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A new solvated complex of the uranyl ion (UO$_2^{2+}$) with 8-hydroxyquinoline

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ABSTRACT

A new solvated complex of the uranyl ion, [UO$_2$(quin)$_2$(H'quin)]·DMF (**1**), (Hquin = 8-hydroxyquinoline and H'quin = quinolinium-8-olate, i.e. the zwitterionic form of H*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 (H*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, [UO$_2$(quin)$_2$(H'quin)]·DMF (**1**), (Hquin = 8-hydroxyquinoline and H'*quin* = quinolinium-8-olate, i.e. the zwitterionic form of H*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 (4000–600 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

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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. 6–8 e$^-$/Å^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 [UO$_2$(quin)$_2$(H'quin)]·DMF (**1**)

Refluxing UO$_2$(CH$_3$COO)$_2$·2H$_2$O (0.5 mmol, 0.21 g) and Hquin (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 C$_{30}$H$_{26}$N$_4$O$_6$U: C, 46.35; H, 4.34; N, 7.21.8%. 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

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

Empirical formula	C$_{30}$H$_{26}$N$_4$O$_6$U
Formula weight (g mol^{-1})	776.58
T (K)	100(2)
Wavelength λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	11.1730(8)
b (Å)	19.2921(13)
c (Å)	13.0426(10)
β (°)	103.546(1)
V (Å^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 × 0.11 × 0.06
θ range (°)	1.87 to 28.25
Reflections collected	47 652
Reflection independent (R_{int})	13 361 (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 (e Å^{-3})	7.230 and −5.353

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 3300–3500 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-hydroxiquinoline 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 °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 °C (found: 9%, calcd 9.4%). In the second stage, the H'quin decomposed at 236 °C (found: 18%, calcd 18.7%) and the third stage at 403 °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 °C.

3.3. Structure of [UO$_2$(8-HQ)$_2$(8-HQH')]·DMF (**1**)

The single crystal X-ray diffraction study reveals that in the asymmetric unit there are two independent [UO$_2$(quin)$_2$(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$_5$N$_2$ 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···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)° for