

Macrocycles Enable Tuning of Uranyl Electrochemistry by Lewis Acids

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Abstract : Capture and activation of the water-soluble uranyl dication (UO_2^{2+}) remains a challenging problem, as few rational approaches are available for modulating the reactivity of this species. Here, we report the divergent synthesis of heterobimetallic complexes in which UO_2^{2+} is held in close proximity to a range of redox-inactive metals by tailored macrocyclic ligands. Crystallographic and spectroscopic studies confirm assembly of homologous $\text{UVI}(\mu\text{-OAr})_2\text{Mn}^+$ cores with a range of mono-, di-, and trivalent Lewis acids (Mn^+). X-ray diffraction (XRD) and cyclic voltammetry (CV) data suggest preferential binding of K^+ in an 18-crown-6-like cavity and Na^+ in a 15-crown-5-like cavity, both appended to Schiff-base type sites that selectively bind UO_2^{2+} . CV data demonstrate that the UVI/UV reduction potential in these complexes shifts positive and the rate of electron transfer decreases with increasing Lewis acidity of the incorporated redox-inactive metals. Moreover, spectroelectrochemical studies confirm the formation of [UV] species in the case of monometallic UO_2^{2+} complex, consistent with results from prior studies. However, unique features were observed during spectroelectrochemical studies in the presence of the K^+ ion, suggesting new insights into electronic structure may be accessible with the heterobimetallic complexes. Overall, these findings suggest that interactions with Lewis acids could be effectively leveraged for rational tuning of the electronic and thermochemical properties of the 5f elements, reminiscent of strategies more commonly employed with 3d transition metals.

Keywords : electrochemistry, Lewis acid, macrocycle, uranyl

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