

# ESI–IT–MS<sup>n</sup> and DFT calculation for electron affinities of bimetallic oxovanadium complexes

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**Abstract** The MS<sup>n</sup> spectra of three bimetallic oxovanadium complexes were obtained using an ion trap. The fragmentation pathways were elucidated. Common features and major differences between ESI–QTOF–MS/MS and ESI–IT–MS<sup>n</sup> spectra were compared. Electron affinities of several radical molecular anions were calculated by DFT and these could be used as an indicator of the ions' stability.

**Keywords** ESI–IT–MS<sup>n</sup> · DFT calculation · Electron affinity · Bimetallic oxovanadium complexes

## Introduction

Oxovanadium complexes play active roles in the fields of pharmaceutical research and organic synthesis. These complexes are potentially useful as orally available

treatments for diabetes mellitus and are used as catalysts in various oxidation reactions [1–9]. Structural characterization of the bimetallic oxovanadium complexes should be a key to the further development of their functions.

Electrospray ionization mass spectrometry (ESI–MS) is a useful approach for the characterization of oxovanadium complexes [10–16]. In mass spectrometry, the fragmentation behavior of radical ions has been found to be rich and fascinating, especially in the field of peptide sequencing [17–19]. However, the detection of radical ions by ESI–MS is very difficult and has therefore attracted much scientific interest. Nevertheless, there are very few reports on the observation of radical ions of vanadium complexes by ESI–MS [20] and none on the radical ions of mononuclear oxovanadium(V) complexes using this method [16]. Surprisingly, we detected radical ions of bimetallic oxovanadium complexes by electrospray ionization quadrupole time-of-flight mass spectrometry (ESI–QTOF–MS) [21]. In order to understand the structural features of bimetallic oxovanadium complexes leading to the formation of radical ions, electron affinities (EAs) of both mono- and bimetallic oxovanadium complexes were calculated by density functional theory (DFT). On the other hand, to verify the previously postulated fragmentation pathway of radical anions by electrospray ionization quadrupole time-of-flight tandem mass spectrometry (ESI–QTOF–MS/MS) [21], three bimetallic oxovanadium complexes **1–3** (Fig. 1) were analyzed by electrospray ionization ion trap multi-stage mass spectrometry (ESI–IT–MS<sup>n</sup>) and ESI–QTOF–MS/MS. The main differences were discussed.

## Results and discussion

Radical molecular anions are rarely observed during ESI. To evaluate the stabilization of radical molecular anions of

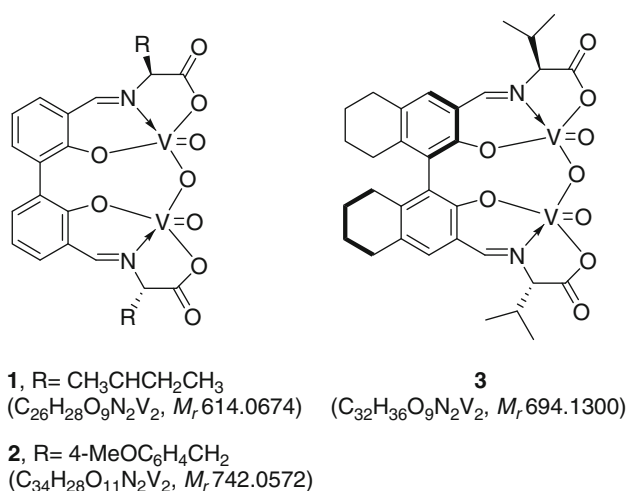
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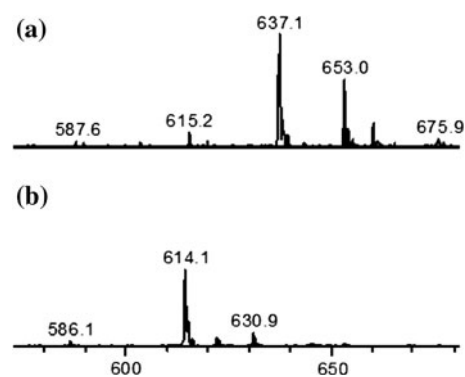
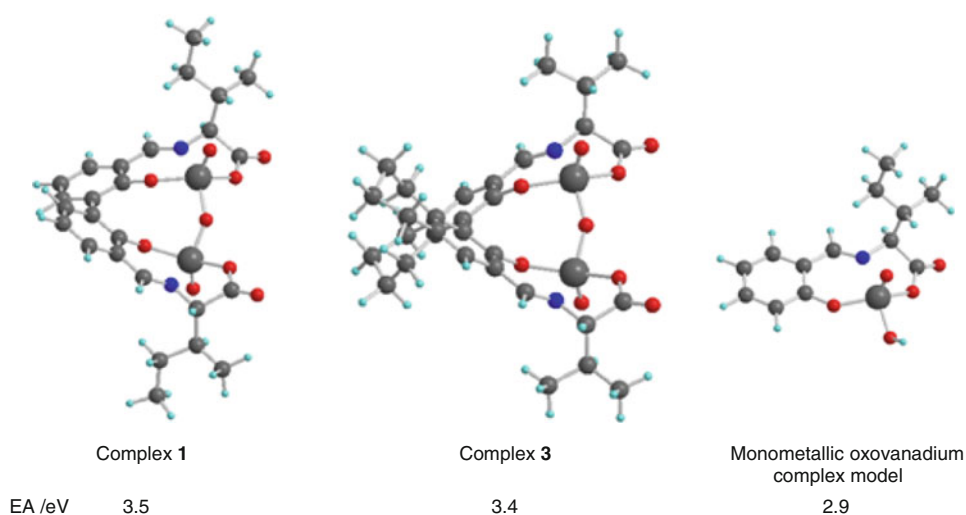
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**Fig. 1** Structures of bimetallic oxovanadium complexes **1–3**

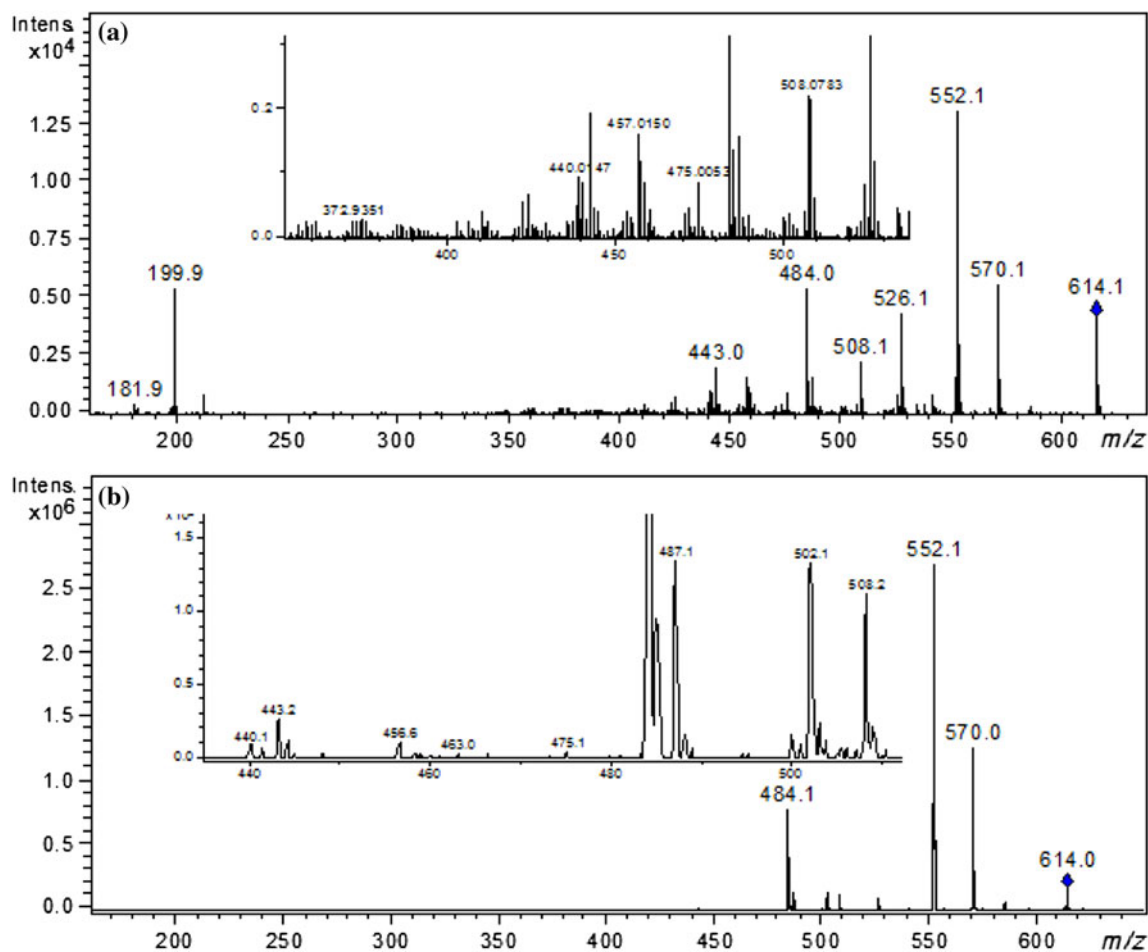
oxovanadium complexes, quantum mechanical calculations were performed for complexes **1** and **3** with the DFT method (U)B3LYP/6-31+G\* as implemented in the Gaussian 03 program suite [22]. The DFT method was demonstrated to efficiently give EAs with errors less than 0.2 eV [23]. The calculated structures and EAs of complexes **1** and **3** are shown in Fig. 2a. Both **1** and **3** contain a bridging V–O–V bond, which is the fundamental structural difference between mono- and bimetallic oxovanadium complexes. To support the previous assumption that the bridging V–O–V bond contributes to the stabilization of the radical [21], a monometallic oxovanadium complex similar to complex **1** was selected for parallel analysis. Bimetallic oxovanadium complexes **1** and **3** were found to have about 0.6 eV higher EAs than the monometallic oxovanadium (Fig. 2b). These results suggest that the bridging V–O–V bond indeed increases the EA significantly.

**Fig. 2** Calculated structures and electron affinities with (U)B3LYP/6-31+G\* method on oxovanadium species



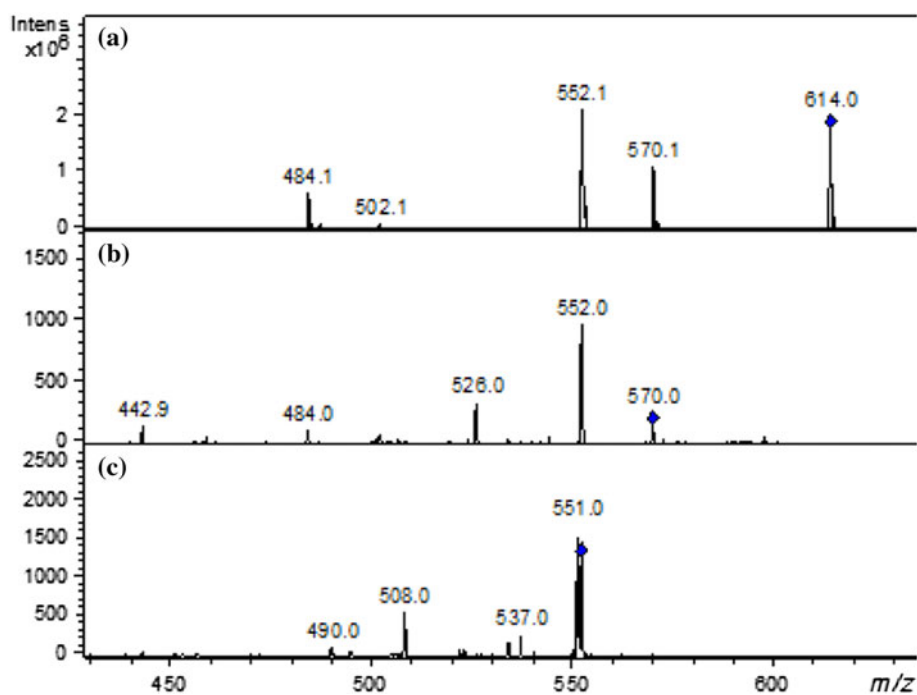
**Fig. 3** ESI-IT-MS spectra of oxovanadium complex **1**: **a** in positive-ion mode ( $[M + H]^+$  at  $m/z$  615,  $[M + Na]^+$  at  $m/z$  637,  $[M + K]^+$  at  $m/z$  653), and **b** in negative-ion mode ( $[M]^-$  at  $m/z$  614)

The MS analyses of complex **1** were performed in both positive- and negative-ion modes by ESI-IT-MS. The radical anion  $[M]^-$  at  $m/z$  614 was detected in negative-ion mode (Fig. 3). The spectra were similar to those detected by QTOF. However, MS<sup>2</sup> spectra obtained by QTOF and by the ion trap were different (Fig. 4). The low  $m/z$  ions at  $m/z$  182, 200, and 214 with large abundance in QTOF spectra were undetectable in the ion trap regime, which can be ascribed to a cutoff at 1/3 of the parent ion's  $m/z$  value in MS/MS experiments in the ion trap [24]. There were also a series of low-abundance peaks in QTOF spectra, which were similar to a normal electron ionization (EI) spectrum. These ions likely indicated the radical character of the precursor ion  $[M]^-$  at  $m/z$  614. On the contrary, they became negligible in the ion trap spectrum. This difference is most likely due to rapid consecutive reactions of these reactive fragments with water and solvent traces present in the ion trap as is observed quite often for metal fragment ions [25].

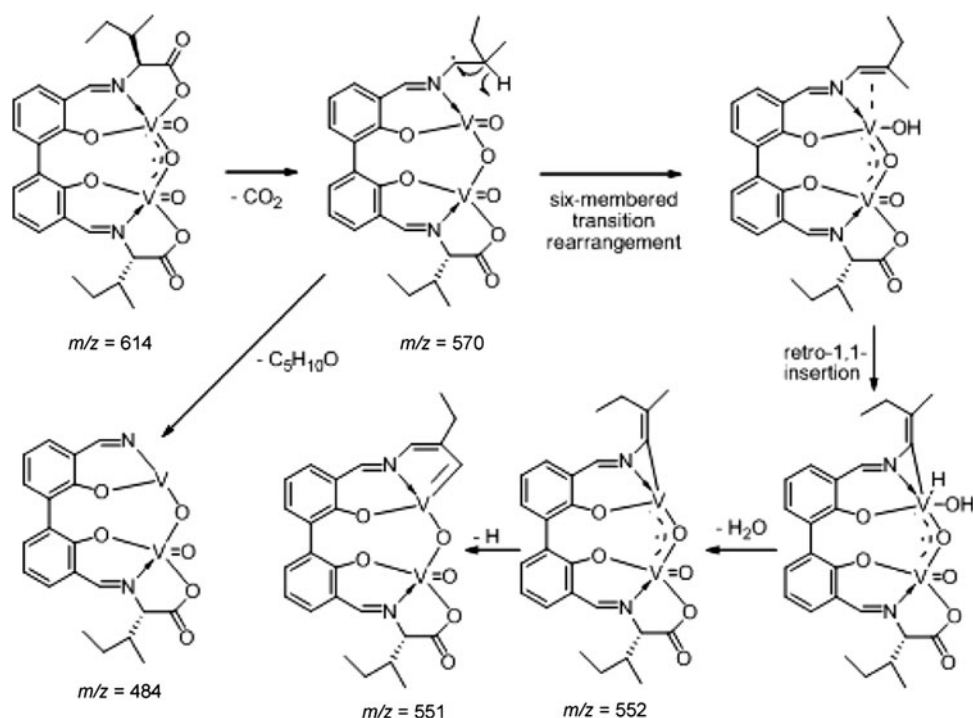


**Fig. 4** MS/MS spectra of oxovanadium complex **1** at  $m/z$  614 in negative-ion mode: **a** obtained in QTOF, and **b** obtained in the ion trap

**Fig. 5** ESI-IT-MS<sup>3</sup> spectra of oxovanadium complex **1** in negative-ion mode: **a** selected  $[M]^-$  at  $m/z$  614, **b** selected ion at  $m/z$  570 from  $m/z$  614, and **c** selected ion at  $m/z$  552 from  $m/z$  614



Scheme 1



Several high-abundance fragment ions from the ion at  $m/z$  614, e.g.,  $m/z$  570, 552, and 484, were detected in both QTOF and the ion trap (Figs. 4, 5). It is necessary to point out that the fragment ion at  $m/z$  484, which was considered to derive from the ion at  $m/z$  552 [21], is more likely formed directly from the ion at  $m/z$  570. The formation of the fragment ion at  $m/z$  552 might involve a rearrangement of the ion at  $m/z$  570 via a six-membered transition state and a retro-1,1-insertion reaction [21]. The fragment ion at  $m/z$  552 readily lost a hydrogen atom to produce an ion at  $m/z$  551 (Fig. 5c). The hydrogen atom might come from amino acids ( $R = \text{alkyl}$ ) of complex **1** (Scheme 1). When  $R$  was a phenyl group (Fig. 1, complex **2**), the loss of a hydrogen atom was not observed.  $\text{MS}^n$  spectra of the precursor ions  $[\text{M} + \text{Na}]^+$  were also obtained in the ion trap. Major fragmentation ions were the same as those obtained from ESI-QTOF-MS/MS.

In summary, EAs of both mono- and bimetallic oxovanadium complexes were calculated by DFT. The higher EA values of bimetallic oxovanadium complexes indicate that the bridging V–O–V bond plays a critical role in the formation of radical ions during ESI-MS analysis. Major high-abundance peaks observed in either negative- or positive-ion  $\text{MS}^n$  spectra basically support the previously postulated fragmentation routes of the bimetallic oxovanadium complexes. In addition, compared with the ion trap,  $\text{MS}^2$  spectra obtained by QTOF generally contained more fragments ions, especially low  $m/z$  and low-abundance  $m/z$  ions.

## Experimental

$\text{MS}^n$  experiments were performed on a Bruker Esquire 6000 ion trap spectrometer (Billerica, MA, USA). The samples were dissolved in acetonitrile before introduction into the mass spectrometer. The capillary voltage was held at 4 kV and the source temperature was maintained at 300 °C. The mass resolution was 0.6 u and the pressure was about  $6 \times 10^{-6}$  mbar. High-purity nitrogen gas was used as the nebulizer gas at a pressure of 1.4 bar. Tandem mass spectra were obtained by collision-induced dissociation (CID) of selected precursor ions with helium as the collision gas, by applying collision voltages between 0.6 and 1.0 V. The collision energy was optimized until sufficient fragmentation was obtained and there was no significant decrease in the intensity of the fragment ions.

High-resolution experiments were performed on a Bruker BioTOF-Q mass spectrometer (Billerica, MA) with a resolution of 20,000 FWHM. High-purity nitrogen gas at a pressure of 2 bar was used as the collision, nebulizer, and auxiliary heated gas. CID was performed in the collision cell, applying collision energy between 25 and 35 eV. The sample introduction rate was 115 mm<sup>3</sup>/h. The ESI source conditions were as follows: capillary voltage 4,000 V, end plate voltage 3,500 V, capillary exit voltage 120 V, and dry gas temperature 150 °C.

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