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Structural variation within uranium^{VI} heterocyclic carboxylates: Solid and solution states studies

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ABSTRACT

The solution chemistry and solid-state structures of two new uranium^{VI} metal–organic compounds, $(tataH)_2[(UO_2)_2(pdtc)_2(\mu\text{-}OH)_2]\cdot 2H_2O$ (**1**) and $(AcrH)_2[(UO_2)(pydc)_2]$ (**2**), [where tata = 1,3,5-triazine-2,4,6-triamine, Acr = acridine, pydc = pyridine-2,6-dicarboxylate and pdtc = pyridine-2,6-bis(monothiocarboxylate)] have been investigated. These compounds were obtained *via* proton-transfer methodology by reacting UO_2^{2+} with the preformed proton-transfer systems $(tataH)_2(pdtc)$ and $(AcrH)_2(pydc)$, respectively, in aqueous solution, after evaporation of the solvent. Our results show that noncovalent interactions such as hydrogen bonds, sulfur···sulfur, and $\pi\cdots\pi$ interactions, when acting cooperatively, are driving forces for the selection of different structures. The protonation constants of Acr, tata, $pdtcH_2$, and $pydcH_2$, the building blocks of the proton-transfer systems $(tataH)_2(pdtc)$ and $(AcrH)_2(pydc)$, and the stability constants of these systems were determined by potentiometric studies in a dioxane/H_2O (1:1 v/v) mixture. The stoichiometry and the formation stability constants of complexes formed on reacting $pydcH_2$/Acr or $pdtcH_2$/tata 1:1 molar mixtures with the UO_2^{2+} ion in dioxane/H_2O (1:1 v/v) were investigated by potentiometric pH titration methods. The stoichiometries of the complex species formed in solution were compared with those observed for the crystalline metal ion complexes **1** and **2**.

1. Introduction

The chemistry of uranium has rapidly expanded over the past decade as the result of several drivers [1–8]. The primary motivation for these new studies is the fact that uranium and other actinides are major contributors to the long-term radioactivity of nuclear wastes with increasing concern for possible environmental and health effects from their contamination. The reduction of nuclear waste from spent reactor fuel along with the extraction of uranium from seawater, groundwater, soil, and the development of actinide decorporation agents (ligands for selective actinide chelation in *vivo*) represent very active areas of research [9–14]. In this respect, knowledge of the binding modes of uranium and actinides under various environmental conditions is very important for long-term nuclear waste disposal and is still relatively limited in comparison to transition metals. Therefore, it is necessary to continue to investigate all aspects of the coordination chemistry in solution and in the solid state of uranium (and actinides). Selected ligands, particularly preorganized bi- or multidentate ligands containing N- and/or O-donors atoms based on chelating units found in siderophores can be used for this purpose. Naturally occurring highly selective sequestering agents for transition metals having similar charge to ionic size ratios and hydrolysis properties can also be employed as models for new ligands.

Over the past decade, our research groups have been interested in the syntheses, structural features and coordination behavior towards metal ions of proton-transfer compounds obtained on reacting organic donor ligands containing N, S, and O atoms and aromatic or aliphatic polycarboxylic acids, including pyridine-2,6-dicarboxylic acid ($pydcH_2$) [15]. It is generally accepted for proton transfer compounds that reaction of an acid with a base will form a proton-transfer salt if the ΔpK_a ($\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid})$) is greater than 2 or 3. $PydcH_2$ has recently attracted much interest in coordination chemistry; $pydcH_2$ has a rigid 120° angle between the central pyridine ring and the two carboxylic(ate) groups and could therefore potentially provide various coordination motifs

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under appropriate synthetic conditions for transition metals and actinides, in particular UO_2^{2+} [9–21]. On the other hand, since carboxylic acids are present in many natural products, metal complexes of $pydcH_2$ in its deprotonated forms could represent useful model systems. Interestingly, the structural analog pyridine-2,6-bis(monothiocarboxylic) acid ($pdtcH_2$) is a unique and powerful naturally-occurring metal chelator produced by soil bacteria *Pseudomonas stutzeri* and *Pseudomonas putida*, and whose physiological role is that of a siderophore, an antibiotic, or both [22]. In this paper, following our interest in the application of proton-transfer compounds of carboxylic acids to the preparation of metal–organic structures featuring multidimensional architectures in the crystal packing *via* weak interactions [23–29], we report the syntheses and structural comparison of the two new uranyl complexes $(tataH)_2[(UO_2)_2(pdtc)_2(\mu\text{-}OH)_2]\cdot 2H_2O$ (**1**) and $(AcrH)_2[(UO_2)(pydc)_2]$ (**2**), starting from the preformed $(tataH)_2(pydc)$ and $(AcrH)_2(pdtc)$ proton-transfer systems. In particular, in order to develop new types of actinide-based coordination compounds with the ability to assemble in the solid-state, we intended to investigate the influence of the differences between $pydcH_2$ and $pdtcH_2$ as multidentate ligands on the structural properties and crystal packing of the resulting coordination compounds with UO_2^{2+}. Furthermore, the behavior of UO_2^{2+} in the presence of $pydcH_2$/Acr or $pdtcH_2$/tata 1:1 molar mixtures in dioxane/H_2O (1:1 v/v) solutions has also been investigated.

2. Experimental

2.1. Instruments and materials

All melting points are uncorrected and were determined using an Electro thermal IA-9100 instrument. Microanalytical data were obtained using a Thermo Finnigan Flash-1112EA microanalyzer. FTIR spectra were recorded on a Bomem B-154 Fourier transform spectrometer as KBr disks. NMR spectra were recorded on a Bruker DRX 300-Avance spectrometer (300 MHz) and chemical shifts are reported on the δ scale relative to TMS. For potentiometric solution studies, a Model 794 Metrohm Basic Titrino was connected to a combined glass–calomel electrode mounted in an air-protected, sealed, thermostated jacketed cell maintained at 25.0 ± 0.1 °C by circulating water, from a constant-temperature bath (Fisherbrand model FBH604, LAUDA, Germany), equipped with a stirrer and a 10.0 mL capacity Metrohm piston burette. The pH meter-electrode system was calibrated to read $-\log [H^+]$ in a dioxane/H_2O (1:1 v/v) solution. Uranyl acetate, $pydcH_2$, Acr, and tata (analytical grade, Merck Chemicals) were used as received. $pdtcH_2$ was prepared according to the reported procedure [30]. In synthetic procedures tataH/pdtc and AcrH/pydc mixtures (2:1 molar ratio) were used.

2.1.1. Synthesis of $(tataH)_2[(UO_2)_2(pdtc)_2(\mu\text{-}OH)_2]\cdot 2H_2O$, 1

Uranyl acetate (0.212 g, 0.5 mmol) was dissolved in distilled water (3 mL). The proton-transfer compound $(tataH)_2(pdtc)$ (0.324 g, 1.0 mmol) was added to boiling distilled water (30 mL) while stirring. The uranyl acetate solution was then added dropwise to the latter solution and heating was continued for 10 min and the resulting hot solution filtered off. After cooling the filtrate, a scarlet participate was obtained. The precipitate was filtered off and dried to obtain 0.46 g product in 93% yield based on uranyl acetate. The crude product was recrystallized from distilled water (100 mL). Yellow single crystals of the title compound were obtained after 3 days: M.p. 260–261 °C. Elem. *Anal.* Calc. for $C_{20}H_{26}N_{14}O_{12}S_4U_2$: C, 19.08; H, 2.08; N, 15.58; S, 10.19. Found: C, 19.05; H, 2.04; N, 15.56; S, 10.23%. IR (KBr pellet, cm^{-1}): 3400–3178(br), 2348(s), 1720–1639(m), 1584(m), 1529(s), 1421(s), 1373(s), 1179(m), 900(s), 780(m), 731(s). ^1H NMR (DMSO-d_6, 300 MHz, δ/ppm): 9.05 (d, J = 7.5 Hz, 4H), 8.57 (t, J = 7.5 Hz, 2H), 6.05 (6H, broad).

2.1.2. Synthesis of $(AcrH)_2[(UO_2)(pydc)_2]$, 2

Compound **2** was obtained by a similar method as used for the preparation of **1** but using the proton-transfer compound $(AcrH)_2(pydc)$ (0.525 g, 1.0 mmol). After cooling, the red participate obtained was filtered off and dried to afford 0.31 g product in 95% yield based on uranyl acetate. The crude product was recrystallized from distilled water (100 mL). Red blocky single crystals of the title compound were obtained after two months: M.p. 300 °C. Elem. *Anal.* Calc. for $C_{40}H_{26}N_4O_{10}U$: C, 50.01; H, 2.73; N, 5.83. Found: C, 50.06; H, 2.79; N, 5.79%. IR (KBr pellet, cm^{-1}): 3435(br), 3057(br), 2885–2830(br), 1703(s), 1652(s), 1588(m), 1575(m), 1442(m), 1400(m), 1376(s), 1236(s), 1141(m), 1064(m), 935(w), 872(m), 795(m), 736(s). ^1H NMR (DMSO-d_6, 300 MHz, δ/ppm): 9.09 (s, 1H), 8.23 (d, J = 7.5 Hz, 2H), 8.15 (d, J = 7.5 Hz, 5H), 7.84 (t, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 2H).

2.1.3. Potentiometric measurements

All pH measurements (pH $-\log [H^+]$) employed for the determination of ligand protonation and uranyl complex stability constants were carried out in 0.1 M $NaClO_4$ dioxane/H_2O (1:1 v/v) solution at 25.0 ± 0.1 °C by means of conventional titration experiments under an inert atmosphere. The choice of the solvent mixture was dictated by the low solubility of Acr in pure water at neutral and alkaline pH values. A jacketed cell containing the test solution was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and 10 mL capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. Atmospheric CO_2 was excluded from the titration cell by purging with a stream of purified nitrogen gas. The concentrations of Acr, $pydcH_2$, $pdtcH_2$ and tata were in the range $2.00 \times 10^{-3} - 3.33 \times 10^{-3}$ M, in the absence and presence of uranyl cation ($1.00 \times 10^{-3} - 1.67 \times 10^{-3}$). A standard carbonate-free NaOH solution (0.097 M) was used in all titrations. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligand protonation constants and stability constants of proton-transfer systems and their complexes with the uranyl cation were evaluated using the program BEST described by Martell and Motekaitis [31]. The value of the autoprotolysis constant for dioxane/H_2O (1:1 v/v) solution ($Ks = [H^+][OH^-]$) was calculated according to the literature [32].

2.1.4. Crystallographic data collection and structure determination for 1 and 2

A summary of the crystal data and refinement details for the compounds discussed in this paper are given in Table 1. Only special features of the analyses are mentioned here. For both compounds, the crystallographic results presented here are the best of several trials. Single-crystal data collection for **1** and **2** was performed on a Bruker SMART 1000 and a SMART APEX II CCD area detector diffractometer, respectively, equipped with an Oxford Cryosystems open-flow nitrogen cryostat, using ω scans and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were mounted on thin glass fibers using paraffin oil. All data sets were corrected for Lorentz, polarization and absorption effects as specified in Table 1. Structure solution in centrosymmetric space groups yielded chemically reasonable and computationally stable refinement models for both compounds. The structures were solved by direct methods using SHELXS97 [33,34], completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2 using SHELXL97 [35]. All non-hydrogen atoms were refined with anisotropic displacement parameters. In **1**, N–H and O–H hydrogen atoms were located from difference maps: the latter were then refined with distance restraints of 0.86(1) Å for O–H and