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Valence Delocalization in a Mixed-Oxidation Divanadium (IV, V) Complex Electrogenerated from Its Structurally Characterized Divanadium (V) Analogue with a Tridentate (ONO) Ligand

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Introduction

Coordination chemistry of vanadium with multidentate ligands is receiving special attention in the past decade because of its catalytic¹² and medicinal³⁻⁵ importance. Structural and/or functional models for vanadate-dependent haloperoxidases, vanadium nitrogenases, and other biologically active vanadium compounds have further stimulated research efforts on vanadium coordination chemistry.⁶ The study of mixed-valence vanadium chemistry is an area of contemporary research interest.^{7,8} Over the past few years, our group has been working on the coordination chemistry of vanadium and has reported the synthesis, characterization, chemical and electrochemical properties of V(III) and V(IV) complexes⁹⁻¹⁴ along with biological activity of some of them.^{15,16} In the present work, we report the synthesis, characterization, and crystal structure of a new complex containing the $\{OV^V(\mu-O) V^VO\}^{4+}$ unit which exhibits the following characteristics. (i) The bridging O atom does not lie on a 2-fold axis, and the two halves of the molecule are not crystallographically equivalent.¹⁷⁻¹⁹ (ii) The V-O-V angle in this compound is quite small (112.06°), and only two other molecules of similar type are known^{19,20} where the V-O-V angles are still smaller. (iii) It is the most stable of the reported complexes^{18,21} containing the $V_2O_3^{4+}$ core as evidenced by the highly negative potentials at which the V^V centers undergo successive reduction. (iv) The two V^V centers of the $V_2O_3^{4+}$ core are found to undergo electrochemical reduction in two distinctly separate steps which are not found in previous reports.^{18,21} We also report here a mixed-oxidation state species $[L(O)V^{IV}OV^V(O)L]^-$ electrogenerated from its divanadium(V) analogue in solution and characterized by IR, EPR, and electronic spectroscopy. To our knowledge, it is a rare example of a mixed-oxidation $[L(O)V^{IV}OV^V(O)L]^-$ species electrogenerated from its divanadium(V) analogue in which the two VOL units are crystallographically nonequivalent.

