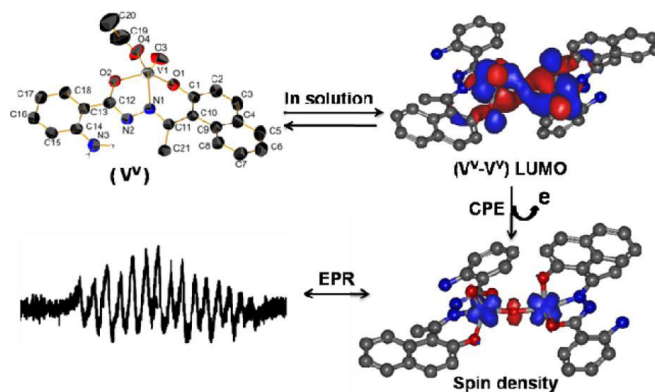


“Versatile Reactivity and Theoretical Evaluation of Mono- and Dinuclear Oxidovanadium(V) Compounds of Aroylazines: Electrogeneration of Mixed-Valence Divanadium(IV,V) Complexes” Rupam Dinda\*, S. P. Dash, S. Roy, M. Mohanty, Department of Chemistry.



The solution behavior of structurally characterized  $[V^V O(OEt)(L)]$  complexes, which transform into the corresponding divanadium(V,V) compounds,  $[\{V^V O(L)\}_2\mu-O]$  is reported. Upon controlled potential electrolysis the corresponding  $[(L)V_2O_3(L)]^-$  mixed-valence species are obtained upon partial reduction of the  $[(V^V O L)_2\mu-O]$  complexes formed in solution. (More in *Inorganic Chemistry*, 2016, 55, 8407–8421)

Details

The substituted hydrazones  $H_2L^{1-4}$  ( $L^{1-4}$  = dibasic tridentate  $ONO^{2-}$  donor ligands) obtained by the condensation of 2-hydroxy-1-naphthaldehyde and 2-aminobenzoylhydrazine ( $H_2hnal-abhz$ ) ( $H_2L^1$ ), 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzoylhydrazine ( $H_2hnal-hbhz$ ) ( $H_2L^2$ ), 2-hydroxy-1-acetonaphthone and benzoylhydrazine ( $H_2han-bhz$ ) ( $H_2L^3$ ), or 2-hydroxy-1-acetonaphthone and 2-aminobenzoylhydrazine ( $H_2hanabhz$ ) ( $H_2L^4$ ) are prepared and characterized. Reaction of ammonium vanadate with the appropriate  $H_2L^{1-4}$  results in the formation of oxidoethoxido vanadium(V)  $[V^V O(OEt)(L^{1-4})]$  (1–4) complexes. All compounds are characterized in the solid state and in solution by spectroscopic techniques (IR, UV–vis,  $^1H$ ,  $^{13}C$ , and  $^{51}V$  NMR, and electrospray ionization mass spectrometry). Single-crystal X-ray diffraction analysis of 1, 3, and 4 confirms the coordination of the corresponding ligands in the dianionic ( $ONO^{2-}$ ) enolate tautomeric form. In solution, the structurally characterized  $[V^V O(OEt)(L)]$  compounds transform into the monooxido-bridged divanadium (V,V)  $[(V^V OL)_2-\mu-O]$  complexes, with the processes being studied by IR and  $^1H$ ,  $^{13}C$ , and  $^{51}V$  NMR. The density functional theory (DFT) calculated Gibbs free energy of reaction  $2[V^V O(OEt)(L^4)] + H_2O \rightleftharpoons [(V^V OL^4)_2-\mu-O] + 2EtOH$  is only 2–3 kcal mol $^{-1}$ , indicating that the dinuclear complexes may form in a significant amount. The electrochemical behavior of the complexes is investigated by cyclic voltammetry, with the  $V^V-V^{IV} E_{1/2}^{red}$  values being in the range 0.27–0.44 V (vs SCE). Upon controlled potential electrolysis, the corresponding  $(L)(O)V^{IV}-O-V^V(O)(L)$  mixed-valence species are obtained upon partial reduction of the  $[(V^V OL)_2-\mu-O]$  complexes formed in solution, and some spectroscopic characteristics of these dinuclear mixed-valence complexes are investigated using DFT calculations and by electron paramagnetic resonance (EPR), with the formation of  $V^{IV}-O-V^V$  species being confirmed by the observation of a 15-line pattern in the EPR spectra at room temperature.