CN; (ii) cation-assisted aerial oxidation, (iii) AgNO<sub>3</sub>/CH<sub>3</sub>CN.

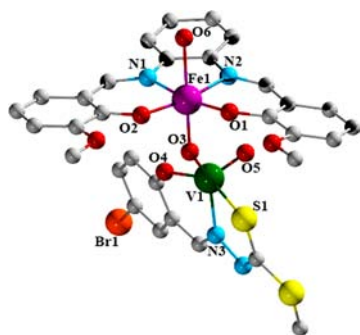
in an acetonitrile solution. Compound 1 displays its molecular-ion peak at 839 cm<sup>-1</sup> due to the [M – H<sub>2</sub>O + Na]<sup>+</sup> ionic species, while for 2, the corresponding peak due to [M – H<sub>2</sub>O – CH<sub>3</sub>CN + H]<sup>+</sup> species appears at 768 cm<sup>-1</sup>. In Figure 1 is



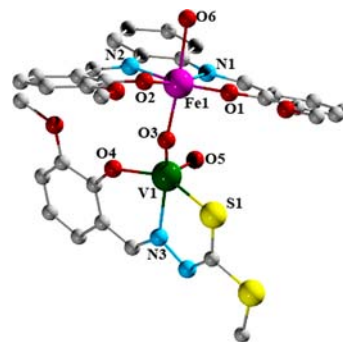
**Figure 1.** Isotopic distribution pattern for compound 1: (a) simulation curve; (b) experimental curve.

displayed the isotope distribution pattern for the molecular-ion peak of compound 1, together with its simulation pattern. Similar results are also obtained for compound 2 (Figure S1 in the Supporting Information), thus providing evidence in favor of the proposed heterobimetallic structure that remains intact in an acetonitrile solution.

The molecular structures and atom-labeling schemes for 1 and 2 are shown in Figures 2 and 3, respectively, which provide confirmatory evidence in support of their discrete  $\mu$ -oxido heterobimetallic structures. Selected metrical parameters of these structures are summarized in Tables S1 and S2 (in the



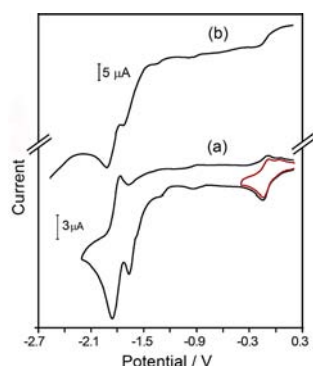
**Figure 2.** Molecular structure and atom-labeling scheme for compound 1. Hydrogen atoms have been omitted for clarity.



**Figure 3.** Molecular structure and atom-labeling scheme for compound 2. Hydrogen atoms and solvent molecule have been omitted for clarity.

Supporting Information). The molecules contain octahedral Fe<sup>III</sup> and square-pyramidal V<sup>V</sup> centers, as is evident from the angles O6–Fe1–O3 168.3(3)<sup>o</sup> [172.3(2)<sup>o</sup> for compound 2] and O5–V1–O3 109.0(3)<sup>o</sup> [107.65(19)<sup>o</sup>]. The metal centers are connected by a bridging atom O3, such that Fe1–O3 1.984(7) Å [1.951(4) Å] and V1–O3 1.684(6) Å [1.688(4) Å] distances differ widely, with the latter being close to a V=O terminal bond. This implies that the oxido bridge (V–O–Fe) in these compounds is best described by the canonical structure V=O→Fe.<sup>7b</sup> The V1–O3–Fe1 bridge angle is 148.4(4)<sup>o</sup> [144.9(2)<sup>o</sup>], close to what is expected when two square-pyramidal metal centers are connected by an oxido bridge.<sup>5g,i</sup> The Fe...V separation is 3.53 Å [3.47 Å], and the dihedral angle between the basal planes surrounding the metal centers is 70.12<sup>o</sup> [64.79<sup>o</sup>].

The redox behavior of 1 and 2 was studied by cyclic voltammetry in *N,N*-dimethylformamide (DMF) solution (0.1 M TBAP) using glassy carbon working and Ag/AgCl reference electrode. The voltammograms involving three redox processes are quite similar, as shown in Figure 4 for a representative compound 1 (Figure S2 in the Supporting Information for 2). It includes a reversible process at  $E_{1/2} = -0.15$  V ( $\Delta E_p = 54$  mV, process I), an irreversible process at  $E_{pc} = -1.67$  V (process II), and a quasi-reversible process at  $E_{1/2} = -1.81$  V ( $\Delta E_p = 90$  mV, process III). All of these processes are cathodic, as judged by steady-state voltammetry. Normal-pulse voltammetry (NPV), also shown in Figure 4,



**Figure 4.** (a) Cyclic and (b) normal-pulse voltammograms of compound **1** in DMF using a glassy carbon working electrode.

indicates process III to involve twice as many electrons as those in process I. Coulometric confirmations of the electron stoichiometry for these processes have failed because of the instability of the electrolysis products in the longer time scale of coulometric experiments. Because  $\text{Fe}^{\text{III}}$  and  $\text{V}^{\text{V}}$  centers are both electroactive, as is the free ligand  $\text{H}_2\text{metsalophen}$ ,<sup>12</sup> we need to record the cyclic voltammogram of the precursor compound  $[\text{Fe}(\text{metsalophen})\text{Cl}]$  under identical conditions as a control to understand the origin of the redox processes, displayed in Figure 4. The control cyclic voltammogram (Figure S3 in the Supporting Information) involved three quasi-reversible processes, all involving identical numbers of electron(s), as judged by the NPV experiment. These include two ligand-based reductions<sup>12</sup> at  $E_{1/2} = -1.56$  and  $-1.78$  V. The third one at  $-0.20$  V is most likely due to a  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  reduction. Taking a cue from this experiment, we now feel confident to conclude that process I in Figure 4 is due to a  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  reduction, process II is due to a ligand-based reduction(s),<sup>12</sup> and process III involves a combination of both vanadium-based ( $\text{VO}^{3+}/\text{VO}^{2+}$ ) and ligand-based reduction, thus accounting for a two-electron involvement. In fact, the observation of  $\text{VO}^{3+}/\text{VO}^{2+}$  reduction at  $E_{1/2} = -1.74$  V of a closely similar vanadium(V) compound  $[\text{L}^3\text{VO}(\text{OCH}_3)]$  ( $\text{H}_2\text{L}^3$  is a similar dithiocarbazate-based tridentate ONS ligand)<sup>8c</sup> vindicates our assignment.

In summary, the synthesis of  $\mu$ -oxido heterodinuclear compounds containing a discrete  $\text{V}^{\text{V}}=\text{O}\rightarrow\text{Fe}^{\text{III}}$  core has been reported for the first time following a targeted synthesis route. The identities of the compounds have been established conclusively by ESI-MS as well as by single-crystal X-ray diffraction analysis. The V1–O3–Fe1 bridge angles in these compounds are ca.  $145^\circ$ , and the  $\text{Fe}\cdots\text{V}$  separations are close to 3.5 Å. Both of the metal centers undergo one-electron reductions at ca.  $-0.15$  ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) and  $-1.81$  V ( $\text{VO}^{3+}/\text{VO}^{2+}$ ) versus a Ag/AgCl reference.

## ■ ASSOCIATED CONTENT

### Supporting Information

Syntheses and characterization data, Tables S1 and S2 containing metrical parameters and CIF files for **1** and **2**, ESI-MS spectrum of **2**, and cyclic voltammograms of **2** and  $[\text{Fe}(\text{metsalophen})\text{Cl}]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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