Uranium(VI) Complexes with a Calix[4]arene-Based 8-Hydroxyquinoline Ligand: Thermodynamic and Structural Characterization Based on Calorimetry, Spectroscopy, and Liquid–Liquid Extraction

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1. UV visible Spectroscopy

![Graph showing UV visible spectra](image)

**Figure S1.** UV visible spectra of 50 μM H₆L in acetonitrile at different uranyl nitrate concentrations (0 – 70.8 μM, 25°C, I = 0.01 M NaClO₄). All spectra are normalized to 1 to show shift of bands.

![Graph showing UV visible spectrum](image)

**Figure S2.** UV visible spectrum of 12.5 μM [UO₂(H₆L)(NO₃)](NO₃)₁ in acetonitrile (25°C, I = 0.01 M NaClO₄).

**Method of Continuous Variations (Job Plot)**

This method provides qualitative insights into the stoichiometries underlying association of m molecules of A and n molecules of B to form complexes of [AₘBₙ].

\[ mA + nB \rightleftharpoons AₘBₙ \]  \hspace{1cm} (1)

In the method of continuous variations usually batch titrations were carried out where the total concentration of component A and B (see equation 1) is constant, only the relative proportions of A and B varies. By monitoring the electronic absorption spectrum (or another physical property that correlates linearly with the concentration of [AₘBₙ]) of these solutions and plotting the absorption values of all spectra at a specific wavelength as a function of mole fraction a bell-shaped curve is resulted. The

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1 J. S. Renny, L. L. Tomasevich, E. H. Tallmadge, D. B. Collum, *Angew. Chem. Int. Ed. Engl.* 2013, 52, 11998–12013.
position of the maximum of the curve provides the stoichiometry of the formed (limiting) complex species. Thus, does the Job Plot display maxima at \( x = 0.5 \) a 1:1 \((m = n)\) complex is formed whereas a maximum at \( x = 0.33 \) reveals a 2:1 species.

This method is proven successfully in the analysis of very stable metal–ligand complexes for several years. However, more complicated cases like a dynamic equilibrium of at least two complex species may provide false results. The resulting Job plot for complexation of \( H_6L \) and \( UO_2(NO_3)_2 \cdot 6H_2O \) in acetonitrile (Figure S3) displays an inflection point at a mole fraction of 0.34 suggesting the formulation only of a 2:1 species. But due to the analysis of the spectrophotometric data with HypSpec there is an equilibrium of more than one complex species in solution, but to the best of our knowledge the 1:1 and 2:1 species are the dominate ones under the chosen conditions. Although various possible complex species \([UO_2]_m(H_6L)_n\) were submitted as input to the HypSpec software, nonlinear least-squares refinements only converged consistently for a speciation model involving 1:1 as well as 2:1 complexes.

Figure S3. Job plot for complexation of \( H_6L \) and \( UO_2(NO_3)_2 \cdot 6H_2O \) in acetonitrile by UV visible spectroscopy at 519 nm; \( c_{total} = 100 \mu M \) (25°C, \( I = 0.01 \) m NaClO₄).

2. Luminescence studies

Verification of Complexation

A sample series with a constant \( UO_2(NO_3)_2 \cdot 6H_2O \) concentration of 50 \( \mu M \) and a \( H_6L \) concentration varying from 0 to 30 \( \mu M \) in acetonitrile was prepared. Samples were measured in a rectangular quartz glass cuvette of 10 mm path length. The sample temperature was adjusted by a Peltier element (TC125 Temperature Control, Quantum Northwest). The luminescence was excited at 266 nm by using a Nd:YAG laser (minilite, Continuum) with 0.3 mJ per 5 ns pulse. The emitted light was transmitted to a spectrometer (HORIBA, slit width 200 \( \mu m \)) via fiber optics. Luminescence spectra were recorded with an ICCD camera (ICCD-3000, HORIBA) in the range from 370 to 669 nm with a resolution of 0.46 nm.
The luminescence spectrum of UO$_2$(NO$_3$)$_2$·6H$_2$O exhibits emission bands at 467, 486, 507, 529 and 552 nm in acetonitrile. The attenuation of the luminescence signal as well as the change in the peak ratios with increasing ligand concentration shown in Figure S4 suggest an interaction between H$_6$L and uranyl ions in acetonitrile. After the addition of 0.6 equivalents of ligand, no luminescence signal for UO$_2$(NO$_3$)$_2$·6H$_2$O could be detected any more. To derive complex formation constants in such a complex system only by exploiting this quenching effect was considered to be too uncertain. UV visible spectroscopy was therefore used for further complexation studies.

Figure S4. Normalized luminescence spectra of 50 µM UO$_2$(NO$_3$)$_2$·6H$_2$O in acetonitrile with increasing concentration of calix[4]arene H$_6$L (I = 0.01 M NaClO$_4$) (left). Normalized luminescence spectra of 50 µM UO$_2$(NO$_3$)$_2$·6H$_2$O and after addition of 0.5 equivalents of H$_6$L in acetonitrile (I = 0.01 M NaClO$_4$) (right).
3. Crystallographic Parameters and Details on Crystal Structure Determination

Table S1. Crystallographic data for [UO$_2$(H$_6$L)(NO$_3$)](NO$_3$)$_2$·6(MeCN) (1·6MeCN).

| Chemical formula | $\text{C}_{80}\text{H}_{92}\text{N}_{14}\text{O}_{16}\text{U}$ |
|------------------|---------------------------------------------------|
| Formula weight   | 1743.70 g/mol                                      |
| Temperature      | 273(2) K                                          |
| Wavelength       | 0.71073 Å                                         |
| Crystal system   | triclinic                                          |
| Space group      | $P\overline{1}$                                   |
| Unit cell dimensions | $a = 15.917(3)$ Å, $\alpha = 66.58(3)^\circ$ |
|                  | $b = 16.576(3)$ Å, $\beta = 81.41(3)^\circ$      |
|                  | $c = 17.131(3)$ Å, $\gamma = 71.83(3)^\circ$     |
| Volume           | 3939.0(17) Å$^3$                                  |
| Z                | 2                                                 |
| Density (calculated) | 1.470 g/cm$^3$                                |
| Absorption coefficient | 2.136 mm$^{-1}$                                |
| $F$(000)         | 1780                                              |
| Theta range for data collection | 2.19 to 19.03$^\circ$                           |
| Reflections collected | 12531                                            |
| Independent reflections | 6348 [R(int) = 0.0185] | 99.9% |
| Coverage of independent reflections | 6348 / 0 / 947 | 1.060 |
| Data / restraints / parameters | 6348 / 0 / 947 | 1.060 |
| Goodness-of-fit on F2 | 5614 data; I>2σ(l) | $R_1 = 0.0520$, $wR_2 = 0.1245$ |
|                  | all data                                          |
|                  | $R_1 = 0.0638$, $wR_2 = 0.1380$                   |
| Largest diff. peak and hole | 4.975 and -1.032 eÅ$^{-3}$ |
| R.M.S. deviation from mean | 0.116 eÅ$^{-3}$ |

* $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, *b* $wR_2 = \sqrt{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table S2. Selected bond distances for [UO$_2$(H$_6$L)(NO$_3$)](NO$_3$)$_2$·6(MeCN) (1·6MeCN).

| atoms | bond length / Å |
|-------|-----------------|
| U1–N14 | 2.921(12) |
| U1–N6  | 2.576(9)  |
| U1–O10 | 1.746(7)  |
| U1–O7  | 2.515(7)  |
| U1–O9  | 1.751(7)  |
| U1–N5  | 2.634(9)  |
| U1–O11 | 2.513(7)  |
| U1–O12 | 2.490(7)  |
| U1–O8  | 2.303(8)  |
Table S3. Selected bond angles for [UO$_2$(H$_2$L)(NO$_3$)](NO$_3$) • 6(MeCN) (1 • 6MeCN).

| atoms          | angle / ° | atoms          | angle / ° |
|----------------|-----------|----------------|-----------|
| O10–U1–O9      | 177.5(3)  | O10–U1–O8      | 89.7(3)   |
| O9–U1–O8       | 92.9(3)   | O10–U1–O12     | 94.1(3)   |
| O9–U1–O12      | 86.8(3)   | O8–U1–O12      | 65.3(3)   |
| O10–U1–O11     | 91.7(3)   | O9–U1–O11      | 87.0(3)   |
| O8–U1–O11      | 116.4(3)  | O12–U1–O11     | 51.2(3)   |
| O10–U1–O7      | 83.6(3)   | O9–U1–O7       | 93.9(3)   |
| O8–U1–O7       | 173.0(3)  | O12–U1–O7      | 113.2(3)  |
| O11–U1–O7      | 62.1(3)   | O10–U1–N6      | 96.9(3)   |
| O9–U1–N6       | 84.3(3)   | O8–U1–N6       | 63.9(3)   |
| O12–U1–N6      | 127.7(3)  | O11–U1–N6      | 171.4(3)  |
| O7–U1–N6       | 118.8(3)  | O10–U1–N5      | 90.5(3)   |
| O9–U1–N5       | 88.3(3)   | O8–U1–N5       | 122.4(3)  |
| O12–U1–N5      | 171.1(3)  | O11–U1–N5      | 121.2(3)  |
| O7–U1–N5       | 59.8(3)   | N6–U1–N5       | 59.0(3)   |
| O10–U1–N14     | 94.9(3)   | O9–U1–N14      | 84.9(3)   |
| O8–U1–N14      | 90.8(3)   | O12–U1–N14     | 25.5(3)   |
| O11–U1–N14     | 25.8(3)   | O7–U1–N14      | 87.9(3)   |
| N6–U1–N14      | 151.8(3)  | N5–U1–N14      | 146.4(3)  |
| N14–O11–U1     | 95.3(7)   | N14–O12–U1     | 96.6(7)   |
Figure S5. Crystal packing of $[\text{UO}_2(\text{H}_6\text{L})\text{NO}_3]\text{NO}_3$ in crystals of 1·6MeCN. Thermal ellipsoids are drawn at 50 % probability. Solvent molecules are omitted for clarity. The parallel arrangement of adjacent heterocyclic units is $d$(centroid−centroid) 3.53 Å manifesting weak stacking interactions.²

² E. A. Meyer, R. K. Castellano, J. F. Diederich, Angew. Chem. Int. Ed. 2003, 42, 1210–1250
4. Liquid-Liquid Extractions

For the distribution experiments a series of solutions containing different concentrations of H₆L (1.0⋅10⁻⁵ – 2.6⋅10⁻⁴ M) in chloroform were prepared (Figure S5). 4 mL of these solutions were mixed with equal volumes of the aqueous phase containing 50 µM U⁶⁺ and shaken for 4 h at 400 rpm. The distribution experiments were performed at pH 6. The pH adjustment and the determination of U⁶⁺ concentrations were carried out as described in manuscript.

![Figure S6. Percentages of U⁶⁺ extracted by H₆L in chloroform as a function of equivalents H₆L at pH 6. Experimental data (black cycles) and linear fit of the experimental data (black lines).](image)

Distribution ratios (D) and separation factors (SF₆⁺/Eu³⁺) were calculated using following equations where \( c₀ \) is the initial concentration and \( c₁ \) the final concentration of the metal cation in the aqueous phase, respectively.

\[
D = \left( \frac{c₀ - c₁}{c₁} \right) \tag{2}
\]

\[
SF_{U/Eu} = \left( \frac{D_U}{D_{Eu}} \right) \tag{3}
\]

| pH | \( c₀ \) [µg/L] | \( c₁ \) [µg/L] | E [%] | D     | SF₆⁺/Eu³⁺ |
|----|----------------|----------------|------|-------|----------|
| 4  | 2040           | 2160           | 161  | 92.1  | 11.7     | 0.02     | 585 |
| 4.85| 2070           | 2200           | 15.9 | 99.2  | 129.2    | 0.02     | 6460 |
| 5.94| 1920           | 1940           | 14.3 | 99.3  | 133.3    | <0.01    | –   |
| 8.2 | 1850           | 2250           | 85.2 | 95.4  | 20.7     | 34.5     | 0.6  |
5. IR Spectroscopy (ATR FT-IR)

ATR FT-IR spectra of crystalline samples of \( \text{H}_6\text{L} \) and \([\text{UO}_2(\text{H}_6\text{L})(\text{NO}_3)](\text{NO}_3) \cdot 6\text{MeCN} \) were measured on a Bruker Vertex 80/v vacuum spectrometer equipped with a mercury cadmium telluride (MCT) detector. The spectra were averaged over 256 scans and the spectral resolution was 4 cm\(^{-1}\). The used ATR unit DURA SampIR II (Smiths Inc.), a horizontal diamond crystal (d = 4 mm) with nine internal reflections on the upper surface and an angle of incidence of 45°, was purged with a current of dry air (dew point < 213 K).

![Normalized ATR FT-IR spectra of H\(_6\)L (black line) and \([\text{UO}_2(\text{H}_6\text{L})(\text{NO}_3)](\text{NO}_3) \cdot 6\text{MeCN} \) (red line). Shifts of \( \nu(C=O) \), \( \nu(C=N) \), and \( \nu(C–O) \) from 1697, 1597, and 1192 cm\(^{-1}\) in H\(_6\)L to 1695, 1601 and 1190 cm\(^{-1}\) indicate the involvement of the carbonyl group, the aromatic N atom, and the hydroxyl group of the 8-hydroxyquinoline hydrazone carbonyl unit in the binding process. Due to hygroscopic property of the compounds it was not possible to identify definite N-H vibrations.](image)

Figure S7. Normalized ATR FT-IR spectra of H\(_6\)L (black line) and \([\text{UO}_2(\text{H}_6\text{L})(\text{NO}_3)](\text{NO}_3) \cdot 6\text{MeCN} \) (red line). Shifts of \( \nu(C=O) \), \( \nu(C=N) \), and \( \nu(C–O) \) from 1697, 1597, and 1192 cm\(^{-1}\) in H\(_6\)L to 1695, 1601 and 1190 cm\(^{-1}\) indicate the involvement of the carbonyl group, the aromatic N atom, and the hydroxyl group of the 8-hydroxyquinoline hydrazone carbonyl unit in the binding process. Due to hygroscopic property of the compounds it was not possible to identify definite N-H vibrations.
6. Isothermal titration calorimetry (ITC)

The blank experiment was the titration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into acetonitrile (Figure S7, lower graph). The heat values of the dilution in the blank experiment correlate with the heat flow in the complexation experiment (Figure S7, upper graph) starting at 150 min (after 20 injections). Thus, the detected heat flow (0 – 100 min) is due to the complexation of the uranyl ion by the ligand $\text{H}_6\text{L}$. Finally, the integrated binding enthalpy was corrected by the heat values of dilution (see Figure 5).

![Graph showing heat flow vs time for ITC experiments](image)

**Figure S8.** Calorimetric titration of 100 µM $\text{H}_6\text{L}$ with 5 mM $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile ($I = 0.01 \text{ M NaClO}_4$) (upper graph). Calorimetric titration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile ($I = 0.01 \text{ M NaClO}_4$) (lower graph).

7. ESI-TOF mass spectrometry

![ESI-TOF mass spectra](image)

**Figure S9.** Negative ion ESI-TOF MS spectra of 100 µM $\text{H}_6\text{L}$ (left) / 100 µM $\text{H}_6\text{L}$ + 200 µM $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (right) in 80 % acetonitrile / 20 % methanol.