

## Bromidovanadium(II, III, and IV) Complexes

Dieter Rehder,<sup>\*,[a]</sup> Henning Nekola,<sup>[a]</sup> Axel Behrens,<sup>[a]</sup> Stephen P. Cramer,<sup>[b]</sup> and Tobias Funk<sup>[b]</sup>**Keywords:** Bromidovanadium; Benzimidazolyl/Pyridyl-dithiahexane; Trithiacyclononane; L-edge XAS; K-edge XAS

**Abstract.** The bromidovanadium complexes *cis*-[V<sup>II</sup>Br<sub>2</sub>(bith)] (**1**) [bith = 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane], *cis*-[V<sup>II</sup>Br<sub>2</sub>(pth)] (**2a**) [pth = 1,6-bis(2-pyridyl)-2,5-dithiahexane], *cis*-[V<sup>II</sup>Br<sub>2</sub>(pth)]Br (**2b**), *trans*-[V<sup>II</sup>Br<sub>2</sub>(tmeda)<sub>2</sub>] (**3**) (tmeda = tetramethylethylenediamine), *fac*-[V<sup>III</sup>Br<sub>3</sub>(9S3)] (**4**) (9S3 = 1,4,7-trithiacyclononane), *mer*-[V<sup>III</sup>Br<sub>3</sub>(thf)<sub>3</sub>] (**5**) (thf = tetrahydrofuran), and *trans*-

[V<sup>IV</sup>OBr<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O] (**6**) were prepared and characterized by, inter alia, XRD (**5**, **6**), K-edge XAS (**3**, **4**) or L-edge XAS (**2a**, **2b**). The complexes are also addressed in the context of the potential of halogenidovanadium compounds in catalytically conducted reactions, including biogenic processes.

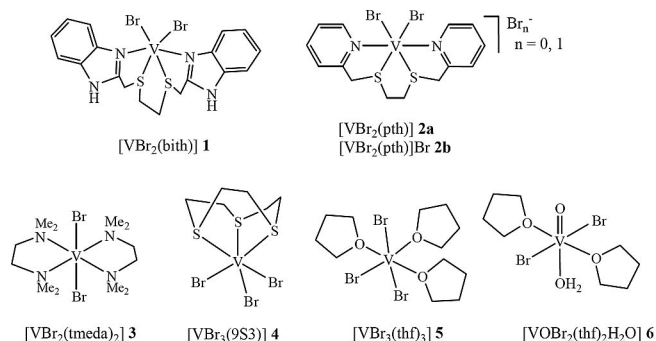
## Introduction

Halogenidovanadium complexes with vanadium in low oxidation states (I, II, and III) have previously been investigated in relation to catalytically conducted reactions such as deoxygenation, hydrogenation, and reductive coupling,<sup>[1]</sup> whereas the corresponding V<sup>IV</sup> and V<sup>V</sup> complexes have been employed in one-electron redox reactions<sup>[2]</sup> as well as in (ep)oxidation and alkene polymerization.<sup>[1,3]</sup> Bromidovanadium(I) and -(II) complexes in particular have been shown to promote the reductive CO and/or CNR coupling to form acetylenes<sup>[4,5]</sup> with subsequent hydrogenation,<sup>[4]</sup> or to be generated as intermediates in the geminal diallylation of carbonyl compounds with allylbromide, e.g., in the presence of catalytic amounts of [VCl<sub>2</sub>(tmeda)<sub>2</sub>] (tmeda = tetramethylethylenediamine).<sup>[6]</sup>

Apart from these applications in organic syntheses and catalysis, biological issues are of interest.<sup>[7]</sup> Vanadium is sequestered by some ascidians (sea-squirts), mainly in its oxidation state +III, in specialized blood cells (vanadocytes), where small amounts can be present, according to XAS investigations, in the form of an aquachloridovanadium(III) species.<sup>[8]</sup> Bromoperoxidases from marine macro-algae contain vanadate(V) coordinated to a histidine residue in the enzyme's active center. The peroxidases catalyze the 2-electron oxidation of bromide to a {Br<sup>+</sup>} species (BrOH, Br<sub>2</sub>, or Br<sub>3</sub><sup>-</sup>), which in turn brominates organic compounds in sea water<sup>[9]</sup> or, in the absence of organics, exert anti-fouling activity (and thus pro-

tect the algae against bacterial infestation) by the formation of singlet oxygen.<sup>[10]</sup> Although Br<sup>-</sup> does not directly interact with vanadium in these enzymatic reactions, the formation of an intermediate with a coordinated hypobromite is likely to occur,<sup>[11a]</sup> mediated by van der Waals contacts between bromide and the active center vanadate.<sup>[11b]</sup> EXAFS<sup>[12a]</sup> and XRD<sup>[12b]</sup> studies of bromoperoxidases soaked with bromide, as well as model investigations with bromoalanine as a ligand constituent for vanadium<sup>[13]</sup> have revealed a V...Br distance of ca. 4 Å.

Further, several of the ligands, which we have employed in the presented study, 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane (bith), 1,6-bis(2-pyridyl)-2,5-dithiahexane (pth), and 1,4,7-trithiacyclononane (9S3) (cf. Figure 1) may be considered to model part of the coordination sphere of vanadium in vanadium nitrogenase from *Azotobacter*,<sup>[14a]</sup> where vanadium, a constituent of the FeV-cofactor (the M cluster) {VFe<sub>7</sub>S<sub>9</sub>}, shuttles between the oxidation states II and IV, and is linked to three bridging sulfide ligands, histidine-Nε, and the vicinal carboxylate and hydroxide functions of homocitrate.<sup>[7,14b]</sup>



**Figure 1.** Ligands and complexes investigated in this work. The complexes **5** and **6** were characterized by XRD, the complexes **2a**, **2b**, **3** and **4** by XAS.

\* Prof. Dr. D. Rehder

E-Mail: rehder@chemie.uni-hamburg.de

[a] Department of Chemistry  
Institute of Inorganic and Applied Chemistry  
Martin-Luther-King-Platz 6  
20147 Hamburg, Germany[b] Department of Applied Science  
University of California  
Davis, CA 95616, USA  
and: Lawrence Berkeley National Laboratory  
Physical Biosciences Division  
Berkeley, CA 94720, USA

The available information on structurally characterized bromidovanadium complexes is comparatively low. Examples include the V<sup>I</sup> complex [VBr(dmpe)<sub>2</sub>(Me<sub>3</sub>SiOC≡COSiMe<sub>3</sub>)] [dmpe = bis(dimethylphosphanyl)ethane],<sup>[4]</sup> the V<sup>II</sup> complexes *cis*-[VBr<sub>2</sub>(bppa)] [bppa = bis(picolyloxy)-oxobenzylamine],<sup>[15a]</sup> *trans*-[VBr<sub>2</sub>(C–N–C)thf] [C–N–C = 2,6-bis(imidazolylidene)-pyridine],<sup>[15b]</sup> *trans*-[VBr<sub>2</sub>(dmpe)<sub>2</sub>]<sup>[15c]</sup> and *trans*-[VBr<sub>2</sub>(CN*t*Bu)<sub>4</sub>],<sup>[15d]</sup> the V<sup>III</sup> complexes *trans*-[VBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>4</sub>]<sup>+</sup>,<sup>[16a]</sup> *trans*-[VBr<sub>2</sub>(teg)]<sup>+</sup> (teg = tetraethyleneglycol),<sup>[16b]</sup> [VBr(OMes)<sub>2</sub>(thf)<sub>2</sub>] (Mes = mesityl)<sup>[16c]</sup> and [VBr(NS<sub>2</sub>S'<sub>2</sub>)] [NS<sub>2</sub>S'<sub>2</sub> = bis(mercaptophenylthio)pyridine],<sup>[16d]</sup> the V<sup>IV</sup> complexes *cis*-[VBr<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>]<sup>[17a]</sup> and [VOBr(tpa)]<sup>+</sup> [tpa = tris(2-pyridyl)amine],<sup>[17b]</sup> and finally the V<sup>V</sup> complexes *trans*-[VBr<sub>2</sub>(*cyclo*-thiazene)(py)<sub>2</sub>]<sup>[18a]</sup> (py = pyridine) and [VOBr<sub>4</sub>]<sup>-</sup>.<sup>[18b]</sup>

The presented study is a comparative investigation of characteristics and structural features of the complexes *cis*-[V<sup>II</sup>Br<sub>2</sub>(bith)] (**1**), *cis*-[V<sup>II</sup>Br<sub>2</sub>(pth)] (**2a**), *cis*-[V<sup>III</sup>Br<sub>2</sub>(bpdh)]Br (**2b**), *trans*-[V<sup>II</sup>Br<sub>2</sub>(tmeda)<sub>2</sub>] (**3**), *fac*-[V<sup>III</sup>Br<sub>3</sub>(9S3)] (**4**), *fac*-[V<sup>III</sup>Br<sub>3</sub>(thf)<sub>3</sub>] (**5**) and *trans*-[V<sup>IV</sup>OBr<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O] (**6**) (Figure 1) based, for compounds **2**–**6**, on single-crystal X-ray diffraction or X-ray absorption features at the K- or L-edges. The X-ray structure of *trans*-[V<sup>II</sup>Br<sub>2</sub>(tmeda)<sub>2</sub>] (**3**) has been reported previously.<sup>[19]</sup> For the preparation and characteristics of **2** see also Ref.<sup>[16d]</sup>, for [VBr<sub>3</sub>(thf)<sub>3</sub>] Ref.<sup>[20]</sup>.

## Results and Discussion

### The Ligands bith and pth, and their Complexes

The ligand bith [1,6-bis(2-benzimidazolyl)-2,5-dithiahexane] was prepared by Phillips condensation from 3,6-dithiooctanedioic acid and 1,2-diaminobenzene.<sup>[21]</sup> A light-brown micro-crystalline powder of bith·THF was obtained from THF solutions layered with pentane.

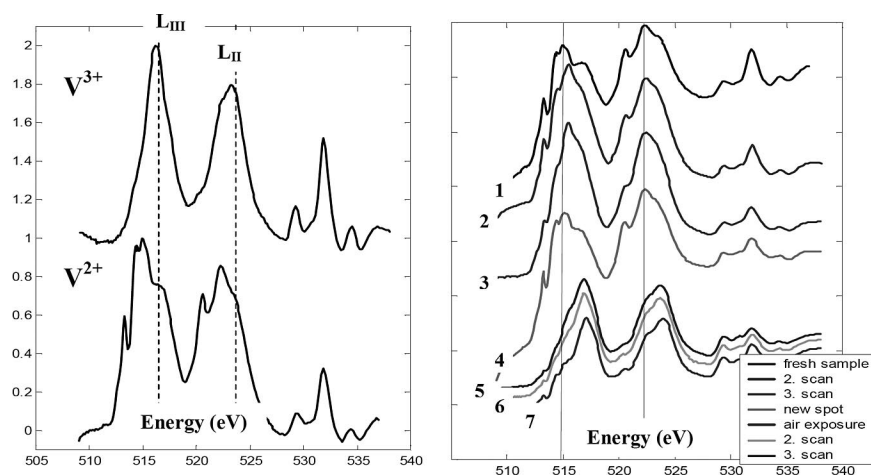
Refluxing equimolar amounts of [VBr<sub>2</sub>(tmeda)] and bith in THF or CH<sub>2</sub>Cl<sub>2</sub> yields light-brown *cis*-[VBr<sub>2</sub>(bith)] (**1**). The complex is insoluble in all common solvents, except of DMSO, where it slowly decomposes. Selected spectroscopic data are collected in Table 1, together with those of the related *cis*-[VBr<sub>2</sub>(pth)] (**2a**) and *cis*-[VBr<sub>2</sub>(pth)]Br (**2b**). The red complex **2a** and the grey-blue **2b** were prepared correspondingly by reaction of pth with *cis*-[VBr<sub>2</sub>(tmeda)] and *cis*-[VBr<sub>3</sub>(thf)<sub>3</sub>], respectively. The assumed structures of **1** and **2**, based on structural evidence for *cis*-[VCl<sub>2</sub>(bith)]<sup>[22]</sup> and *cis*-[VCl<sub>2</sub>(pth)]<sup>[23]</sup> are depicted in Figure 1. The conductivity of **2b** dissolved in DMSO is 8.3 S·cm<sup>2</sup>·mol<sup>-1</sup>, indicating strong ion-pairing between the [VBr<sub>2</sub>(bpth)]<sup>+</sup> cation and the Br<sup>-</sup> anion.

Complexes **2a** and **2b** represent several of the features of the vanadium site in the *M* cluster of vanadium-nitrogenase, viz. the coordination of sulfur functions (μ<sub>3</sub>-S<sup>2-</sup> in the *M* clus-

**Table 1.** Selected spectroscopic data for the complexes **1**, **2a**, and **2b**.

	$\nu(\text{C}=\text{C}, \text{C}=\text{N}); \delta(\text{CH}_2-\text{S}) / \text{cm}^{-1}$	$\nu(\text{V}-\text{S}, \text{V}-\text{Hal}) / \text{cm}^{-1}$	$\delta(^1\text{H}) \text{ArCH}_2\text{S}^{\text{a)}$ ; $\text{SCH}_2\text{CH}_2$	$\delta(^{13}\text{C}) \text{ArCH}_2\text{S}^{\text{a)}$ ; $\text{SCH}_2\text{CH}_2$
bith	1622, 1589, 1534; 1456, 1446, 1437		3.96; 2.79	30.7; 27.7
[VBr <sub>2</sub> (bith)] ( <b>1</b> )	1620, 1593, 1522; 1449, 1396	345, 293	b)	b)
pth	1592, 1565; 1474, 1434		3.82; 2.66	36.5; 30.7
[VBr <sub>2</sub> (pth)] ( <b>2a</b> )	1600, 1561; 1477, 1436	377, 363, 301	b)	b)
[VBr <sub>2</sub> (pth)]Br ( <b>2b</b> )	1613, 1534; 1463, 1415	376, 356, 295	3.85; 2.66	36.1; 30.6

a) Ar (aryl) stands for the benzimidazolyl and pyridyl moiety, respectively. b) The complexes are paramagnetic.



**Figure 2.** Left: The L<sub>III</sub> and L<sub>II</sub> bands of [VBr<sub>2</sub>(pth)]Br (**2b**, top) and [VBr<sub>2</sub>(pth)] (**2a**, bottom). The feature at ca. 532 eV represents oxygen. Right: Variations in the L-edge spectra of [VBr<sub>2</sub>(pth)], **2a**: Traces 1 and 4: fresh samples; traces 2 and 3: variations with increasing irradiation time; traces 5–7: after up to ca. 0.5 h of exposure to air (oxidation to [VBr<sub>2</sub>(pth)]<sup>+</sup>).

ter) and aromatic nitrogen (N $\epsilon$  of histidine in the *M* cluster). For vanadium nitrogenase, a change of the vanadium oxidation state between +II and +IV has been inferred from the energy position of the K-edge in K-edge XAS.<sup>[14a]</sup> L-edge XAS can provide more reliable information on the oxidation state of a central metal atom in a complex compound. In Figure 2, left, L-edge XANES spectra of **2a** and **2b** are provided. The spectra show two absorptions corresponding to the electronic 2p<sub>3/2</sub> → 3d (L<sub>III</sub>) and 2p<sub>1/2</sub> → 3d (L<sub>II</sub>) transitions, with the energy positions for the V<sup>3+</sup> complex **2b** (L<sub>III</sub> = 516.5, L<sub>II</sub> = 523.9 eV) clearly at higher energies than for the V<sup>2+</sup> complex **2a** with maxima at 515.6 (L<sub>III</sub>) and 522.5 eV (L<sub>II</sub>). The spectral feature for **2b** remains constant over time, i.e., the V<sup>3+</sup> complex is essentially stable under the conditions of the experiment. This is not the case for the V<sup>2+</sup> complex **2a**: Figure 2, right, provides a collation of spectra of **2a**, showing that the sample becomes radiatively damaged, mainly indicated by a slight high-energy shift of L<sub>III</sub> (traces 1–3), and is gradually oxidized to the V<sup>3+</sup> complex on exposure to air (traces 5–7).

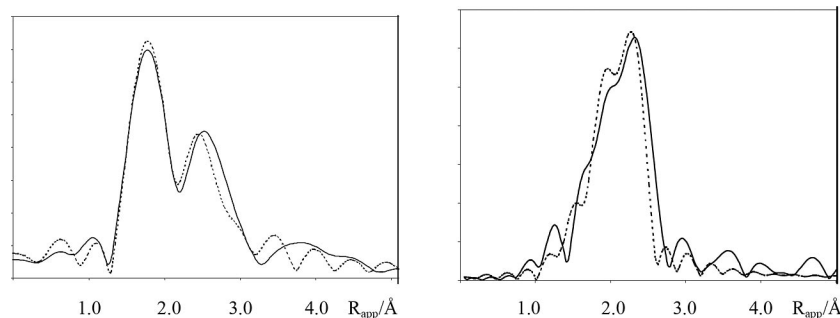
### The Complexes 3, 4, 5, and 6

The complexes [VBr<sub>2</sub>(tmeda)] (**3**), prepared from [V<sub>2</sub>(μ-Br)<sub>3</sub>(thf)<sub>6</sub>][AlBr<sub>2</sub>Et<sub>2</sub>] and tmeda,<sup>[19]</sup> and [VBr<sub>3</sub>(9S3)] (**4**), obtained by reacting 9S3 with [VBr<sub>3</sub>(thf)<sub>3</sub>] (**5**) (see Experimental Section), were investigated by K-edge XAS. Complexes **5** and **6** were also structurally characterized by single-crystal X-ray diffraction. Table 2 summarizes K-edge and EXAFS data for the complexes **3** and **4**; the Fourier transformed EXAFS spectra are shown in Figure 3.

**Table 2.** XAS data for the complexes [VBr<sub>2</sub>(tmeda)] (**3**) and [VBr<sub>3</sub>(9S3)] (**4**).

	[VBr <sub>2</sub> (tmeda)] <b>3</b>	[VBr <sub>3</sub> (9S3)] <b>4</b>
K-edge (inflection point) /eV	5466.3	5468.5
K-edge relative to V foil (5465.0) /eV	1.3	3.5
Pre-edge peak (1s→3d) /eV	5461.3	5462.6
<i>d</i> (V–N) /Å	2.244 [2.313 and 2.324] <sup>a)</sup>	
<i>d</i> (V–S) /Å		2.516
<i>d</i> (V–Br) /Å	2.528 [2.656] <sup>a)</sup>	2.482
Coordination number	4 (N) and 2 (Br)	3 (S) and 3 (Br)
Debye–Waller factor σ <sup>2</sup>	0.012822 (N) and 0.000897 (Br)	0.011117 (S) and 0.006803 (Br)

a) Values in square brackets are from XRD.<sup>[19]</sup>



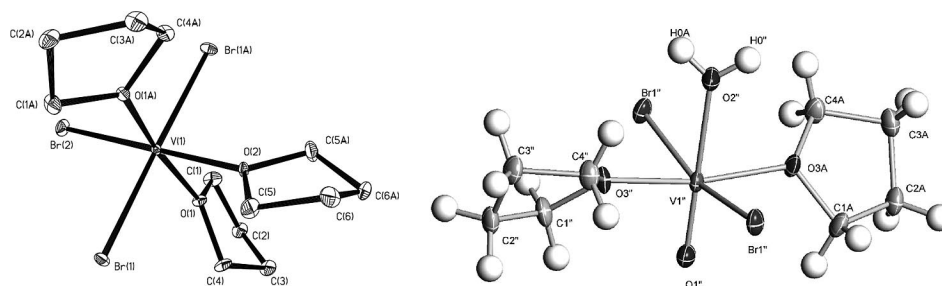
**Figure 3.** EXAFS regions of the XAS spectra of the complexes [VBr<sub>2</sub>(tmeda)<sub>2</sub>] (**3**, left) and [VBr<sub>3</sub>(9S3)] (**4**, right); R<sub>app</sub> is the apparent (i.e. uncorrected) distance in Å; for the corrected distances see Table 2. The dashed lines represent the fits, based on the XDS structure in the case of **3**,<sup>[19]</sup> and a plausible structure in case of complex **4**. The less than ideal fit in the case of **4** may be due to partial oxidation.

The K-edge for the V<sup>3+</sup> complex **4** is shifted to high energy by 2.2 eV with respect to that of the V<sup>2+</sup> complex **3**. Both complexes also exhibit a distinctive pre-edge peak of rather low energy, with a shift difference of 1.3 eV. The energy difference between the K-edges of the two complexes is in the order of magnitude to be expected for V<sup>2+/3+</sup> complexes; the absolute values are at low energies when compared with, e.g., oxides of V<sup>2+/3+</sup>,<sup>[24]</sup> reflecting the softness of the bromide and thioether ligands in **3** and **4**. While the distances *d*(V–Br) = 2.482 Å in **4** correspond to the mean *d*(V–Br) = 2.485 Å found by XRD for **5** (vide infra), the *d*(V–N) and *d*(V–Br) for **3** found by EXAFS are somewhat shorter than those determined for the same complex by XRD (Table 2 and Table 3). The structure of **3** otherwise compares to that of [VCl<sub>2</sub>(tmeda)<sub>2</sub>].<sup>[25a]</sup>

The molecular structures of complexes **5** (red hexagonal crystals) and **6** (green crystals) are displayed in Figure 4, se-

**Table 3.** Selected structure data /Å, ° of complexes **3**, **5** and **6**.

[VBr <sub>2</sub> (tmeda)] ( <b>3</b> ) <sup>[19]</sup>	[VBr <sub>3</sub> (thf) <sub>3</sub> ] ( <b>5</b> )	[VOBr <sub>2</sub> (thf) <sub>2</sub> H <sub>2</sub> O] ( <b>6</b> )
V–Br 2.656(1)	V–Br1 2.546(2)	V–Br 2.54274(19)
	V–Br2 2.454(3)	V–O1 1.5940(17)
V–N1 2.313(7)	V–O1 2.045(5)	V–O2 2.2095(17)
V–N2 2.324(7)	V–O2 2.069(6)	V–O3 2.0667(12)
Br–V–Br# 179.76(12)	Br1–V–Br2 90.80(3)	Br–V–Br# 165.21(2)
Br–V–N1 89.9(2)	Br1–V–O1 89.78(16)	Br–V–O1 97.395(10)
Br–V–N2 90.1(2)	Br1–V–O2 89.20(3)	Br–V–O2 82.605(10)
	Br2–V–O1 95.43(13)	Br–V–O3 91.14(4)
N1–V–N2 81.0(3)	O1–V–O2 84.57(13)	O1–V–O2 180.0
		O1–V–O3 95.30(3)
		O2–V–O3 84.70(3)
		O3–V–O3# 169.40(7)



**Figure 4.** The molecular structures of the complexes *mer*-[VBr<sub>3</sub>(thf)<sub>3</sub>] (**5**, left) and [VOBr<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O] (**6**, right; hydrogen atoms shown).

lected structure data, together with those for complex **3**, in Table 3. The difference in the bond lengths  $d(\text{V}-\text{Br})$  of **3** and  $d(\text{V}-\text{Cl})$  in [VCl<sub>2</sub>(tmeda)], 0.15 Å, correspond to the difference of the ionic radii of the two halogenido ligands. Complex **5** crystallizes in the orthorhombic space group *Pbcn*; the point symmetry for the molecule is  $C_{2v}$ , with the twofold axis defined by O2, V, and Br2. Compound **5** is iso-structural with the chlorido complex *mer*-[VCl<sub>3</sub>(thf)<sub>3</sub>].<sup>[25b]</sup> The bonds  $d(\text{V}-\text{Br})$  for the bromide ligands mutually *trans* [Br1 and Br1A, 2.546(2) Å] are slightly longer than  $d(\text{V}-\text{Br}2)$  [2.454(3) Å] and  $d(\text{V}-\text{Br})$  in **3** [2.656(1) Å], but compare to the  $d(\text{V}-\text{Br}) = 2.5427(2)$  Å for **6**. The bromido complex **6** is iso-structural to the chlorido complex [VOCl<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O].<sup>[26]</sup> As in the chlorido complex, infinite one-dimensional double chains are present, with the molecules linked together via intermolecular V–Br···H<sub>2</sub>O–V (2.481 Å) hydrogen bonds between the two strands of the double chain, plus weak interactions between protons of neighboring THF rings within neighboring molecules of the same strand,  $d(\text{H}\cdots\text{H}) = 2.398$  Å.

## Conclusions

Six bromidovanadium complexes with vanadium in the oxidation states II, III, and IV were characterized by X-ray diffraction or absorption spectroscopy (K-edge XANES and EXAFS, L-edge XANES) to provide clues for the exploration of low-valent, ligand-stabilized vanadiumhalide-based catalysts. Supporting ligands in the complexes are *O*-functional (THF), *N*-functional (tmeda), *S*-functional (1,4,7-trithia-cyclo-nonane), or *N,S*-functional [bis(pyridyl/benzimidazolyl)-2,5-dithiahexane, pth/bith], and thus cover the range from hard to soft ligands. The complexes *cis*-[VBr<sub>2</sub>(pth)]<sup>*n*+</sup> ( $n = 0$  and 1) in particular mimic structural features of the iron-vanadium-sulfide cluster (the *M* cluster) in vanadium nitrogenase, for which changes of the vanadium oxidation state between II and IV during turn-over were inferred. K-edge XAS reveals rather low-energy edge and pre-edge peaks reflecting, along with the low vanadium oxidation state, the softness of Br<sup>−</sup> and the *S*-functional ligands. L-edge XAS, which has previously been employed as a symmetry- and valence-selective probe to characterize vanadium-based minerals,<sup>[27]</sup> has been shown herein to be a sensitive probe for the distinction between the oxidation states +II and +III in the vanadium complexes *cis*-[VBr<sub>2</sub>(pth)]<sup>*n*+</sup>.

## Experimental Section

**Materials and Methods:** Standard chemicals were obtained from commercial sources and used without further purification. The following ligands were prepared by literature procedures: bith,<sup>[21]</sup> pth,<sup>[28]</sup> and 9S3.<sup>[29]</sup> Elemental analyses: CNH-O rapid analyzer (Heraeus and Carlos Erba). IR spectra: KBr mulls, Perkin-Elmer FTIR spectrometer 1720 FT; IR spectra were recorded as KBr or CsI mulls with a Perkin-Elmer 1700 XFT spectrometer. NMR spectra: Bruker AM 360 or Varian Gemini 200 spectrometer with the usual instrument settings. Conductivity measurements were performed at room temp. in 2.5 mM DMSO solution with a WTW LF 410 conductometer, employing a platinum electrode (WTW LTA 100).

Single crystal X-ray measurements were carried out with a Hilger and Watts Y290 (**5**;  $\theta/2\theta$  scan mode) and a Bruker SMART Apex CCD diffractometer (**6**;  $\omega$ -scan mode), equipped with graphite monochromator and Mo- $K_{\alpha}$  source. For the solution and refinement of the structures the program systems SHELXL-93<sup>[30]</sup>, SHELXS-97,<sup>[31]</sup> and SHELXL-97<sup>[32]</sup> were used. Frames were read with the program SAINT, absorption corrections (**6**) were carried out with DIFABS. For the determination of the space group, the program XPREP was employed. Hydrogen atoms were found (H<sub>2</sub>O in **6**) or calculated into ideal positions. Crystal data and details of the data collection and refinement are summarized in Table 4.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-921752 (**5**) and CCDC-218130 (**6**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

K-edge XAS measurements of compounds **3** and **4** were accomplished at room temp. at the beamline E4 of the Hamburger Synchrotron-Strahlungslabor (HASYLAB) at the Deutsche Elektronen Synchrotron (DESY) in Hamburg, Germany. The compounds were pressed into polyethylene pellets (containing ca. 20% w/w of the complex). Energy calibration was carried out by referencing against vanadium metal foil, with the first inflection point set to 5465 eV. EXAFS analyses were carried out with the software SimX for single scattering least-squares curve fittings. Phases were calculated using the FEFF7 software<sup>[33]</sup> (see also Ref.<sup>[12a]</sup>). L-edge XAS data were collected at the beamline 4.02 of the Stanford Synchrotron Radiation Laboratory, CA, USA, at an energy of ca. 520 eV. Calibration was implemented with a Ti mesh. The samples, fixed to adhesive tape in a nitrogen atmosphere, were measured at 20–30 K.

**Preparation of Complexes:** All reactions were carried out in inert gas atmosphere and absolute solvents, employing Schlenk techniques. All

**Table 4.** XRD structure and refinement data.

	[VBr <sub>3</sub> (thf) <sub>3</sub> ] ( <b>5</b> )	[VOBr <sub>2</sub> (thf) <sub>2</sub> H <sub>2</sub> O] ( <b>6</b> )
Empirical formula	C <sub>12</sub> H <sub>24</sub> Br <sub>3</sub> O <sub>3</sub> V	C <sub>8</sub> H <sub>18</sub> Br <sub>2</sub> O <sub>4</sub> V
Formula weight /g·mol <sup>-1</sup>	506.98	388.98
Temperature /K	153(2)	153(2)
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbcnb</i>	<i>C2/c</i>
<i>a</i> /Å	8.684(12)	12.2122(4)
<i>b</i> /Å	13.646(12)	17.3747(5)
<i>c</i> /Å	14.267(14)	8.1772(2)
<i>a</i> /°		
<i>β</i> /°		131.5850(10)
<i>γ</i> /°		
<i>V</i> /Å <sup>3</sup>	1691(3)	1277.78(6)
<i>Z</i>	4	4
Density (calcd) /g·cm <sup>-3</sup>	1.992	1.991
Absorption coefficient /mm <sup>-1</sup>	7.677	6.914
<i>F</i> (000)	992	764
Crystal size /mm	0.8 × 0.7 × 0.3	0.41 × 0.31 × 0.24
<i>θ</i> range /°	2.78–30.07	2.52–32.49
Index ranges	–2 < <i>h</i> < 12 –5 < <i>k</i> < 19 –4 < <i>l</i> < 20	–18 < <i>h</i> < 18 –26 < <i>k</i> < 26 –12 < <i>l</i> < 12
Reflexions collected	4194	17555
Independent reflexions		2341
<i>R</i> (int)	0.0813	0.0567
No. of parameters	89	74
Final <i>R</i> indices <i>I</i> > 2σ( <i>I</i> ), <i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub>	0.0647; 0.1481	0.0270; 0.0620
<i>R</i> indices all data, <i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub>	0.1060; 0.1690	0.0329; 0.0628
Largest diff. peak and hole / e·Å <sup>-3</sup>	1.462 and –1.934	1.290 and –0.734

products were stored in an argon or nitrogen atmosphere at room temp. The following complexes were prepared according to published procedures: [VBr<sub>2</sub>(pth)] (**2a**) and [VBr<sub>2</sub>(pth)]Br (**2b**),<sup>[16]</sup> [VBr<sub>2</sub>(tmeda)<sub>2</sub>] (**3**),<sup>[19]</sup> [VBr<sub>3</sub>(thf)<sub>3</sub>] (**5**).<sup>[20]</sup>

**[VBr<sub>2</sub>(bith)] (1):** [VBr<sub>2</sub>(tmeda)<sub>2</sub>] (220 mg, 0.5 mmol) and bith (180 mg, 0.5 mmol) were dissolved in THF (20 mL) and refluxed for 1 h. Complex **1** was obtained as a yellow precipitate, which was filtered off, washed with THF and dried. Yield: 250 mg (88%). **IR** (KBr):  $\tilde{\nu}$  = 3172–2818 ( $\nu_{\text{NH}}$ ,  $\nu_{\text{CH}}$ ); 1620, 1593, 1522 ( $\nu_{\text{C=C}}$ ,  $\nu_{\text{C=N}}$ ); 1449, 1396 ( $\delta_{\text{HCS}}$ ); 1276 (CHS wagging); 748 (arom. subst.); 433, 345, 293 ( $\nu_{\text{VS}}$ ,  $\nu_{\text{VBr}}$ ) cm<sup>-1</sup>. **<sup>1</sup>H NMR** ([D<sub>6</sub>]DMSO):  $\delta$  = 7.63–7.34 (*m*, 8 H, *H*<sub>arom</sub>), 4.16 (*s*, 4 H, arom-CH<sub>2</sub>-S), 2.83 (*s*, 4 H, S-CH<sub>2</sub>-CH<sub>2</sub>-S). C<sub>18</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>4</sub>S<sub>2</sub>V (565.25 g·mol<sup>-1</sup>): calcd. C 38.37, H 3.29, N 9.96%; found C 37.96, H 3.54, N 10.02%.

**[VBr<sub>3</sub>(9S3)] (4):** [VBr<sub>3</sub>(thf)<sub>3</sub>] (460 mg, 0.91 mmol) and 9S3 (160 mg, 0.90 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and refluxed for 2 h. A dark-red precipitate was obtained, which was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> and dried. Yield: 330 mg (77%). **IR** (KBr):  $\tilde{\nu}$  = 1440, 1407 ( $\delta_{\text{HCS}}$ ); 963, 902, 827; 436, 308, 275, 262 ( $\nu_{\text{VS}}$ ,  $\nu_{\text{VBr}}$ ) cm<sup>-1</sup>. **<sup>1</sup>H NMR** ([D<sub>6</sub>]DMSO):  $\delta$  = 3.05 (*s*, S-CH<sub>2</sub>-CH<sub>2</sub>-S). C<sub>2</sub>H<sub>12</sub>Br<sub>3</sub>S<sub>3</sub>V (471.01 g·mol<sup>-1</sup>): calcd. C 15.30, H 2.57%; found C 15.97, H 2.60%.

**[VOBr<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O] (6):** A few crystals of this complex were obtained as a by-product from the reaction between [VOBr<sub>2</sub>(thf)<sub>2</sub>] and bis(2-methylpyridyl)-2-thioethylamine (N<sub>3</sub>S):<sup>[22]</sup> A solution of N<sub>3</sub>S (200 mg, 0.77 mmol) in THF (10 mL) was cooled in a liquid N<sub>2</sub>/EtOH bath and treated dropwise with an equivalent amount (0.5 mL) of a 1.6 M hexane solution of *tert*-butyl-lithium. This mixture was slowly warmed to room temp. and stirred for 1 h, followed by treatment with

[VOBr<sub>2</sub>(thf)<sub>2</sub>] (297 mg, 0.80 mmol) dissolved in THF (10 mL). After stirring overnight at room temp., a grey precipitate (approximate composition [VOBr<sub>3</sub>(N<sub>3</sub>S)(N<sub>3</sub>)]·7LiCl [N<sub>3</sub> = bis(2-methylpyridyl)ethylamine] was filtered off, but not further characterized due to insufficient reproducibility. The filtrate was concentrated to about 1/3 of its original volume, treated with hexane (5 mL) and stored at 4 °C. Green crystals of [VOBr<sub>2</sub>(thf)<sub>2</sub>H<sub>2</sub>O] suitable for X-ray analysis formed within several weeks.

## References

- [1] T. Hirao, *Chem. Rev.* **1997**, *97*, 2707–2724.
- [2] T. Hirao, *J. Inorg. Biochem.* **2000**, *80*, 27–33.
- [3] a) E. C. E. Rosenthal, H. Cui, J. Koch, P. Escarpa Gaede, M. Hummer, S. Dechert, *Dalton Trans.* **2005**, 3108–3117; b) E. C. E. Rosenthal, H. Cui, K. C. H. Lange, S. Dechert, *Eur. J. Inorg. Chem.* **2004**, 4681–4685.
- [4] J. D. Protasiewicz, S. J. Lippard, *J. Am. Chem. Soc.* **1991**, *113*, 6564–6570.
- [5] a) D. Rehder, H. Gailus, *Trends Organomet. Chem.* **1994**, *1*, 397–413; b) C. Collazo, D. Rodewald, H. Schmidt, D. Rehder, *Organometallics* **1996**, *15*, 4884–4887.
- [6] Y. Kataoka, I. Makihira, H. Akiyama, K. Tani, *Tetrahedron* **1997**, *53*, 9525–9540.
- [7] D. Rehder, *Bioinorganic Vanadium Chemistry*, Wiley & Sons, Chichester, **2008**.
- [8] a) P. Frank, E. J. Carlson, R. M. K. Carlson, B. Hedman, K. O. Hodgson, in: *ACS Symposium Series 974* (Eds.: K. Kustin, J. Costa Pessoa, D. C. Crans), American Chemical Society, Washington DC, **2007**, 281–295; b) P. Frank, E. J. Carlson, R. M. K. Carlson, K. O. Hodgson, *Coord. Chem. Rev.* **2003**, *237*, 31–39.
- [9] a) A. Butler, J. N. Carter-Franklin, *Nat. Prod. Rep.* **2004**, *21*, 15060–15066; b) B. S. Moore, *Nat. Prod. Rep.* **2006**, *23*, 615–629.
- [10] I. F. Persoon, M. A. Hoogenkamp, A. Bury, P. R. Wesselink, A. F. Hartog, R. Wever, W. Crielaard, *J. Endodontics* **2012**, *38*, 72–74.
- [11] a) O. Bortolini, M. Carraio, V. Conte, S. Moro, *Eur. J. Inorg. Chem.* **2003**, 42–46; b) G. Zampella, P. Fantucci, V. L. Pecora, L. De Gioia, *J. Am. Chem. Soc.* **2005**, *127*, 953–960.
- [12] a) U. Christmann, H. Dau, M. Haumann, E. Kiss, P. Liebisch, D. Rehder, G. Santoni, C. Schulzke, *Dalton Trans.* **2004**, 2534–2540; b) J. Littlechild, E. G. Rodriguez, M. Isupov, *J. Inorg. Biochem.* **2009**, *103*, 617–621.
- [13] V. Kraehmer, D. Rehder, *Dalton Trans.* **2012**, *41*, 5225–5234.
- [14] a) J. M. Arber, B. R. Dobson, R. R. Eady, S. S. Hasnain, C. D. Garner, T. Matsushita, T. M. Nomuras, B. E. Smith, *Biochem. J.* **1989**, *258*, 733–737; b) R. R. Eady, *Coord. Chem. Rev.* **2003**, *273*, 23–30.
- [15] a) W. A. Chomitz, S. G. Minasian, A. D. Sutton, J. Arnold, *Inorg. Chem.* **2007**, *46*, 7199–7209; b) D. Pugh, J. A. Wright, S. Freeman, A. A. Danopoulos, *Dalton Trans.* **2005**, 775–782; c) F. Stüßmilch, F. Olbrich, H. Gailus, D. Rodewald, D. Rehder, *J. Organomet. Chem.* **1994**, *472*, 119–126; d) C. Böttcher, D. Rodewald, D. Rehder, *J. Organomet. Chem.* **1995**, *496*, 43–48.
- [16] a) F. A. Cotton, G. E. Lewis, W. Schwotzer, *Inorg. Chem.* **1986**, *25*, 3528–3529; b) R. Neumann, I. Assael, *J. Am. Chem. Soc.* **1989**, *111*, 8410–8413; c) K. Thiele, H. Görls, W. Imhof, W. Seidel, *Z. Anorg. Allg. Chem.* **2002**, *628*, 107–118; d) H. Nekola, D. Wang, C. Grüning, J. Gätjens, A. Behrens, D. Rehder, *Inorg. Chem.* **2002**, *41*, 2379–2384.
- [17] a) E. L. Jones, J. G. Reynolds, J. C. Huffman, G. Christou, *Polyhedron* **1991**, *10*, 1817–1825; b) Y. Tajika, K. Tsuge, Y. Sasaki, *Dalton Trans.* **2005**, 1438–1447.
- [18] a) W. Willig, R. Christophersen, U. Müller, K. Dehnicke, *Z. Naturforsch. B* **1986**, *41*, 831–833; b) U. Müller, A.-F. Shihada, K. Dehnicke, *Z. Naturforsch. B* **1982**, *37*, 699–701.

- [19] P. B. Hitchcock, D. L. Hughes, L. F. Larkworthy, G. J. Leigh, C. J. Marmion, J. R. Sanders, G. W. Smith, J. S. de Souza, *J. Chem. Soc. Dalton Trans.* **1997**, 1127–1135.
- [20] G. W. A. Fowles, P. T. Greene, T. E. Lester, *J. Inorg. Nucl. Chem.* **1967**, *29*, 2365–2370.
- [21] P. J. M. W. L. Birker, J. Helder, G. Henkel, B. Krebs, J. Reedijk, *Inorg. Chem.* **1982**, *21*, 357–363.
- [22] C. P. Marabella, J. H. Enemark, K. F. Miller, A. E. Bruce, N. Pariyadath, J. L. Corbin, E. I. Stiefel, *Inorg. Chem.* **1983**, *22*, 3456–3461.
- [23] M. Farahbakhsh, H. Nekola, H. Schmidt, D. Rehder, *Chem. Ber. Recueil* **1997**, *130*, 1129–1133.
- [24] P. Wong, F. W. Lytle, R. P. Messmer, D. H. Maylotte, *Phys. Rev. B* **1984**, *30*, 5596–5610.
- [25] a) J. J. H. Edma, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W. J. J. Smeets, A. L. Spek, *Inorg. Chem.* **1990**, *29*, 1302–1306; b) F. A. Cotton, S. A. Duraj, G. L. Powell, W. J. Roth, *Inorg. Chim. Acta* **1986**, *113*, 81–85.
- [26] a) W. Priebsch, D. Rehder, *Inorg. Chem.* **1990**, *29*, 3013–3019; b) D. Paputsakis, A. S. Ichimura, V. G. Young Jr., J. E. Jackson, D. G. Nocera, *Dalton Trans.* **2004**, 224–228.
- [27] G. Cressey, C. B. M. Henderson, G. van der Laan, *Phys. Chem. Minerals.* **1993**, *20*, 111–119.
- [28] S. E. Livingstone, J. D. Nolan, *Aust. J. Chem.* **1970**, *23*, 1553–1558.
- [29] P. K. Baker, S. J. Coles, M. C. Durrant, S. D. Harris, D. L. Hughes, M. B. Hursthouse, R. L. Richards, *J. Chem. Soc. Dalton Trans.* **1996**, 4003–4010.
- [30] G. M. Sheldrick, *SHELXL-93*, Program of Crystal Structure Refinement, University of Göttingen, **1993**.
- [31] G. M. Sheldrick, *SHELXL-97*, Program of Crystal Structure Solution, University of Göttingen, **1997**.
- [32] G. M. Sheldrick, *SHELXL-97*, Program of Crystal Structure Refinement, University of Göttingen, **1997**.
- [33] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, M. J. Eller, *Phys. Rev. B* **1995**, *52*, 2995–3009.

Received: January 28, 2013  
Published Online: March 25, 2013