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Elucidating the secondary effect in the Lewis acid mediated anodic shift of electrochemical oxidation of a Cu(II) complex with a N₂O₂ donor unsymmetrical ligand†

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A metalloligand [CuL] (H₂L = *N*- α -methylsalicylidene-*N'*-salicylidene-1,3-propanediamine) was reacted with a series (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Pr³⁺, Nd³⁺ and Sm³⁺) of redox-inactive metal ions (in excess) with different Lewis acidities in acetonitrile to form heterometallic complexes *in situ*. In the cases of K⁺ and Zn²⁺, single crystals were isolated from their respective solutions and solved. The complexes were found to be trinuclear with the phenoxido bridge between the redox-inactive metals and the copper center having closest equilibrium distance. In solution, some metal ions (Na⁺, K⁺, Mg²⁺ and Ca²⁺) formed predominantly 1 : 1 [CuL] : Mⁿ⁺ adducts whereas others did not. Spectroscopic studies revealed that both the energy and intensity of the LMCT band of [CuL] at 363 nm were influenced by the Lewis acidity of the guest metal ions. The blue shift and the hypochromic shift of this band showed a linear dependence on the Lewis acidity of the corresponding redox-inactive metal ions only for 1 : 1 adducts. A combined EPR and d–d transition spectral analysis of these 1 : 1 adducts in acetonitrile at 298 K indicates that there is a change in the coordination geometry around Cu(II) on proximal cation binding of free [CuL]. The correlation of the half wave potential ($E_{1/2}$) of the first oxidation of [CuL] with pK_a of the corresponding metal(aqua)ⁿ⁺ ion as a measure of its Lewis acidity revealed that the potentials were linearly dependent for 1 : 1 adducts whereas in the case of the other metal ions an unexpected deviation from linearity was observed. An incremental addition of water to some of these mixtures revealed a decrease in the corresponding oxidation peak potential with a concomitant increase in the molar absorptivity. The molar absorptivities of different mixtures with their corresponding $E_{1/2}$ values show a linear dependence with better correlation suggesting that the modulation of electron density around Cu(II) regulates the electrochemical oxidation of the metalloligand.

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Introduction

One of the common structural features of active sites of natural redox active metalloproteins is the presence of redox-inactive metal ions in close proximity, as for instance, Ca²⁺ in a highly hydrated Mn₄-oxygen evolving complex (OEC).^{1,2} It is now well known that Ca²⁺ controls the binding and activation

of a water substrate as well as the redox properties of the Mn-cluster of the OEC.^{3,4} These observations in natural systems open up a new way of activating a synthetic metal ion catalyst. For example, the addition of strongly Lewis acidic metal ions (Al³⁺ or Sc³⁺) in multiple equivalents causes a remarkable improvement in the efficiency of oxidation of sluggish high valent metal complex catalysts.^{5–8} In fact, the Lewis acid interaction by redox-inactive metal ions facilitates the rate of electron transfer with a positive shift of the reduction potential of the corresponding redox active metal complexes.^{9,10} To address the role of Ca²⁺ in the OEC and various redox-inactive Lewis acidic metal ions in synthetic models, Agapie *et al.*^{11–15} demonstrated that the reduction potentials of the isostructural redox active heterometallic clusters containing a redox-inactive metal ion are linearly correlated with pK_a of the corresponding metal aqua ion as a measure of its Lewis acidity. Similar investigations by several other groups have also suggested this trend for different dinuclear species.^{16–19} All these results indi-

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† Electronic supplementary information (ESI) available: Benesi–Hildebrand plot, representative ESI-mass spectrum, $\Delta\lambda_{\max}$ vs. pK_a plot, cyclic voltammetry and DPV analyses, UV-vis spectra, correlation of ΔE_{pa} vs. equiv. of water added and $\Delta\epsilon$ vs. equiv. of water added, ΔE_{pa} vs. $\Delta\epsilon$ correlation for incremental addition of aqueous acetonitrile, bond lengths and angles of complexes 1 and 2, some literature reports of redox potential vs. pK_a correlation diagrams. CCDC 1896197 and 1896198. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT03323H