Thermodynamic Evaluation of the bis(μ-oxo)/μ-η^2:η^2-peroxo Equilibrium

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An interesting phenomenon in copper-dioxygen chemistry, is the rapid equilibrium between a $[Cu_2^{II}(O_2)]^{2+}$ μ-η^2:η^2-peroxo, and a $[Cu_2^{III}(O)_2]$ bis(*μ*-oxo) species, which can be influenced by several factors (e.g. temperature, solvent, electronic effects). Previously we have shown that by tuning the redox potential of a copper(I) complex $[Cu(R\text{-}PYAN)(CH_3CN)]B(C_6F_5)_4$ (R-PYAN = *N*-[2-(4-R-pyridin-2-yl)-ethyl]-N,N',N'-trimethyl-propane-1,3-diamine) the equilibrium shifts towards the bis(*μ*-oxo) isomer when R = electron donating groups. Full stopped-flow kinetic characterization of the oxygenation reaction of $[Cu(OMe\text{-}PYAN)(CH_3CN)]B(C_6F_5)_4$ (**1**) has been conducted in different solvents to further investigate the thermodynamics of oxygen binding and the ensuing $[Cu_2^{II}(O_2)]^{2+}/[Cu_2^{III}(O)_2]$ equilibrium. In acetone, **1** reacts with O_2 at low temperature (–90 °C) predominantly forming the dicopper(III) bis(*μ*-oxo) ($\mathbf{2^{oxo}}$) complex, while at higher temperatures (> –30 °C) the side-on peroxo ($\mathbf{2^{peroxo}}$) isomer is the major species formed. This temperature dependence allowed for the calculation of the thermodynamic parameters for $\mathbf{2^{peroxo}} \rightleftarrows \mathbf{2^{oxo}}$: $\Delta H° = -14.7$ kJ/mol ± 0.1, $\Delta S° = -68.2$ J/mol ± 0.4.