CATALYTIC FOUR-ELECTRON REDUCTION OF OXYGEN TO WATER BY A MOLECULAR COBALT COMPLEX CONSISTING OF A PROTON EXCHANGING SITE AT THE SECONDARY COORDINATION SPHERE

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In this study, we designed and synthesized a mononuclear Co^{III} complex (1) of a bis-pyridine-bis-oxime ligand where the oxime site can participate in reversible proton exchange reactions. Electrocatalytic ORR of 1 was investigated in aqueous buffer solutions and acetonitrile containing trifluoroacetic acid as the proton source. We observed that in a 0.1 M phosphate buffer solution (PBS), 1 is selective for $4e^-/4H^+$ reduction of O_2 at pH 4, and the selectivity decreases with increasing the buffer medium's pH, producing ca. 75% H_2O at pH 7. However, in a 0.1 M acetate buffer solution (ABS), 1 remained highly selective for the cleavage of the O−O bond to produce H_2O at pH 4 and pH 7. The overpotential (η) of H_2O formation (ca. 0.8−0.65 V) decreased proportionally with increasing pH in PBS and ABS. In acetonitrile, 1 remained highly selective for $4e^-/4H^+$ reduction for electrocatalytic and chemical ORR. An overpotential of 760 mV was estimated for H_2O production in acetonitrile. Kinetic analysis suggests the first-order dependence of catalyst concentration on the reaction rate at 25 °C. However, the formation of a peroxo-bridged dinuclear cobalt(III) complex was noted as a reaction intermediate in the ORR pathway in acetonitrile at −40 °C. We conjecture that the oxime scaffold of the ligand works as a proton exchanging site and assists in the proton-coupled electron transfer (PCET) reactivity to cleave the O−O bond in the acidic buffer solutions and acetonitrile, further corroborated by theoretical studies. Density functional theory (DFT) calculation suggests that the acetate ion works as a mediator at pH 7.0 for transferring a proton from the oxime scaffold to the distal oxygen of the $Co^{III}(OOH)$ intermediate, responsible for high selectivity toward $4e^-/4H^+$ reduction of O_2.