



A new solvated complex of the uranyl ion (UO_2^{2+}) with 8-hydroxyquinoline



Masoud Mirzaei^{a,*}, Azam Hassanpoor^a, Antonio Bauzá^b, Joel T. Mague^c, Antonio Frontera^{b,*}

^a Department of Chemistry, Ferdowsi University of Mashhad, 917751436 Mashhad, Islamic Republic of Iran

^b Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Balears), Spain

^c Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

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ABSTRACT

A new solvated complex of the uranyl ion, $[\text{UO}_2(\text{quin})_2(\text{H}'\text{quin})]\cdot\text{DMF}$ (**1**), ($\text{H}'\text{quin}$ = 8-hydroxyquinoline and $\text{H}'\text{quin}$ = quinolinium-8-olate, i.e. the zwitterionic form of $\text{H}'\text{quin}$) was synthesized and investigated by means of elemental analysis, IR spectroscopy and X-ray crystallography. Interestingly one coordinated 8-hydroxyquinoline is protonated, thus provoking the simultaneous existence of an electron rich and electron poor ring in the same molecule. This clearly enhances the ability of this ring to form antiparallel stacking interactions that are responsible for the solid state architecture of compound **1**. This aspect has been analyzed by means of density functional theory calculations (DFT), molecular electrostatic potential (MEP) tool and Bader's theory of "atoms in molecules".

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1. Introduction

The coordination chemistry of actinide ions is very important for the development of new extractants for the separation and purification of actinide ions from irradiated nuclear fuel and also for the technology concerning the storage of highly radioactive waste materials [1,2]. Uranium is the second most common naturally occurring actinide after thorium, however the former has more applications than the latter [3]. Uranium is most commonly used as nuclear fuel in fission reactors for civilian purposes. It has a strong preference for binding two axial O atoms to form the linear uranyl species UO_2^{2+} in its +6 oxidation state. The uranyl ion exhibits good stability and forms complexes with various O-, N- and S-donor ligands. 8-Hydroxyquinoline ($\text{H}'\text{quin}$), which typically behaves as a bidentate (N, O) ligand, has a great ability to form luminescent coordination compounds either for light-emitting devices [4] or sensors [5]. Since 8-hydroxyquinoline and its anion have been used to construct LEDs and sensors, it appeared interesting to analyze its coordination ability with an actinide element such as uranium, since it might show interesting structural arrangements and properties. As a continuation of our previous research [6–8], we report the synthesis of a new solvated complex

of the uranyl ion (UO_2^{2+}) with 8-hydroxyquinoline, $[\text{UO}_2(\text{quin})_2(\text{H}'\text{quin})]\cdot\text{DMF}$ (**1**), ($\text{H}'\text{quin}$ = 8-hydroxyquinoline and $\text{H}'\text{quin}$ = quinolinium-8-olate, i.e. the zwitterionic form of $\text{H}'\text{quin}$). This structure is characterized by X-ray crystal structure determination, elemental analysis and IR spectroscopy. Moreover, we have studied the noncovalent interaction observed in the solid state by means of density functional theory calculations (DFT), molecular electrostatic potential (MEP) analysis and the Bader's theory of "atoms in molecules" (AIM).

2. Experimental

2.1. Materials and methods

All reagents used in the syntheses were purchased from commercial sources and were used as received without further purification. Infrared spectrum in the range ($4000\text{--}600\text{ cm}^{-1}$) was recorded on a Buck 500 Scientific spectrometer using KBr discs. Elemental analysis was carried out with a Thermo Finnigan Flash-1112EA microanalyzer. The X-ray diffraction data were collected with a Bruker-AXS Smart APEX CCD diffractometer. Absorption corrections were performed with SADABS [9], the structure solved by Patterson methods (SHELXS [10]) and refined with SHELXL [10]. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with

* Corresponding authors.

E-mail addresses: mirzaeesh@um.ac.ir (M. Mirzaei), toni.frontera@uib.es (A. Frontera).

independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined riding on their parent atoms. Data collection with structure refinement parameters are given in Table 1.

In the final refinement, significant residual peaks (ca. $6\text{--}8\text{ e}^{-}/\text{\AA}^3$) remained in the vicinity of the U2 atom. Two possible sources were considered, “whole molecule” disorder or the presence a minor twin domain. Careful inspection of difference maps did not provide enough evidence to establish an alternate location for the molecule containing U2 and refinement of the largest residual peak as an alternate location of U2 did not improve the model. The relatively high value for R_{int} (0.055) suggests that a minor twin domain (non-merohedral twinning) may be present although no direct evidence for it could be obtained with CELL_NOW. Such a situation could generate “ghost” peaks of the uranium atoms from those reflections overlapped to various extents by reflections from the minor domain.

2.2. Synthesis of $[\text{UO}_2(\text{quin})_2(\text{H'quin})]\cdot\text{DMF}$ (**1**)

Refluxing $\text{UO}_2(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.21 g) and H'quin (1.5 mmol, 0.22 g) in 30 mL of a mixture of DMF and water (2:1) for 3 h at 353 K produced a deep orange solution. By slow evaporation of the solvent at room temperature, orange block single crystals of **1** were obtained after one month. Yield: 68% (based on U). Anal. Calc. for $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_6\text{U}$: C, 46.35; H, 4.34; N, 7.218%. Found: C, 46.15; H, 3.53; N, 6.95%. IR (KBr, cm^{-1}): 1624, 1612, 1520, 1470, 1431, 1283, 982, 877, 842.

2.3. Theoretical methods

The energies of all complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory. For uranium, the def2-TZVPP basis set was used. The geometries have been obtained from the crystallographic coordinates apart from the preliminary study where the geometries are optimized. The calculations have been performed by using the program TURBOMOLE version 6.5 [11]. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique [12]. For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3). The “atoms-in-molecules” (AIM) [13] analysis was performed

at the BP86/def2-TZVP level of theory. The calculation of AIM properties was done using the AIMAll program [14].

3. Results and discussion

3.1. Spectroscopic studies

Besides elemental analysis, compound **1** was initially characterized by its IR spectrum. This reveals that the broad band due to phenolic hydroxyl stretching at $3300\text{--}3500\text{ cm}^{-1}$ is absent but absorption bands located at 1431, 1470, 1520 and 1612 are seen which are assigned as characteristic absorptions of the 8-hydroxyquinoline moiety. [15] The strong band at 1624 cm^{-1} is attributed to C=N bond stretching [16] while the symmetric and antisymmetric absorptions of the U=O stretching modes are at 877 and 982 cm^{-1} respectively [17,18].

3.2. Thermogravimetric study

Thermogravimetric analysis for **1** was performed from 5 to $1000\text{ }^{\circ}\text{C}$ (see Fig. S1) and three decomposition stages are observed. In the first stage, the graph shows a weight loss that corresponds to the removal of DMF that occurs at $129\text{ }^{\circ}\text{C}$ (found: 9%, calcd 9.4%). In the second stage, the H'quin decomposed at $236\text{ }^{\circ}\text{C}$ (found: 18%, calcd 18.7%) and the third stage at $403\text{ }^{\circ}\text{C}$ is related to the weight loss of two quin ligands (found: 38.5%, calcd 37.1%). From the remaining weight (found: 38.6%, calcd 37.1%) it could be confirmed that only UO_2 particles remained in the system at temperatures above $500\text{ }^{\circ}\text{C}$.

3.3. Structure of $[\text{UO}_2(8\text{-HQ})_2(8\text{-HQH}')]\cdot\text{DMF}$ (**1**)

The single crystal X-ray diffraction study reveals that in the asymmetric unit there are two independent $[\text{UO}_2(\text{quin})_2(\text{H'quin})]$ complexes and two solvent DMF molecules (see Fig. 2). The coordination around each uranium metal center consists of two nitrogen atoms and two phenolic oxygen atoms from two quin units acting as bidentate (N1, N2, O3, O4 for U1 and N4, N5, O6 O8 for U2) ligands and one phenolic oxygen atom from an H'quin unit acting as monodentate (O5 for U1 and O10 for U2) ligand. The organic ligands occupy the equatorial positions while the axial sites are occupied by two oxo groups (O1, O2 for U1 and O6, O7 for U2). The uranyl (UO_2^{2+}) fragment is uniquely characterized by short U–O (oxo) bond lengths and a linear O–U–O geometry [19]. Each U atom has a coordination number of seven and is in the center of a pentagonal-bipyramid formed by the UO_5N_2 bond set (Fig. 1). The U–N distances are longer than the U–O phenolic distances, a behavior which can be explained by Pearson’s hard and soft acid–base concept [20,21] (see Table 2). That is, since the (UO_2^{2+}) moiety can be considered as a hard acid, it has higher affinity for oxygen than for nitrogen [22].

It should be mentioned that related systems have been previously reported in the literature. For instance, the UO_2^{2+} complexes of 7-substituted derivatives of 8-hydroxyquinoline [23] and adducts of bis(8-hydroxyquinolinato)dioxouranium(VI) [24]. Moreover, a chloroform solvate [25] and unsolvated [26] analogs have been published where the three ligands are coordinated to the uranium, two as bidentate through the nitrogen and the phenolic oxygen atoms, and the third as a monodentate through the oxygen only. Similarly to these previous works, in compound **1** each independent molecule contains an intramolecular N–H \cdots O hydrogen bond (Table 3) which aids in establishing the approximate coplanarity of the monodentate H'quin ligand with the two quin ligands. The dihedral angles between the mean coordination plane and the mean plane of the H'quin ligand are $10.5(2)^{\circ}$ for

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_6\text{U}$
Formula weight (g mol^{-1})	776.58
T (K)	100(2)
Wavelength λ (\AA)	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a (\AA)	11.1730(8)
b (\AA)	19.2921(13)
c (\AA)	13.0426(10)
β ($^{\circ}$)	103.546(1)
V (\AA^3)	2733.1(3)
Z	4
D_{calc} (mg m^{-3})	1.887
$F(000)$	1496
ρ (mm^{-1})	5.991
Crystal size (mm^3)	$0.13 \times 0.11 \times 0.06$
θ range ($^{\circ}$)	1.87 to 28.25
Reflections collected	47652
Reflection independent (R_{int})	13361 (0.0548)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0520, 0.1120
R_1, wR_2 (all data)	0.0611, 0.1168
Goodness-of-fit (GOF) on F^2	1.092
Largest differences peak and hole ($\text{e } \text{\AA}^{-3}$)	7.230 and -5.353

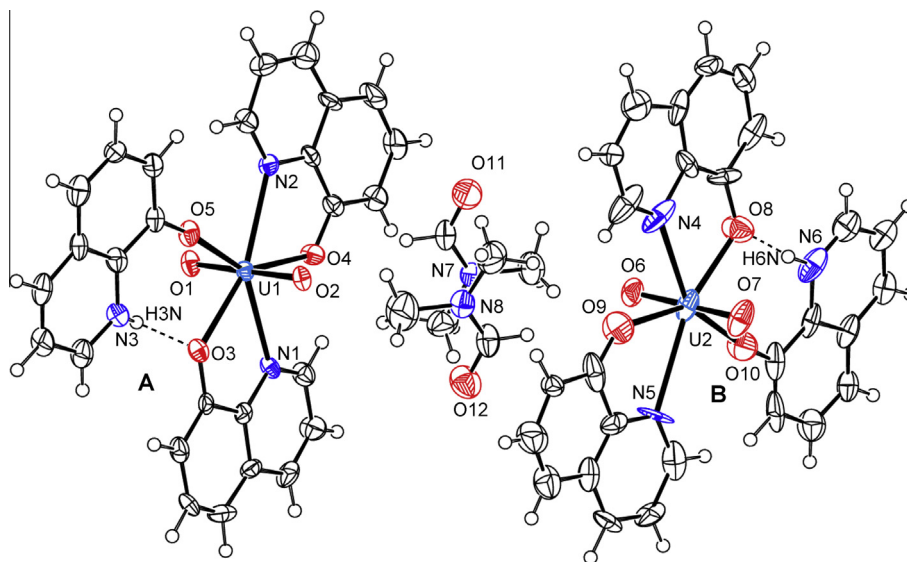


Fig. 1. Perspective view of the asymmetric unit of **1**. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are represented by spheres of arbitrary radius.

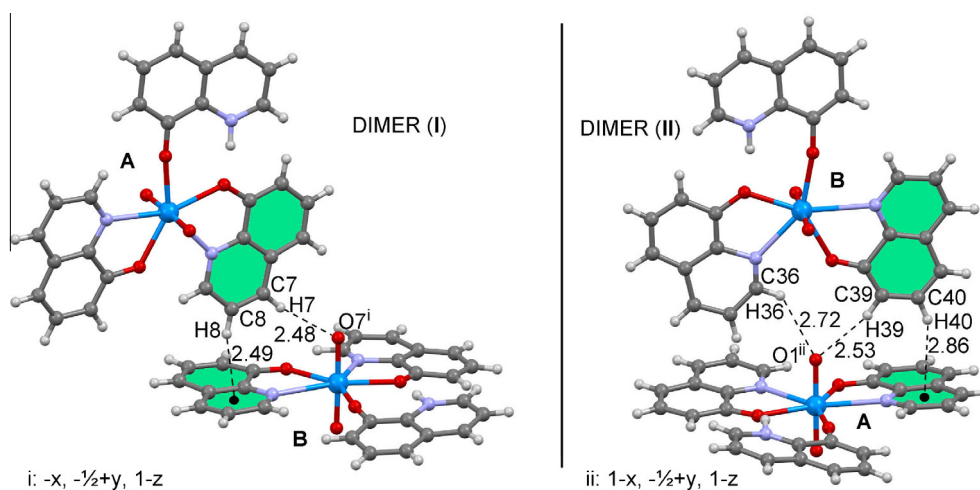


Fig. 2. Partial views of compound **1** with indication of the C–H...O and C–H/π interactions. Distances in Å.

molecule **A** and $8.3(2)^\circ$ for molecule **B**. The solvent DMF molecules lie between the two independent molecules of the complex and appear to be involved in very weak C–H...O interactions with the latter. Regarding the noncovalent interactions, it should be mentioned that intermolecular C–H...O and C–H/π are relevant for the crystal packing (see Fig. 2). The C–H...O interactions involve the UO_2^{2+} moieties of complexes **A** and **B**: C7–H7...O7ⁱ (2.48 Å), C39–H39...O1ⁱⁱⁱ (2.53 Å) and C36–H36...O1ⁱⁱ (2.72 Å). These reported distance values are similar to previously described for C–H...O interactions, where the hydrogen atom is not bonded to an atom with strong electronegativity [27]. The distances observed for C–H/π interactions are very short, especially the C8–H8...Cg (2.49 Å, see Fig. 2, left). As a matter of fact, the conventional C–H/π interaction distance ranges from 3.0 to 3.5 Å [28]. The binding energy associated to these interactions is further analyzed below in the theoretical study.

Another interesting feature of the solid state structure of compound **1** is the antiparallel stacking interaction involving the monocoordinated H'quin ligand (see Fig. 3) that strongly influences the solid state architecture. It should be emphasized that the ligand

that participates in π–stacking interactions is the zwitterionic monodentate one. A likely explanation is that it has an enhanced ability to form self-assembled π–π stacking complexes involving the electron poor (protonated) ring and the electron rich (phenolate) ring. We have also analyzed this behavior in the theoretical part of the manuscript.

3.4. Theoretical study

We have focused our theoretical study on an analysis of the energetic features of the interesting noncovalent interaction observed in the supramolecular assemblies described above (see Figs. 2 and 3). Particularly, one relevant feature of the π–π interaction is the antiparallel arrangement of the H'quin moiety. We have performed a preliminary study to analyze the electronic properties of the quinolinium-8-olate ring by computing the Molecular Electrostatic Potential (MEP) surface. The dual π-electronic character of the molecule can be observed from the energetic data of Fig. 4. The protonated pyridine part is π-acidic (π^+) and the phenolate part is π-basic (π^-). In fact, the MEP values over the ring centers are

Table 2
Distances (Å) and angles (°) around the U metal centers in compound **1**.

U(1)–O(1)	1.786(7)	U(2)–O(7)	1.778(9)
U(1)–O(2)	1.795(7)	U(2)–O(6)	1.790(9)
U(1)–O(5)	2.254(7)	U(2)–O(8)	2.291(9)
U(1)–O(4)	2.310(7)	U(2)–O(10)	2.296(9)
U(1)–O(3)	2.356(7)	U(2)–O(9)	2.328(9)
U(1)–N(2)	2.596(7)	U(2)–N(4)	2.501(10)
U(1)–N(1)	2.607(8)	U(2)–N(5)	2.710(8)
O(1)–U(1)–O(2)	177.6(4)	O(7)–U(2)–O(6)	178.1(4)
O(1)–U(1)–O(5)	91.5(3)	O(7)–U(2)–O(8)	89.9(4)
O(2)–U(1)–O(5)	90.6(3)	O(6)–U(2)–O(8)	91.1(4)
O(1)–U(1)–O(4)	89.9(3)	O(7)–U(2)–O(10)	91.3(4)
O(2)–U(1)–O(4)	87.8(3)	O(6)–U(2)–O(10)	90.5(4)
O(5)–U(1)–O(4)	146.8(3)	O(8)–U(2)–O(10)	78.4(3)
O(1)–U(1)–O(3)	90.4(3)	O(7)–U(2)–O(9)	89.7(4)
O(2)–U(1)–O(3)	91.1(3)	O(6)–U(2)–O(9)	88.4(4)
O(5)–U(1)–O(3)	76.7(3)	O(8)–U(2)–O(9)	140.3(4)
O(4)–U(1)–O(3)	136.5(2)	O(10)–U(2)–O(9)	141.3(4)
O(1)–U(1)–N(2)	87.3(3)	O(7)–U(2)–N(4)	90.8(4)
O(2)–U(1)–N(2)	92.0(3)	O(6)–U(2)–N(4)	88.0(4)
O(5)–U(1)–N(2)	81.8(3)	O(8)–U(2)–N(4)	68.6(4)
O(4)–U(1)–N(2)	65.1(3)	O(10)–U(2)–N(4)	147.0(4)
O(3)–U(1)–N(2)	158.3(3)	O(9)–U(2)–N(4)	71.6(4)
O(1)–U(1)–N(1)	87.4(3)	O(7)–U(2)–N(5)	89.6(4)
O(2)–U(1)–N(1)	91.6(3)	O(6)–U(2)–N(5)	90.1(4)
O(5)–U(1)–N(1)	141.4(3)	O(8)–U(2)–N(5)	156.8(4)
O(4)–U(1)–N(1)	71.8(2)	O(10)–U(2)–N(5)	78.4(4)
O(3)–U(1)–N(1)	64.8(2)	O(9)–U(2)–N(5)	62.9(4)
N(2)–U(1)–N(1)	136.6(3)	N(4)–U(2)–N(5)	134.6(4)

Table 3
Hydrogen bonds for **1** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(3)–H(3N)···O(3)	0.93	1.86	2.708(11)	151
N(6)–H(6N)···O(8)	0.92	1.79	2.708(14)	170

12 kcal/mol for the protonated ring and –24 kcal/mol for the phenolate ring. Therefore an antiparallel π -stacked arrangement of this molecule is electrostatically favored, in agreement with the experimental X-ray structure (see Fig. 4).

Using this model compound H'quin and the non-zwitterionic form we have performed a computational study to analyze their complexation energies in parallel and antiparallel stacking orientations. The energetic results are gathered in Fig. 5 together with the optimized geometries (C_i or C_s symmetry imposed). The interaction energies are in good agreement with the previously mentioned MEP analysis. That is, the zwitterionic H'quin has a higher ability to form π -stacked complexes in the antiparallel disposition ($\Delta E_3 = -19.6$ kcal/mol, distance = 3.05 Å) than in the parallel one

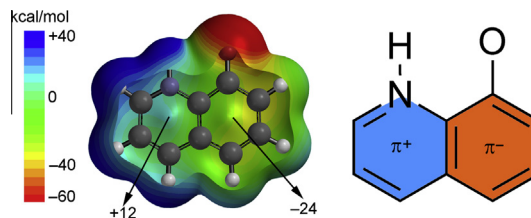


Fig. 4. MEP surface of quinolinium-8-olate ring (H'quin). Energies over the ring centers are provided in kcal/mol.

($\Delta E_4 = -3.0$ kcal/mol, distance = 3.70 Å). Similar behavior is observed for Hquin, however the energetic difference between both orientations is smaller compared to the zwitterionic case. In addition the parallel stacked complex is more favorable in Hquin ($\Delta E_1 = -5.6$ kcal/mol, distance = 3.70 Å) than in H'quin ($\Delta E_4 = -3.0$ kcal/mol, distance = 3.70 Å) due to a stronger electrostatic repulsion in the latter.

In addition to this preliminary computational analysis, we have used a fragment of the crystal structure to evaluate the contribution of the antiparallel π - π interaction in the solid state. The theoretical models A (complete dimer) and B (H'quin dimer) are shown in Fig. 7. The interaction energy of model A (left) is very large and favorable, $\Delta E_5 = -32.3$ kcal/mol, because secondary interactions are also involved (see blue dashed lines). They consist of bifurcated C–H···O interactions between two aromatic C–H bonds and one oxygen atom the UO_2^{2+} moiety. We have also computed a model (B) where the coordinated U and the rest of ligands have been eliminated. The interaction energy of this isolated H'quin dimer is $\Delta E_5 = -19.3$ kcal/mol, very similar to the one computed for the optimized dimer (see Fig. 6). In addition, the X-ray geometry is very similar to the optimized one ($\Delta E_3 = -19.6$ kcal/mol), emphasizing the importance of this antiparallel π -stacking interaction in the solid state. We have also computed the interaction energy of the dimers shown in Fig. 2, where a combination of C–H···O and C–H/ π interactions is present. For dimer (I) the interaction energy is $\Delta E_7 = -8.2$ kcal/mol and for dimer (II) it is $\Delta E_7 = -11.8$ kcal/mol. The interaction energy in the latter is greater because an additional C–H···O interaction is present (see Fig. 2).

Finally, we have used the Bader's theory of “atoms in molecules”, which provides an unambiguous definition of chemical bonding, to further describe the antiparallel noncovalent π - π interaction. The AIM theory has been successfully used to characterize and understand a great variety of interactions; therefore it is adequate to analyze the interactions described above. In Fig. 7 we show the AIM analysis of the theoretical model B using the crystallographic coordinates (see Fig. 7). It can be observed that

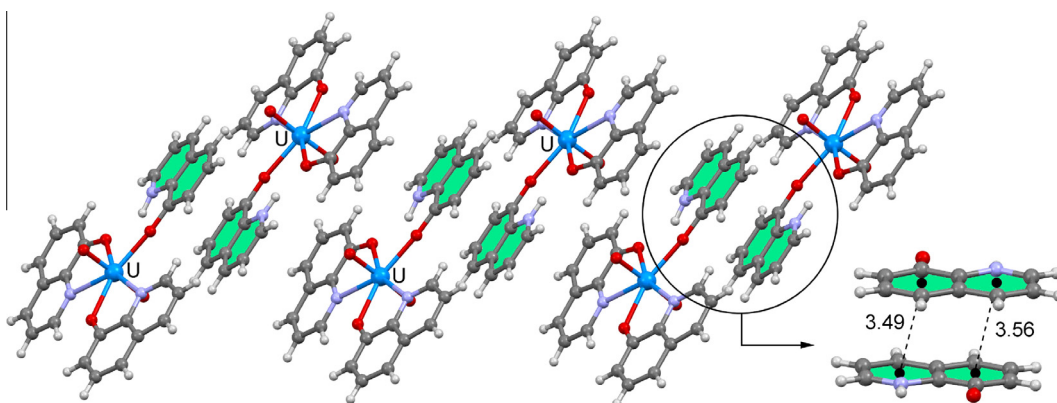


Fig. 3. Partial view of the crystal packing of **1** with indication of the antiparallel stacking interaction of the H'quin ligand.

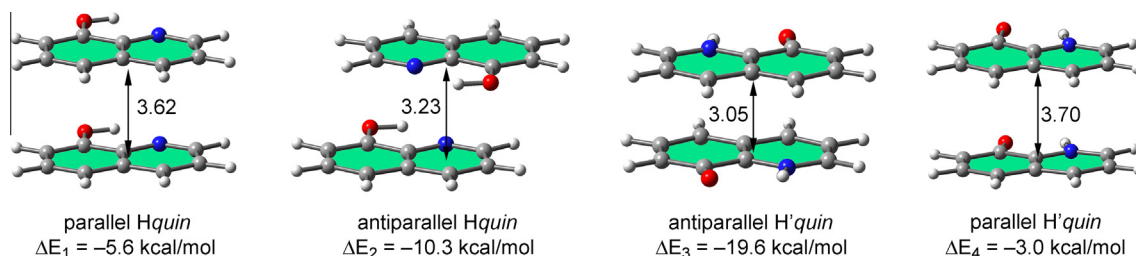


Fig. 5. BP86-D3/def2-TZVP optimized geometries and interaction energies of several π - π complexes. Distances in Å.

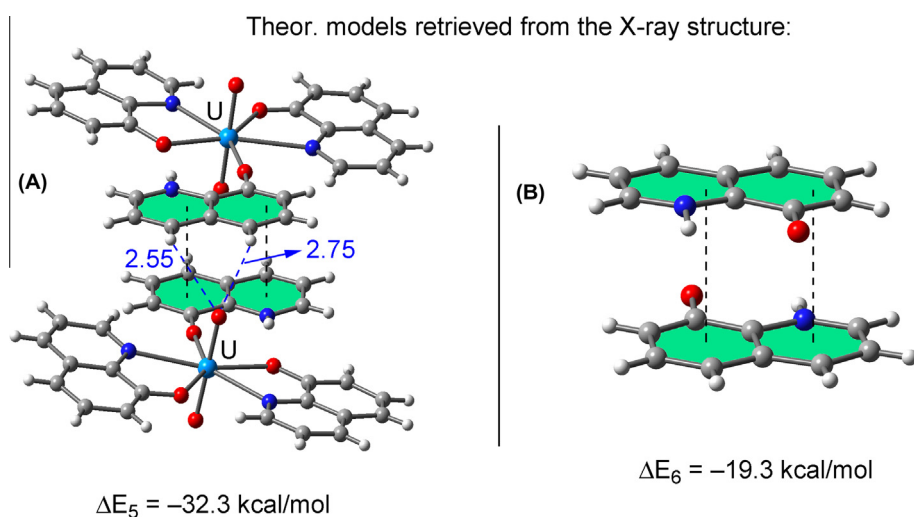


Fig. 6. X-ray fragment considered in the theoretical study and the interaction energies. Distances in Å.

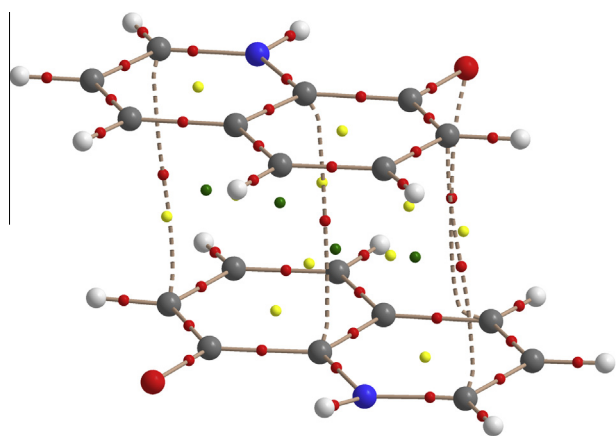


Fig. 7. AIM analysis of the antiparallel π - π interactions in compound **1**. Bond and ring critical points are represented by red and yellow spheres, respectively. The bond paths connecting bond critical points are also represented by dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the stacking interaction is characterized by the presence of four bond critical points that connect three carbon and one oxygen atoms of one H_{quin} molecule with four aromatic carbon atoms of the other H_{quin} molecule. In addition six ring and four cage critical points further characterize the interaction, indicating a strong overlap of the π -clouds. The value of the Laplacian of the charge

density computed at the bond critical points is positive, as is common in closed-shell interactions.

4. Conclusions

In conclusion, a new solvated uranyl complex has been synthesized and structurally characterized by means of elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The coordination number of each uranium center is seven with the U atom located in the center of a pentagonal-bipyramid formed by a UO_5N_2 bond set consisting of two axial oxygen atoms and three oxygen and two nitrogen atoms from UO_2 , H_{quin} and H'_{quin}, respectively. The DFT study confirms the importance of the antiparallel π - π interaction that is very strong due to the simultaneous π -acidity/basicity of the rings in the zwitterionic ligand, as demonstrated in the preliminary energetic and MEP studies. In addition, further energetic calculations on the X-ray structure and the AIM analysis demonstrate the importance of the interaction in the solid state structure of compound **1**.

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Appendix A. Supplementary material

CCDC 821409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2014.10.032>.

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