Studies on the Mechanism of Reduction of Vanadium (V) Dipicolinate Compounds by L-Ascorbic Acid: The Ascidia nigra story

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Introduction
It has long been recognized that various species of tunicates (ascidians) actively accumulate heavy metals, including manganese, magnesium, iron, molybdenum, niobium, tantalum, chromium, titanium, and most commonly, vanadium [1]. The concentration of vanadium species in sea water is 35 nM, whereas the concentration in the blood cells of several species of ascidians can approach 350 mM [2]. Ascidia gemmata, reported with 350 mM vanadium in blood cells contains $10^7$ times the vanadium in seawater [3]. The coordination chemistry of vanadium in the tunicate is yet to be completely clarified. We now report the very first High-Frequency and -Field (HFEPR) studies on selected V(V) complexes in the presence of L-ascorbic acid (H$_2$A), and V(III) complexes in the solid state, where these studies will be used to model the oxidation state of vanadium in the tunicates.

Experimental
NH$_4$[VO$_2$(dipic)] (H$_2$dicpic = dipicolinic acid), Na[VO$_2$(dipicNH$_2$)]H$_2$O, NH$_4$[VO$_2$(dipic-OH)]H$_2$O, NH$_4$[VO$_2$(dicpic-Br)], NH$_4$[VO$_2$(dicpic-Cl)].H$_2$O, [V(dipic)(Hdicpic)(OH)$_2$], [V(dipic)(H$_2$O)$_2$F]. 1.5 H$_2$O, and H$_2$A were used in this study. Experiments were carried out on reaction mixtures containing V(V) complexes and H$_2$A in water, and V(III) complexes in the solid state. In most cases, [V(V)] = 100 mM and [H$_2$A] = 500 mM. The experiments were performed using the EMR Facility and in particular its 15/17 T superconducting magnet.

Results and Discussion
It was found that H$_2$A reduced all of the V(V) complexes to V(III) species in aqueous solution when H$_2$A was kept as five equivalents to that of the V(V) complexes. This was proven on acquisition of HFEPR spectra. A comparative study was carried out on the V(III) species, [V(dipic)(Hdicpic)(OH)$_2$] and [V(dipic)(H$_2$O)$_2$F]. All the investigated samples produced well-defined EPR spectra at sufficiently high frequencies and fields. The spectra can be interpreted as originating from a ground $S = 1$ state, as expected for V(III). In particular, the solid complex [V(dipic)(Hdicpic)(OH)$_2$] yielded spectra of an unprecedented quality for V(III) (Figure 1), which could be almost perfectly simulated using a powder pattern for the triplet state, with a positive value for the zero-field parameters.

Conclusions
We have successfully acquired the first HFEPR spectra for V(III) complexes with dipicolinic acid and its analogs as ligands. It was found that H$_2$A, a two electron reductant, reduces V(V) species to form V(III) species.

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References