Reaction of Cu(II) Chelates with Uranyl Nitrate to Form a Coordination Complex or H-Bonded Adduct: Experimental Observations and Rationalization by Theoretical Calculations

Pradip Bhunia, Soumavo Ghosh, Rosa M. Gomila, Antonio Frontera,* and Ashutosh Ghosh*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Four new heterometallic Cu(II)−U(VI) species, $[\{(CuL^1)\text{-}(CH_3CN)\}UO_2(NO_3)_2]$ (**1**), $[\{(CuL^2)(CH_3CN)\}UO_2(NO_3)_2]$ (**2**), $[\{(CuL^3)(H_2O)\}UO_2(NO_3)_2]$ (**3**), and $[UO_2(NO_3)_2(H_2O)_2]\cdot2[CuL^4]\cdot H_2O$ (**4**), were synthesized using four different metalloligands ($[CuL^1]$, $[CuL^2]$, $[CuL^3]$, and $[CuL^4]$, respectively) derived from four unsymmetrically dicondensed N,O-donor Schiff bases. Single-crystal structural analyses revealed that complexes **1**, **2**, and **3** have a discrete dinuclear $[Cu−UO_2]$ core in which one metalloligand, $[CuL]$, is connected to the uranyl moiety via a double phenoxido bridge. Two chelating nitrate ions complete the octa-coordination around uranium. Species **4** is a cocrystal, where a uranyl nitrate dihydrate is sandwiched between two metalloligands $[CuL^4]$ by the formation of strong hydrogen bonds between the H atoms of the coordinated water molecules to U(VI) and the O atoms of $[CuL^4]$. Spectrophotometric titrations of these four metalloligands with uranyl nitrate dihydrate in acetonitrile showed a well-anchored isosbestic point between 300 and 500 nm in all cases, conforming with the coordination of $[CuL^1]$, $[CuL^2]$, $[CuL^3]$, and the H-bonding interaction of $[CuL^4]$ with $UO_2(NO_3)_2$. This behavior of $[CuL^4]$ was utilized to selectively bind metal ions (e.g., Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and La^{3+}) in the presence of $UO_2(NO_3)_2\cdot2H_2O$ in acetonitrile. The formation of these Cu(II)−U(VI) species in solution was also evaluated by steady-state fluorescence quenching experiments. The difference in the coordination behavior of these metalloligands toward $[UO_2(NO_3)_2(H_2O)_2]$ was studied by density functional theory calculations. The lower flexibility of the ethylenediamine ring and a large negative binding energy obtained from the evaluation of H bonds and supramolecular interactions between $[CuL^4]$ and $[UO_2(NO_3)_2(H_2O)_2]$ corroborate the formation of cocrystal **4**. A very good linear correlation ($r^2 = 0.9949$) was observed between the experimental U≡O stretching frequencies and the strength of the equatorial bonds that connect the U atom to the metalloligand.
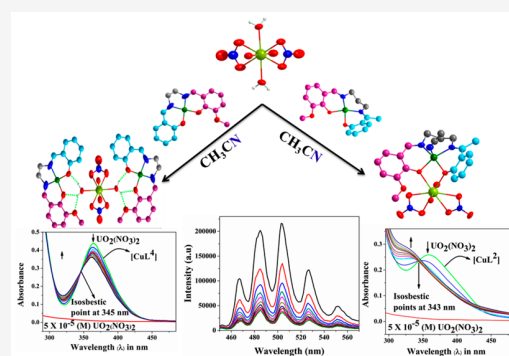
■ INTRODUCTION

The coordination and organometallic chemistry of actinides, especially uranium, have been explored extensively over last two decades.[1−7] These studies have important applications not only in the extraction of actinides,[8−10] nuclear fuel processing,[11] environmental remediation,[12] and nuclear forensics[13] but also in the fields of magnetism,[14,15] optics,[16,17] catalysis,[18,19] and electrochemistry.[20−22] Among these, the sequestration of uranium from its daughter nuclides in a spent nuclear fuel is of potential concern in terms of economic and environmental issues, such as recycling and radioactive waste handling.[23−26] During the nuclear fission process, a number of radioactive fission products, e.g., cesium, strontium, barium, lanthanides, etc., are formed and need to be separated from the spent nuclear fuel in a timely manner.[27] One of the convenient ways to separate these metal ions is to use a ligand that can selectively bind either uranium or these metal ions.[28−30] The selectivity of such a ligand exploits the key differences of size and chemistry between the linear triatomic uranyl cation,

which allows the coordination of the ligand only to the equatorial plane from these metal ions with no coordination site preference. Moreover, if the ligand is stereochemically rigid, then it often shows unusual coordination behavior toward metal ions with a coordination preference due to the mismatch in cavity size and denticity of ligand vs the size and available coordination site of the guest, which is crucial for selectivity.[31]

On the other hand, N,O-donor ligands have been used widely for the synthesis of heterometallic complexes in past few decades. The relatively softer N-donor sites of such ligands bind the soft metal ions (e.g., transition metal), and harder O-