Structural and Spectroscopic Characterization of V^V-Imidazole Complexes

The structure and spectroscopy of vanadium coordination compounds is receiving increased attention in light of the recent discoveries of vanadium-dependent enzymes. To understand fully the role of vanadium in biological systems, the relationships between structure, spectroscopy, and reactivity must be elucidated. To this end we have undertaken the synthesis and complete characterization of vanadium coordination compounds which have presumed structural and/or spectroscopic similarities to naturally occurring vanadium complexes. In particular, we have focused on the active site of vanadium bromoperoxidase and the role of vanadium in tunicates and the mushroom Amanita muscaria. The tunicates and A. muscaria are known to accumulate vanadium to high concentrations, relative to the surrounding environment, possibly utilizing siderophore type molecules which contain noninnocent ligands such as hydroxamates and/or hydroxy-DOPA. Vanadium haloperoxidases, which have been isolated from several species of marine algae and a terrestrial lichen, catalyze the reaction shown as eq 1. These haloperoxidases differ from the more widely recognized heme enzymes in three important ways: First, they use vanadium in place of iron. Second, they do not contain a prosthetic group such as a porphyrin. Third, the catalytic cycle apparently may not require metal-centered redox conversions. Thus, the vanadium haloperoxidases represent a unique biological approach to the activation of halides using hydrogen peroxide. Several spectroscopic techniques have been utilized to probe the structure of the vanadium site in vanadium bromoperoxidase. The structure that is emerging for the active site of vanadium bromoperoxidase and the role of vanadium-catalyzed air oxidation of Br^- to Br_2 (Neumann, R.; Assael, I.) are as follows: V=O(Br) = 1.591 (3), V-O2 = 1.912 (3), V1-O3 = 1.898 (2), V1-O4 = 2.193 (3), V1-N1 = 2.119 (3), V1-N2 = 2.119 (3); O1-V1-O2 = 103.1 (1), O1-V1-O3 = 96.6 (1), O1-V1-O4 = 169.7 (1), O1-V1-N1 = 95.4 (1), O1-V1-N2 = 92.8 (1), O2-V1-O3 = 88.6 (1), O2-V1-O4 = 84.9 (1), O2-V1-N1 = 86.3 (1), O2-V1-N2 = 163.1 (1), O3-V1-O4 = 76.9 (1), O3-V1-N1 = 167.8 (1), O3-V1-N2 = 95.1 (1), O4-V1-N1 = 91.5 (1), O4-V1-N2 = 80.0 (1).

Imidazole coordination has been inferred on the basis of ESEEM measurements on the reduced catalytically inactive enzyme. It is probable that the balance of the coordination sphere is rich in carboxylate ligands. Below we report the structural and spectroscopic characterization for a series of complexes which contain the V=O-imidazole moiety and o xo, catecholato, or hydroximate ligands. The large ^{31}V NMR chemical shift range for this homologous series is unprecedented for vanadium complexes with oxygen and nitrogen donor ligands.

Although high-valent vanadium complexes containing the tris(pyrazolyl)borato ligand have appeared, crystallographically characterized V(V)-imidazole compounds, which are not limited to the sterically constrained facial coordination, have not been reported. Such materials may provide models for both the structure and reactivity of this unique vanadoenzyme. The neutral V=O(SALIMH)(CAT)HACAC (2) by the addition of 1 equiv of catechol to an
acetonitrile, dichloromethane, or methanol solution of the vanadium(V) precursor. Compound 1 has been characterized by X-ray crystallography, and an octamer picture is presented as Figure 1. Important bond lengths and angles are provided in the caption and are comparable to other vanadium catechol complexes reported in the literature. The vanadium to terminal oxo group (O1) distance is 1.59 Å which is slightly shorter than the VIV=O bond (1.64 Å) in 2. EXAFS results for the native enzyme yield a 1.63 Å V=O distance. There is also a slight shortening of the phenolate to vanadium distance in 1 (V=O2 = 1.91 Å) versus 2 (V=O2 = 1.98 Å), consistent with metal-centered oxidation. Little change is seen with the vanadium to imidazole nitrogen ligation (V, V-N2 = 2.11 Å; 2, V-N2 = 2.10 Å). The vanadium-imidazole nitrogen distance in 1 is the same as that reported for the native enzyme on the basis of EXAFS. The elongation of the V=O bond (trans to terminal oxo) relative to V=O in the native enzyme is in keeping with 1 (V=O4 = 2.10 Å; V=O5 = 1.91 Å) than 2 (V=O4 = 2.20 Å; V=O3 = 1.97 Å), and as a consequence, the vanadium to imine nitrogen distance in 1 increases to 2.15 Å from 2.05 Å seen in 2.

Reaction of 2 with acetoxyhydroxamic acid (AHAMH2) in a manner similar to that described above affords V+O(SALIMH)AHI (3) as a microcrystalline solid in 80% yield. Pyrogallol also reacts with 1 to yield a 1.63 Å V=O distance. There is also a slight elongation of the V=O bond (trans to terminal oxo) relative to V=O in the native enzyme, with a slightly higher V=O4 distance in 1 (V=O4 = 2.10 Å; V=O5 = 1.91 Å) than 2 (V=O4 = 2.20 Å; V=O3 = 1.97 Å), and as a consequence, the vanadium to imine nitrogen distance in 1 increases to 2.15 Å from 2.05 Å seen in 2.

Strong ligand to metal charge-transfer (LMCT) excitations are observable in the visible region for $V^{+}O_{2}$ (SALIMH)AHI (4), and as a consequence, the vanadium to imine nitrogen distance in 1 increases to 2.15 Å from 2.05 Å seen in 2.

Figure 2. $^{51}$V NMR spectra of acetonitrile solutions of (A) $^{51}$V(O) (SALIMH)AHI (4), (B) $^{51}$V(O)(SALIMH)AHI (3), and (C) $^{51}$V(O)(SALIMH)CAT (4). All spectra were collected at 52,200 Hz and referenced to external VOCl3. The sweep width was 125,000 Hz, and 8000 data points were used for the typical acquisition. Signal/noise was improved by exponential multiplication of the FID, inducing 50 Hz of line broadening. The asterisk denotes an impurity in the external $^{51}$VOCl3 standard, which was run with every spectrum.

weak q-d transitions [539 nm ($\epsilon = 59$ cm$^{-1}$ M$^{-1}$) and 743 nm ($\epsilon = 34$ cm$^{-1}$ M$^{-1}$)] in the visible region and 4 is transparent at wavelengths above 400 nm. Ligand to metal charge-transfer excitations have been reported for the "naked" vanadium(V) complex $K^+(CAT)^{+}$ and strong charge-transfer excitations associated with $V^{+}O$-phenoxy (tyrosine) motifs in the native enzyme.

Butler has presented a referencing scale based on the correlation of $^{51}$V NMR shifts with the sum of the ligand electronegativities, $\Sigma X$, for a wide variety of V(V) complexes with coordination numbers 4, 5, and 6. A listing of vanadium complexes containing exclusively oxygen and nitrogen ligands reveals that, with rare exception, the chemical shifts are upfield of the standard, VOCl3, and that the bulk of these resonances occur between -400 and -600 ppm. In the course of our work, we have found that vanadium complexes of noninnocent ligands, such as catechol and hydroxocyanic acid, can fall well outside this range. This finding is important since many biomolecules contain these functional groups. In the vanadium-accumulating tunicates maintain a high level of hydroxy-dopa-based molecules known as tunicohromes, which have recently been isolated and characterized.

Furthermore, the mushroom A. muscaria accumulates vanadium to form the $\pi$-hydroxyl amine complex amavadin22 and vanadate has been shown to strongly coordinate the polyhydroxamic acid siderophore desferrioxamine B.23 Butler has utilized desferriferrioxamine B to selectively extract vanadate from the phosphate binding site of an ATPase.24

The $^{51}$V NMR chemical shift range for the complexes of $^{51}$V(O) (SALIMH)Cl, where L is a noninnocent ligand or an oxo group, extends over a remarkable 1020 ppm. The spectra of 4, 3, and 1 are presented in Figure 2 from top to bottom, respectively. The $^{51}$V(IV) complex, 4, has a single resonance at -542 ppm. This shift is typical for dioxovanadium(V) complexes of oxygen/nitrogen ligands. Utilizing the Zhang formalism, one would cal-
Gold(III) Glycyl-L-histidine Dipeptide Complexes: Preparation and X-ray Structures of Monomeric and Cyclic Tetrameric Species

Metal complexes of histidine-containing peptides have been widely used as models for interactions between metal ions and proteins. As to the simple dipeptide glycyl-L-histidine (gly-L-his), its reactivity toward Zn(II) has been studied with regard to the phenomenon of increased oxygen affinity for hemoglobin on Zn(II) binding, for example. Various solution studies on binary systems have favored a binding pattern in which gly-L-his acts as a tridentate chelating ligand with the metal coordinated to the aminogroup of glycine, the deprotonated peptide N, and the N3 site of the imidazole ring. In the case of Cu(II), this conclusion has been confirmed by an X-ray structure determination. As reported by Morris and Martin, monocyclic gly-L-his complexes of Cu(II), Ni(II), and Pd(II) associate into...