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Electronic structure and characterization of a uranyl di-15-crown-5 complex with an unprecedented sandwich structure[†]

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Understanding of the nature and extent of chemical bonding in uranyl coordination complexes is crucial for the design of new ligands for nuclear waste separation, uranium extraction from seawater, and other applications. We report here the synthesis, infrared spectroscopic characterization, and quantum chemical studies of a molecular uranyl-di-15-crown-5 complex. The structure and bonding of this unique complex featuring a distinctive 6-fold coplanar coordination staggered sandwich structure and an unusual non-perpendicular orientation of the uranyl moiety are evaluated using density functional theory and chemical bonding analyses. The results provide fundamental understanding of the coordination interaction of uranyl with oxygen-donor ligands.

The interaction of crown ethers¹ with uranyl(vı) has been previously explored in the framework of f-element separation studies.² Condensed phase studies have shown two possible isomers depending on the experimental conditions: those with direct metal–crown interactions and those with the crown ether hydrogen-bonded to metal-coordinated water molecules.³ Anhydrous conditions are required for the formation of inclusion complexes in which uranyl(vı) is encapsulated by the crown ether.^{3c,d} Despite the fact that there have been several published experimental studies for uranyl(vı)–crown ether complexes, information about structures of uranyl–crown ether complexes has been rather limited.^{3a,4} Studies of gas-phase complexes eliminate perturbations present in condensed phases and provide an

opportunity to evaluate intrinsic metal-ligand binding from an elementary perspective that illuminates key features.⁵ On the basis of the hydration behaviour it was concluded that in the gaseous $UO_2(18C6)^{2+}$ complex ("3nCn" denotes 3n-crown-n ether), the uranyl moiety inserts into the crown and is coordinated in the equatorial plane by the six oxygen donor sites.⁵ This is rather different from the nature of this complex in aqueous solution where hydration effects destabilize the inclusion complex.⁴ Experimental evidence for the formation of a 1:2 $UO_2(15C5)_2^{2+}$ complex in the gas-phase has been reported.⁵ An intriguing aspect of the gas-phase results is the bonding motifs of uranyl(v1) complexes coordinated by two crown ether ligands. In the present work, the synthesis and gas-phase IR spectrum and structure of $UO_2(15C5)_2^{2+}$ is reported, and the structure and bonding in this unique complex are evaluated using Density Functional Theory (DFT). This $UO_2(15C5)_2^{2+}$ complex features an exceptional sandwich structure that is unknown in chemistry.

The infrared multiphoton dissociation (IRMPD) experiments were performed at the Free Electron Laser for Infrared eXperiments (FELIX) Laboratory.⁶ The $UO_2(15C5)_2^{2+}$ complex was produced by electrospray ionization of a solution of $\sim 100 \ \mu M$ uranyl perchlorate and ~400 μ M 15C5 (Sigma-Aldrich, 98%) in methanol (<10% water). The IRMPD spectra were acquired using a quadrupole ion trap (QIT) MS similar to that previously employed to study hydration of uranyl-crown complexes.⁵ The QIT/MS has been modified⁷ such that the high-intensity tunable IR beam from FELIX can be directed into the ion packet, resulting in multiphoton dissociation that is appreciable only when the IR frequency is in resonance with an adequately highabsorption vibrational mode of the particular mass-selected complex being studied. The FEL produces $\sim 5 \ \mu s$ long IR pulses with an energy of typically 40 mJ, which are in the form of a sequence of ~ 5 ps long micropulses at a 1 GHz repetition rate. The wavelength of the radiation was tuned between 6.22 and 15.7 µm in these experiments. This IRMPD approach was previously employed to study organo-uranyl complexes.8

Theoretical calculations were performed at the level of density functional theory with scalar relativistic corrections using the

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computational chemistry software packages Gaussian 09^9 and ADF 2013.¹⁰ In searching for the most stable isomer, the generalized gradient approximation (GGA) with the PBE¹¹ functional and LDA¹² with Slater-VWN¹³ functional was used. To balance between accuracy and time cost of the calculations, in the ADF calculations we applied the frozen core approximation for $[1s^2-5d^{10}]$ of the U atom and Slater-type basis sets of valence triple- ζ plus two polarization functions (TZ2P)¹⁴ quality and DZP basis sets for C and O atoms with a frozen $[1s^2]$ shell. The relativistic effects were accounted for by using the scalar relativistic (SR) zero-orderregular approximation (ZORA).¹⁵ Optimized geometric structures were verified to be true minima on the potential energy surfaces by analytical vibrational frequency analysis, which was also used to analyze the experimental IR spectra.

To test the dependence of the results on the density functional employed, hybrid-GGA (B3LYP¹⁶), hybrid meta-GGA (M06¹⁷), and local-meta-GGA (M06-L¹⁸) methods were also used to optimize the geometries and electronic structure using the Gaussian 09 code. The quasi-relativistic small-core pseudo-potential ECP60MWB along with the corresponding ECP60MWB-SEG valence basis sets¹⁹ was applied for uranium and the 6-311G** basis²⁰ for C, H and O atoms, which has been shown to provide reliable results for actinide systems. The Weinhold's natural bond orbitals (NBO)²¹ and natural localized molecular orbitals (NLMOs)²² analyses were performed at the PBE/6-31G* level on optimized geometries from a PBE calculation by using the NBO 6.0 program.²³

Further chemical bonding analyses were performed with ADF 2013 at the PBE level. Energy decomposition analyses (EDA)²⁴ and combined Extended Transition State (ETS) with the Natural Orbitals for Chemical Valence (NOCV) theory^{24a,25} were carried out to assess different bonding orbital contributions to the total bonding energies. Electron localization functions (ELF)²⁶ were determined based on the PBE results from ADF calculations. The details are available in ESI.[†]

Five different density functionals were employed, which gave similar results, so that only geometries optimized at the B3LYP level are presented. In the DFT calculations, geometric optimizations were performed on all the possible structures of $UO_2(15C5)_2^{2+}$. The low-energy structures are shown in Table S1 and Fig. S1 (ESI[†]). The most stable structure, isomer A, is also shown in Fig. 1. In this "sandwich" structure, uranyl is coordinated to six almost coplanar crown ether oxygen atoms (C_i symmetry) with U-Oe bond lengths of 2.566 Å, 2.658 Å, 2.695 Å, respectively (Table S1, ESI⁺), while distances between U and the other crown ether oxygen atoms are larger than 3.7 Å. Here Oe represents the oxygen atoms from the crown ether. The uranium atom in isomer B is also coordinated to six Oe atoms, with the U-Oe bond lengths of 2.565, 2.613 and 2.677 Å, respectively. This C_2 -symmetry structure is more compacted than isomer A. Therefore, these six coordinated Oe are in three different planes rather than coplanar and each Oe-U-Oe bond is not linear, due to a Jahn-Teller distortion. Therefore, isomer C exhibits a chiral bis-inclusion structure with D_5 symmetry, in which all ten of the crown oxygen atoms coordinate the uranium with a U-O_e distance of 2.816 Å. The fourth isomer D, another sandwich complex, has two Oe atoms terminally bonded to uranium with



Fig. 1 Optimized geometrical structure of isomer A (top and side view).

 C_{2h} symmetry. Isomer A is 8.9, 17.3 and 34.5 kcal mol⁻¹ lower in energy than isomers B, C and D, respectively, at the B3LYP level of theory.

The experimental and computed IR spectra for isomer A are shown in Fig. 2; those for isomers B, C and D are shown in Fig. S2 in ESI.† A scaling factor of 0.98 has been applied to the computed frequencies due to well-known overestimation by the approximate exchange–correlation functionals and harmonic approximation to the vibrational frequencies. Higher-energy isomers C and D can be eliminated based on significant disparities between the experimental and computed IR spectra and the much higher relative energies. The B3LYP spectra for structurally similar isomers A and B are in rather good accord with the experimental spectrum. Both predicted spectra show several intense peaks in the 1000–1150 cm⁻¹ region; in the experimental spectrum, there are indeed intense peaks in this region, with shoulders that indicate closely-spaced features. The peak splitting near 1290 cm⁻¹ suggests isomer A. The characteristic sharp



Fig. 2 Experimental IR spectrum (blue), and B3LYP computed (red) spectrum of the ground-state $[UO_2(15C5)_2^{2+}]$ isomer A. A scaling factor of 0.98 has been applied to the computed spectrum.

uranyl asymmetric stretch mode, ν_3 , observed at 976 cm⁻¹, is also in better agreement with the computed spectrum for isomer A than for isomer B.

The 842 cm^{-1} band is assigned to the asymmetric $O_e UO_e$ stretching mode. The bands around 1050 cm⁻¹ correspond to C-O crown ether bond stretching modes. The 765, 910-931 and 1006 cm⁻¹ bands are also assigned to vibrational modes of 15C5. Additional assignments are given in Table S2 (ESI^{\dagger}). The uranyl ν_3 mode at 976 cm⁻¹ is only slightly less red-shifted than the most extreme previously reported red-shift to 965 cm⁻¹ for a dipositive gas-phase uranyl complex.¹² This large red-shift of ν_3 indicates substantial electron donation to the uranium metal center from the ligands and a corresponding weakening of the uranyl bonds, consistent with hexadentate equatorial oxygen coordination. An unusual feature of isomer A is that the uranyl moiety is not perpendicular to the six-fold coplanar oxygen atoms, but with an angle of 76° to the O₁UO₃ plane. This intriguing distortion is attributed to steric repulsion between the uranyl oxygen atoms and crown ether oxygen atoms (Fig. 1, side-view).

To provide insight into the interactions between uranyl and the crown ether ligands of $UO_2(15C5)_2^{2+}$, several bonding analyses were performed, including the Nalewajski-Mrozek (N-M)²⁷ bond orders, Mulliken charges²⁸ and natural population analysis (NPA),²⁹ energy decomposition approach (EDA), the extended transition-state method with the natural orbitals for chemical valence (ETS-NOCV), Kohn-Sham orbital interaction, natural localized molecular orbitals (NLMOs) analysis and electron localization function (ELF). The calculated N-M bond order (Table 1) of U–O_e is four times smaller than that of U–O_{vl}, indicating weak U-Oe dative-bonding interactions. In addition, Mulliken charge analysis shows that for O_e atoms the charges (between -0.72 and -0.75) are more negative than in isolated 15C5, for which the charge on the oxygen atoms is -0.69; this is due to rearrangement of electrons in the 15C5 ligands to stabilize the U-Oe dative bonds. In 15C5, each Oe oxygen atom has two C-Oe single bonds and two lone-pairs. Upon coordination to uranyl, there are dative electron donations from Oe lone pairs to the 5f and 6d orbitals of uranyl, with the formation of weak σ and π bonding between O_e atoms and U. NBO analysis indicates the expected presence of σ_{O_a-U} and π_{O_a-U} NLMOs (Table S3, ESI[†]), which is consistent with the ELF result shown in Fig. 3.

As shown earlier, the EDA results for $UO_2^{2^+} + 2(15C5) \rightarrow UO_2(15C5)_2^{2^+}$ (Table S4, ESI†) show that electrostatic and orbital interactions account for almost equal contributions to the total bonding energy, consistent with the bonding character of the U–O_e bonds. Inspection of the Kohn–Sham orbitals of



Fig. 3 Two-dimensional ELF contours for the O–U–O planes containing the U–O interactions. The results are based on the SR-ZORA calculated densities.

 $UO_2(15C5)_2^{2^+}$ (Fig. S4, ESI[†]) reveals that the U–O_e bonds mainly result from the orbital interaction between U $6d_{\delta}$, $5f_{\delta}$ and $5f_{\phi}$ orbitals in uranyl and 2p orbitals of crown–ether oxygen atoms, which is confirmed by additional ETS-NOCV analysis. This analysis (Fig. S5, ESI[†]) further substantiates that the key bonding interactions between the U and O_e atoms are due to uranium 5f and 6d atomic orbitals as the principal contributors to the σ and π bonding molecular orbitals, consistent with the results obtained from NLMO bond analysis. The results for $UO_2(15C5)_2^{2^+}$ thus bear resemblance for the very stable uranyl tetrahalide dianions.^{30,31}

In summary, a unique uranyl-crown-ether sandwich complex is identified via experimental and computational studies. Comparison of experimental and computed IR spectra of the gas-phase $UO_2(15C5)_2^{2+}$ complex indicate that it displays a distinctive 6-fold coplanar coordination structure. Such a highly coordinated uranium center in uranyl is enabled by a structure in which the two 15C5 ligands each coordinate via three oxygen atoms, but with minimal repulsive interactions. The sandwich structure is further stabilized by an unusual non-perpendicular orientation of the uranyl moiety to reduce O-O repulsion. Although each of the six U-O_e bonds is not particularly strong in comparison to two-center single-bonds, the overall bonding interaction is substantial, as indicated by an extreme red-shift in the uranyl asymmetric stretch frequency and significant binding energies. A juxtaposition of factors that include six-fold equatorial coordination of uranyl, a high electron density on the ligands, and the availability U 5f and 6d acceptor orbitals create an unusually favorable ligand-field effect, which

Table 1 Selecte	d bond lengths, bon	d orders, Mulliken	charges, and na	tural population a	nalysis (NPA)	charges of the	$UO_2(15C5)_2^{2+}$	isomer A
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	Bond length	Bond order		
U–O _{yl} (Å) U–O _e (Å)	1.742 2.566, 2.658, 2.695, 3.703, 3.823	2.721 0.320, 0.491, 0.398, 0.081, 0.084		
	Mulliken charge	NPA		
$\begin{array}{c} q(\mathrm{U}) \\ q(\mathrm{O}_{\mathrm{yl}}) \\ q(\mathrm{O}_{\mathrm{e}}) \end{array}$	2.25 -0.59 -0.72, -0.72, -0.74, -0.75	$\begin{array}{c} 1.46 \\ -0.57 \\ -0.51, -0.54, -0.53, -0.53, -0.5 \end{array}$		

results in substantial covalent bonding character that provides stabilization beyond electrostatic interactions. The stabilization of this uranyl sandwich complex can thus be attributed to the unique bonding characteristics of this 5f-element. The results here add to the fundamental understanding of uranyl-ligand interactions and aid in rational design of crown–ether ligands for lanthanide/actinide separations.

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