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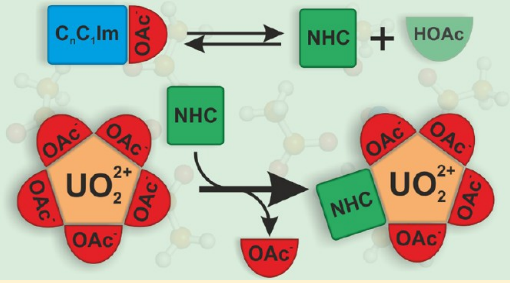
Uranyl(VI) Complexes in and from Imidazolium Acetate Ionic Liquids: Carbenes versus Acetates?

Oldamur Hollóczki*,[†]

[†]Mulliken Center for Theoretical Chemistry, University of Bonn, Beringstrasse 4 + 6, D-53115 Bonn, Germany

Supporting Information

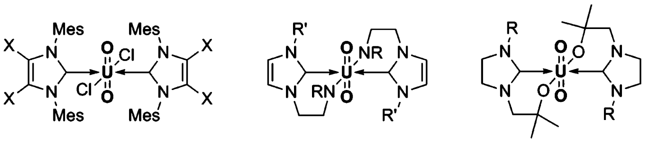


ABSTRACT: Formation of uranyl(VI)-N-heterocyclic carbene complexes from 1-alkyl-3-methylimidazolium acetate ionic liquid carbene sources was investigated by theoretical methods, combining classical molecular dynamics *ab initio* molecular dynamics and static DFT calculations. The interaction between the UO_2^{2+} cation and the acetate anion was found to be very strong, in accordance with the hard and soft acids and bases principle. The calculations, however, indicate that the preference of the acetate anions to coordinate monodentately, together with the Coulombic repulsion between these anionic ligands, provides accessible sites for the carbene in the corresponding uranyl-acetato complexes. According to the calculations the carbene is bound to the uranium atom of the $[UO_2(OAc)_3]^-$ complex with significant strength; ΔE value of −79.4 kJ mol^{-1} was obtained. Comparison with the analogous, but experimentally confirmed, reaction between the present ionic liquid and CO_2 indicates that this binding strength should be enough for the reaction to occur. The analogous aqua complexes exhibit lower stability, showing that traces of moisture should not prohibit the reaction via competitive coordination. The results obtained suggest a mild and very convenient method for preparing carbene complexes of metals in general, including those with the uranyl cation, which have been so far limited to a few exotic examples.

1. INTRODUCTION

Complexes of the uranyl(VI) (UO_2^{2+}) cation are of high interest, partly due to their role in the separation and recycling of nuclear waste,[1,2] and in the migration and retardation of these substances in natural systems.[3] Beyond the mere technological and environmental significance, increasing scientific attention has been drawn to these compounds throughout the past decade, as novel aspects of their chemistry with considerable potential[4] have been discovered in the field of coordination chemistry,[5,6] supramolecular chemistry,[6−8] and catalysis as well.[6,9,10]

Due to its high charge at the uranium atom, the UO_2^{2+} cation is a hard Lewis acid; therefore, it generally forms stable complexes with hard bases.[5] The preferred ligands, therefore, mostly involve halogenides, or oxygen containing, often anionic Lewis bases (carboxylates, nitrate, carbonate, hydroxide, water), forming in most cases 4−6 coordinative bonds.[5] According to the principle of hard and soft acids and bases (HSAB), the relatively soft N-heterocyclic carbene (NHC) ligands[11] can be expected to bind to the uranyl cation very weakly, despite the NHCs' general ability in forming prominently stable[12,13] complexes with metals, and even with silicon derivatives.[14−16] Indeed, the corresponding synthesized uranyl-carbene complexes are limited to a few examples (Figure 1),[17−20] with rather weak C→U bonds.[17,19] This rather loose binding prompted in the synthesis either the attachment of an additional, highly basic coordinating functionality to the side chain of the NHC (amide, alkoxide)[19,20] (see Figure 1), or the use of the free carbene itself as reagent.[17] Hence, the hitherto applied methods to prepare uranyl-NHC complexes are rather case-specific and inconvenient, which may limit their preparation and also the further investigation of their chemistry in general. To overcome this obstacle, the design of simple and convenient routes toward these species is required, which could trigger a significant advance in the field, by providing the possibility of adopting more of the powerful and versatile NHC complex chemistry[12,13,21−26] in the field of uranyl(VI) derivatives.



1 X = H
2 X = Cl

3 R = ^tBu; R' = Mes
4 R = R' = ^tBu

5 R = Mes
6 R = Dipp

Figure 1. Hitherto synthesized NHC complexes of the uranyl cation.

In the past few years it has been shown[27,31] that 1,3-dialkylimidazolium acetate ionic liquids (ILs) are mild and excellent carbene sources, and the divalent species is available via a single proton transfer from the cation to the basic anion without the addition of external bases (Figure 2), defining, therefore, the concept of "carbenes from ILs". After the initial theoretical and vapor phase experimental characterization of the process,[27] in a series of subsequent studies trapping reactions with elemental chalcogens,[28] benzaldehyde,[28] and CO_2[30] could be performed, while the NHC-like organocatalytic activity of these ILs has also

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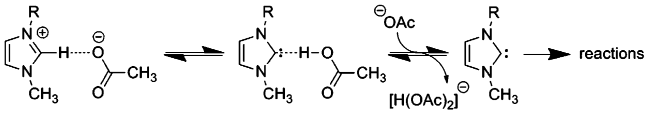

Figure 2. Formation of carbenes from imidazolium acetate-based ionic liquids.[27−31]

been observed,[29] and later applied in biomass processing.[32] Most remarkably, in an early work it had already been shown that, in the presence of external acetate ions, NHC complexes of palladium can be prepared from palladium salts and imidazolium-based ILs.[33,34] In light of the aforementioned principle of “carbenes from ILs”,[31] the formation of such complexes has been reproduced also in imidazolium acetates.[28,35] Nevertheless, interestingly, this process has never been considered as a general way to prepare NHC complexes, despite the simplicity of a possible application. The material just needs to be dissolved in the appropriate IL without any external, reactive, and possibly coordinating base, and then the desired reaction with the forming NHC complex catalyst/reagent can be performed either directly within the parent IL as a one pot synthesis (exploiting the often advantageous properties of ILs[36−41] in the process) or in a stepwise fashion after separation. The further advantage of this method could be that the carbene is continuously available from the IL, while it is mainly encapsuled and stabilized in the form of imidazolium cations; hence, in the case of weakly bound NHC complexes (like those presumably with the uranyl cation) the dissociation of the forming carbene complex can also be reversible, without the degradation of the NHC ligand.

Very recently the direct interaction of metal oxide surfaces with the carbene content of imidazolium acetates has also been precedented,[35] suggesting the possibility of carbene complex formation already at the interface. Nevertheless, for the application of such a process, it would be more advantageous if the initial metal salt had a reasonable solubility in the given IL. Unfortunately, metal salts in general are very poorly soluble in ILs, including those of f-elements and uranyl derivatives in particular as well.[42,43] Theoretical studies showed that the positively charged uranyl (and other f-element) ions in ILs are interacting mainly with the anion of the IL solvent;[44−48] therefore, by boosting up the strength of the metal−anion interaction higher solubilities can be achieved. Accordingly, ILs with strongly coordinating anions (e.g., nitrate, halogenides)[42,45,46] or with coordinating functionalities at the cation[49] have been shown to dissolve its salts to a significant extent; thus, considering the formation of stable UO_2^{2+} complexes with carboxylates in aqueous solutions,[3,50,51] it can be assumed that in acetate-based ILs also considerable solubilities can be achieved. Moreover, in the basic environment provided by the acetate anions, no decomposition of the solute by redox processes is expected.[52]

In the system of uranyl(VI) salts dissolved in an imidazolium acetate IL, a competition between the accessible carbenes and the acetate anions can be assumed for the binding to the uranium atom. Although according to the aforementioned HSAB concept it seems clear that the hard−hard interaction between the acetate anion and the uranyl cation will overcome the weak binding of the carbene to the metal, ILs are known to have unique properties in terms of solvation that can greatly influence such competitions. First, the “charge screening” of the IL ions generally enhances the dissociation of oppositely charged solute ions of any associates,[53,54] and has, therefore, a “super-dissociating” effect, which may be able to disrupt the charge-driven formation of acetate-UO_2^{2+} complexes. Second, somewhat related to this, it has also been suggested that stronger interactions of solutes with the acetate anion in imidazolium-acetate ILs are significantly weakened by the imidazolium cations,[55] or in other words the hard−hard interplay between the uranyl and the acetate may compete not only with the formation of carbene-uranyl complexes, but also with the very strong anion−cation interactions,[55] including hydrogen bonding.[56−59] The effect of such ligand−solvent interactions in decreasing the stability of uranyl complexes has also been observed for aqueous systems.[60,61] These considerations, together with the often similarly influental Coulombic[62−65] and steric[66] repulsion between the anionic ligands around the uranium atom, allow the conclusion that the neutral carbene may compete successfully with the acetate for binding to the metal atom.

In the present contribution the possible formation of uranyl-NHC complexes from 1,3-dialkylimidazolium acetate ionic liquids will be discussed, together with bonding and other structural features in the expectedly forming structures. Since this cation is known to form weaker NHC complexes[18] than most of the other metal ions, if the formation of the present complexes is predicted, presumably this synthetic approach is feasible for many other metals as well. Thus, the present results can contribute not only to the development of the uranyl cation’s coordination chemistry, but may also provide a valuble benchmark for the application of metal-NHC complexes, in terms of suggesting a novel general and convenient method for the synthesis of these compounds. Moreover, the formation of NHC complexes with metals can also result in the solubilization of the corresponding substances, opening new perspectives in the catalytic or extraction processes of inorganic salts involving IL solutions.

2. APPLIED METHODS

The solvation of the uranyl cation by the IL ions in the liquid phase was investigated by classical molecular dynamics (MD) simulations. This method does not explicitly treat the bond formation between the acetate ligands and the uranium atom, but estimates it via the nonbonding Coulombic and dispersion terms of the force field. Nevertheless, since the hard−hard interaction between the uranium atom and anionic ligands in such complexes shows very low covalency,[62] this approach has been proven to be applicable for similar problems,[44,45,47,67,68] including analogous complex formation reactions with the uranyl cation in IL media.[45,47,68]

Classical MD simulations on systems **I**−**II** (Figure 3) were performed with periodic boundary conditions at 398 K by the LAMMPS program package.[69,70] In recent studies excellent force fields were developed for the uranyl cation on the basis of high level *ab initio* calculations,[71,72] taking into account the polarization and flexibility of this species. However, due to the lack of polarizable force field for the present ionic liquid, for the sake of consistency in this study a nonpolarizable, flexible force field by Maginn and co-workers from 2013 was applied for the uranyl cation,[73] together with the force field developed by the Pádua group for the IL.[74−77] The simulations were repeated by using a rigid force field of Wipff (with the U=O bond lengths and the O−U−O bond angle fixed at 1.80 Å and 180°, respectively),[78] which has been shown in several studies to give accurate results on solute−solvent interactions combined with Pádua’s IL force fields. In the solvation of the UO_2^{2+}, characterized by the RDFs and CDFs described in the next section, only minor differences

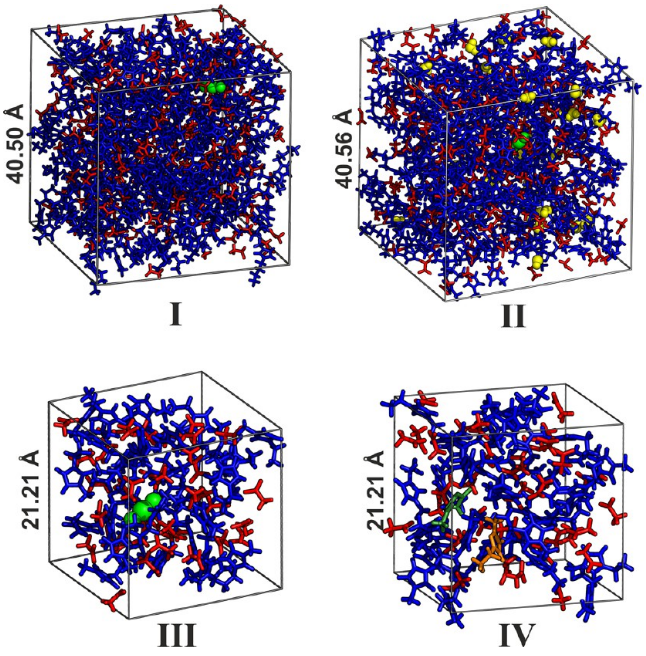

Figure 3. Snapshot of the simulation box that was investigated by classical (**I** and **II**) and *ab initio* (**III** and **IV**) MD simulations. System **I**: containing one UO_2^{2+} (green), 202 acetate anions (red), 200 1-butyl-3-methylimidazolium cations (blue). System **II**: system **I** with 27 additional water molecules (yellow). System **III**: one UO_2^{2+} (green), 37 acetate anions (red), 35 1-ethyl-3-methylimidazolium cations (blue). System **IV**: one 1-ethyl-3-methylimidazol-2-ylidene (orange), one $[(OAc)_2H]^-$ (dark green), 34 acetate anions (red), 35 1-ethyl-3-methylimidazolium cations (blue).

were observed (see Supporting Information), which do not affect the main conclusions of this study. For water the SPC/E force field was applied,[79] which was successfully used in previous MD simulations on IL/uranyl/water systems.[47]

It has to be noted that, according to recent studies, the quality of the results on dynamic properties obtained by classical MD simulations can be increased significantly, if the total charges on the anions and on the cations are scaled down by a factor of 0.8.[80−82] This can be rationalized by a real physical effect of a charge transfer via hydrogen bonding, as has been shown by a systematic quantum chemical study.[82] However, such scaling would break the consistency either in charge between the uranyl and the IL ions, or in the force field fitted for the uranyl at the given charges; thus, it was not applied here. Nevertheless, to check the effect of a possibly somewhat faster motion of the particles, further simulations were performed at elevated temperatures (600 K). Since the obtained graphs were essentially similar (otherwise noted explicitly), the lack of such downscaling should not result in any significant error in the general findings. Thus, the figures in the Article correspond to the lower temperature simulations (at 398 K), while the data and graphs for the higher temperature can be seen in the Supporting Information.

To describe nonbonding interactions, the Lorentz−Berthelot mixing rules were used. For the calculation of van der Waals and Coulombic interactions, a 1 nm cutoff radius was chosen. The periodic simulation box with an initial density of 1 g cm^{-3} was simulated in an NPT ensemble for 1 ns. The average cell vector of the last 0.5 ns was then used for further equilibration (1 ns) and for the production run (10 ns) within an NVT ensemble. Nosé−Hoover barostats (p = 1 bar, τ = 1000 fs) and Nosé−Hoover thermostats (T = 398 or 600 K, τ = 100 fs) were applied for the simulations in the NPT and NVT ensembles, respectively.[83−85]

Ab initio molecular dynamics (AIMD) simulations were performed by the CP2K program package[86] with periodic boundary conditions on systems **III**−**IV**, derived from the previously published[56] simulation box of the 36 ion pairs of 1-ethyl-3-methylimidazolium acetate. System **III** was built by the removal of a cation from the box, and insertion of a single uranyl cation and an extra acetate anion. System **IV** was prepared by removing a proton from one of the cations of the original system, and adding it to one of the acetate anions. These systems were equilibrated for 10 ps by using massive thermostat in an NVT ensemble. The production run was performed at 350 K by a Nosé−Hoover thermostat[83−85] for 20.1 and 63.1 ps. For the simulations the BLYP GGA-type density functional was applied with the dispersion correction D3 by Grimme,[87] since the BLYP-D3 functional has been shown to provide results of excellent quality for ionic liquids.[88−90] At the uranium atom a pseudopotential of Krack was applied.[104,105] System **III** showed essentially very similar $U(UO_2^{2+})-O(OAc)$ RDFs to those obtained with the classical MD, also with the first and second peak positions matching within 0.05 Å, showing the accuracy of the applied force field (for the graphs, see Supporting Information). The analysis of all classical and *ab initio* MD trajectories was performed by using the TRAVIS program.[91]

Static quantum chemical DFT calculations have also shown great potential and value in exploring the coordination within uranyl(VI) complexes.[50,51,60,92,93] For example, solvation in water has been explored,[60] and the competition of water with chloro and acetonitrile ligands has been rationalized,[93] as well as the binding modes of carboxylate ligands in aqueous solutions.[50,51] The provided results were in good accordance with experimental data in terms of coordination number, and ligand exchange equilibrium, providing an excellent benchmark for this study as well, showing that GGA functionals describe the uranyl-ligand interaction with a reasonable accuracy.[60,93] Thus, to evaluate the possible formation of the NHC complexes, and to structurally characterize the compounds that are likely to form, static quantum chemical calculations were performed by the TURBOMOLE 6.4 program package.[94] In these calculations various DFT functionals were considered (BP88, BLYP, B97-D, B3LYP, PBE0, TPSSh), together with the def-TZVPP basis set for all atoms with the RI approach, and with the dispersion correction DFT-D3.[87] For uranium an effective core potential was applied, including scalar relativistic correction.[95] For the optimized structures the eigenvalues of the Hessian were checked in order to characterize the stationary point found. To reduce the number of possible conformations, the alkyl chain of the carbene's ring was replaced by a methyl group, as this slight simplification should not affect the bonding at the coordinating hypovalent center,[27] and, thus, should not alter the main conclusions. Since in a series of test calculations for the $[(UO_2)(OAc)_3]^-$ system all GGA DFT functionals showed similar interaction energies between the carbene and the $[(UO_2)(OAc)_3]^-$ complex (see the Supporting Information), the (RI)B97-D/def-TZVPP results will be shown throughout the Article. To further test the accuracy of these calculations in evaluating uranyl-ligand interactions, a previously published[71] CASPT2 UO_2-H_2O potential was reproduced by using this method. The depth of the obtained energy well showed only ca. 10 kJ mol^{-1} energy difference, at an also very similar position. Shared electron number (SEN) data, electrostatic potential-fitted charges, and vibrational frequencies (with a nonharmonic

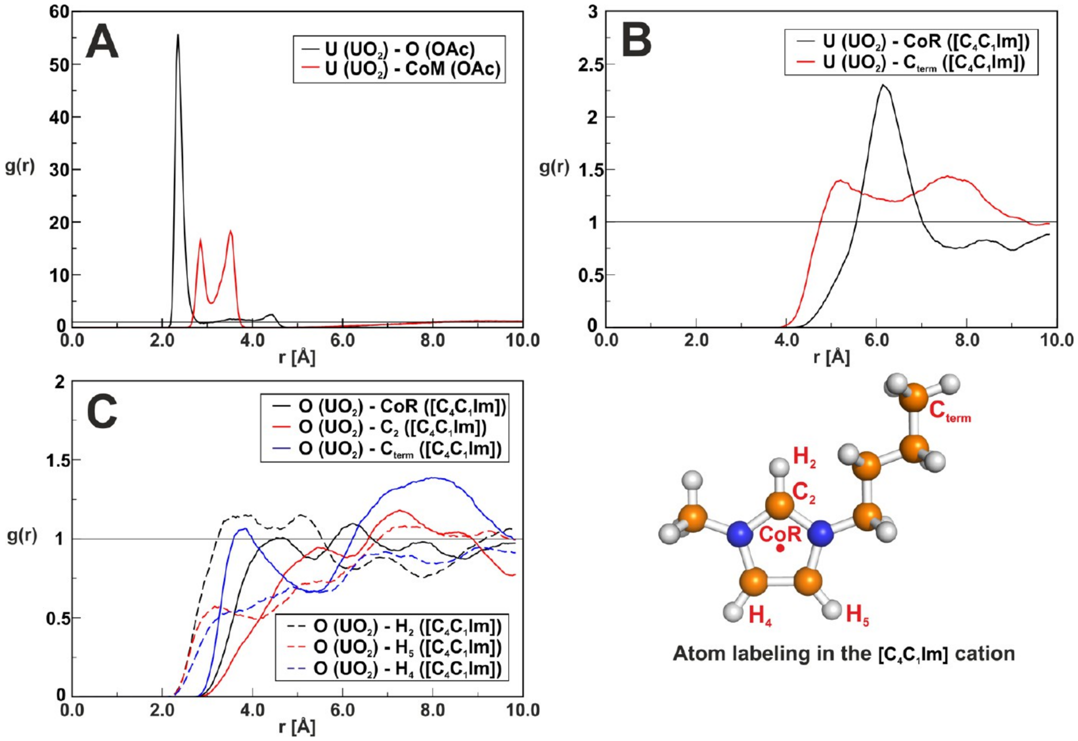

Figure 4. Radial distribution functions (RDFs) of characteristic distances between the uranium and the anion (top left), the uranium and the cation (top right), the UO_2^{2+}'s oxygen and the cation (bottom left). CoR = Center of ring. CoM = Center of mass.

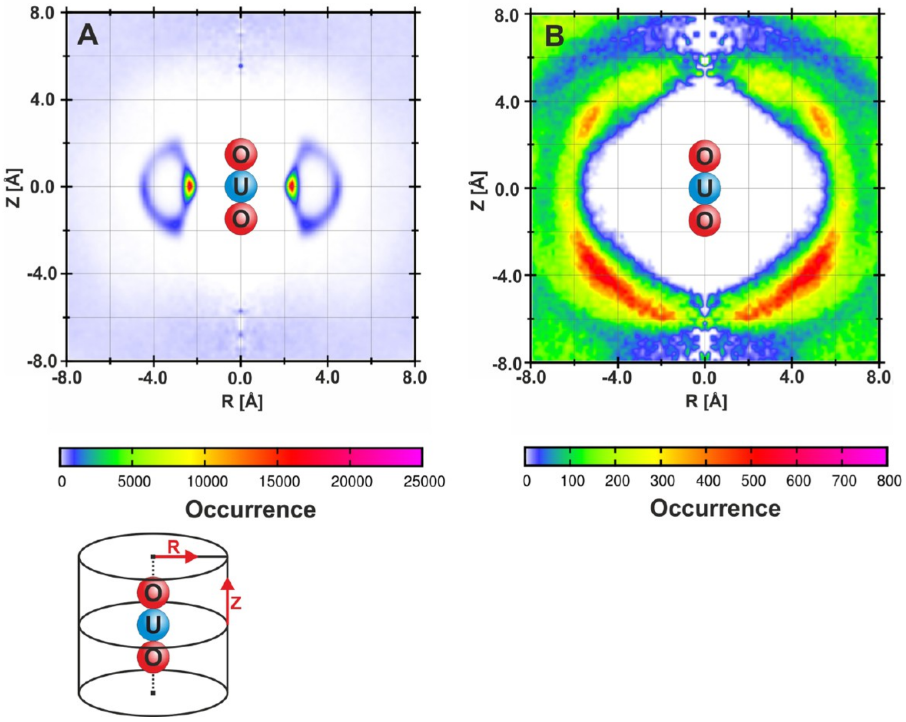

Figure 5. Pseudospatial distribution functions of the anion's oxygen atoms (A) and the cation's ring center (B) around the uranyl cation.

scaling factor of 0.9744[96]) were calculated at the (RI)B97-D/def-TZVPP geometry at the same level. Gibbs free energies are calculated at 298 K and under 1 atm pressure.

3. RESULTS AND DISCUSSION

3.1. Part I. Solvation of the Uranyl Cation in the IL. Coordination of the Acetate Anions. It is reasonable to assume that the first step of forming NHC complexes from the imidazolium acetate-based ionic liquid should be the solvation of the UO_2^{2+} cation in the IL, including the coordination of acetate ions to the metal atom. Since a competition between the acetate and NHC ligands is expected (see above), to assess if the complex formation with the NHC is possible, first the solute–solvent interactions in this initial stage should be characterized, with a special emphasis on the coordination number and mode of the acetate ions.

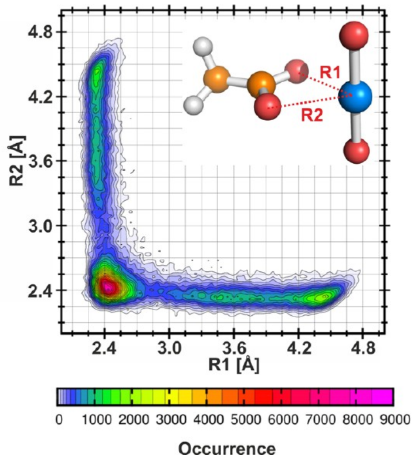

Figure 6. Combined distribution function (CDF) of the two $U(UO_2^{2+})-O(OAc^-)$ distances considering each coordinating acetate anion.

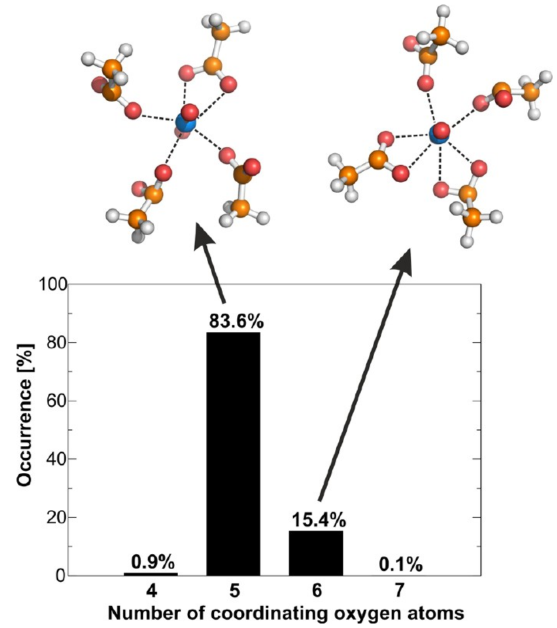

Figure 7. Occurrences of different numbers of acetate oxygen atoms within 2.9 Å around the uranium, together with two snapshots representing the two most often occurring coordination numbers.

A sharp and prominently high peak can be observed in the $U(UO_2^{2+})-O(OAc^-)$ radial distribution functions (RDFs) at a distance of ca. 2.35 Å (see Figure 4A; for comparison with the AIMD results, see Supporting Information), in the same range as the O→U bond lengths in literature for $[UO_2(OAc)_3]^-$ from both calculations[51,97] and experiments.[98] The peak height in the RDFs in Figure 4A is significantly larger than obtained for other IL anions previously,[46] indicating a much stronger interplay between these two atoms, in agreement with the HSAB theory above, and with the known high stability of the uranyl acetato complexes.[3,50,51] Moreover, the lack of exchange between the coordinating and bulk anions even at higher temperature (600 K) also supports the remarkable strength of the uranyl-acetate interplay, despite the "superdissociating" power[53,54] of the IL. The pseudospatial distribution function (pSDF, Figure 5A) shows that the interacting acetate oxygen atoms are, as expected, located in a very narrow ring around the uranium atom. However, interestingly, despite the fact that in other systems often the formation of $[(UO_2)(OAc)_3]^-$-like complexes has been reported,[3,48,50,51] the uranyl cation is in this case sorrounded by four acetate anions. Among these ligands, however, only one or two are acting as bidentate at a time, and [according to the combined distribution function (CDF) in Figure 6, and also in agreement with the double peak in the $U(UO_2^{2+})-COM(OAc^-)$, and the shoulder of the first peak in the $U(UO_2^{2+})-O(OAc^-)$ RDF in the 2.9 – 5.0 Å region (Figure 4A)] the anions are often monodentates, viz. they form a single O→U bond, while they turn out with their noncoordinating oxygen atom toward the bulk of the solvent. It should be noted here that similar preference for monodentate arrangement has been predicted in aqueous solutions for $[(UO_2)(OAc)(H_2O)_{3-4}]^+$ complexes by recent DFT calculations.[51] Therefore, these altogether four coordinating acetate anions form mostly five (83.6%, see Figure 7), and only sometimes six (15.4%), O→U bonds. This distribution in preferred coordination numbers has some resemblance to that observed for water;[47,60,78] nevertheless, it is very surprising, since in such high concentration of the very basic and strongly coordinating acetate anion saturated, 6-fold coordination could be expected, as has been shown eperimentally for UO_3 in ILs with carboxyl-functionalized cations.[49]

Regarding the noncoordinating oxygen atoms of the ligands it should be noted that in 1,3-dialkylimidazolium acetate ILs significant anion–cation interplay can be observed;[56] therefore, these "free" oxygen atoms are strongly interacting with the surrounding cations. This picture is fully supported by the high occurrence of the cations' ring centers close to the regions where the "free" oxygen atoms of the coordinating acetate ions are located, as shown in the pSDF in Figure 5B. It is also worth pointing out that the higher occurences of the anions' oxygen atoms at the lower half of the graph correspond to higher occurences of the cations in the neighboring regions (Figure 5), which also underpins the structural importance of the $OAc^- - [C_4C_1Im]^+$ interactions in the arrangement of the ligands. This asymmetry above can be rationalized by a rather strong and also rigid coordination and solvation. Consequently, the coordinating acetate ligands are partly shared by the uranyl cation and the IL cations, which results in a competition for the acetate anions between these two cationic species,[55] contributing to the decrease in higher coordination, and to the increase in the monodentate complexation.

The orientation of the cations' ring centers around the uranyl exhibits some resemblance to the cation cage that is known for the physically absorbed CO_2 in this IL from *ab initio* molecular dynamics simulations.[99] In the present case, however, four anions are surrounding the solute's equatorial region instead of the average of 1.38 observed for CO_2,[99] which induces a gap at these areas in the cation cage. The imidazolium cations seem to be located in the regions where they can interact with both the acetate anions and the uranyl cation (Figure 5B), which prompts the necessity of investigating the $[C_4C_1Im]^+-UO_2^{2+}$ interplay. According to the observed RDFs (Figure 4A), the $[C_4C_1Im]^+$ cation's ring hydrogen atoms approach the uranyl cation's oxygen atom as close as 2.1–2.2 Å, which indicates the presence of (weak) hydrogen bonds.

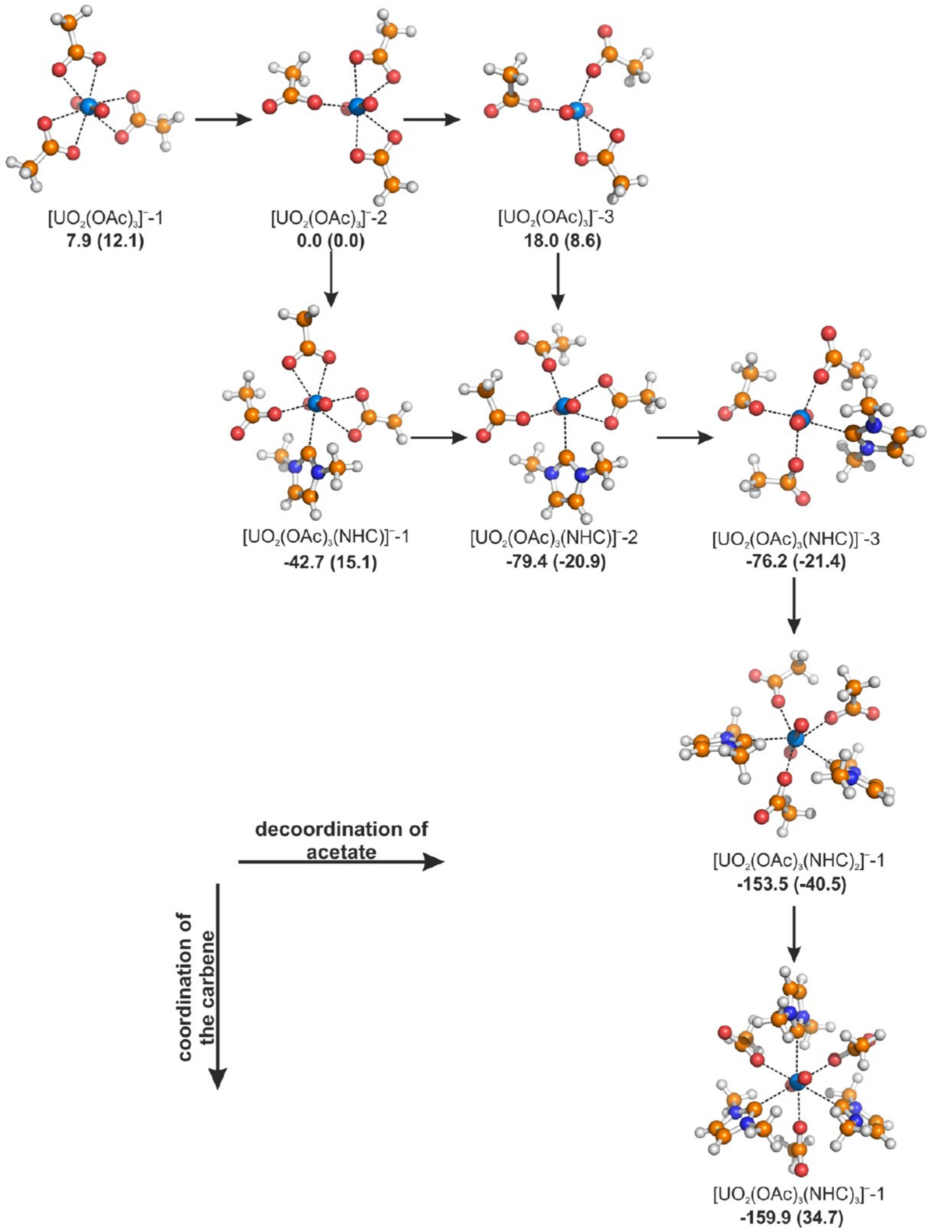

Figure 8. Optimized complexes of the uranyl cation with 3 acetate molecules and 1−3 carbenes, together with the corresponding (RI)B97-D/def-TZVPP relative energies and Gibbs free energies (in parentheses) with respect to $[UO_2(OAc)_3]^-$ and the free NHC ligands. Only the most stable conformations are shown here; for the full list, see Supporting Information.

As can be seen above, the UO_2^{2+}-IL interactions are very strong, and include both imidazolium-uranyl and acetate-uranyl interplay, which implies that uranyl(VI) salts may dissolve in these solvents to a considerable extent, even without considering the effect of the carbene's coordination. Furthermore, the formation of monodentate acetate-UO_2^{2+} complexes mostly with 5-fold coordination is predicted, which may open the possibility of coordination for the approaching carbene ligand.

3.2. Part II. Coordination of Carbenes to Uranyl-Acetate Complexes.

Although the MD simulations above indirectly suggest the possibility of further coordination, the sufficient strength of the C→U bond is also necessary for the formation of the NHC complexes in the present IL. Since force fields, in principle, cannot account for the breaking and formation of covalent bonds, and the C→U bond is assumingly less charge-induced than the O→U, static quantum chemical DFT calculations were applied to investigate the energetics of the complex formation with the NHC, and for the structural characterization of the corresponding molecules.

Considering structures with charges between +2 and −1, and with the most often occurring coordination numbers for uranyl complexes (between four and six),[4,6,60,93] several structures were optimized (see Supporting Information). However, according to the MD data above, the uranyl cation is coordinated mostly by five and six acetate oxygen atoms; hence, the complexes with 0−2 acetate ligands are of minor importance, and therefore, here only the derivatives with more acetate ions will be discussed.

Three acetate ligands can form a complex with 6-fold coordination ($[UO_2(OAc)_3]^-$−1, Figure 8), which can be decreased to 5-fold by the rupture of a O→U bond ($[UO_2(OAc)_3]^-$−2). Interestingly, in agreement with previous gas phase IRMPD measurements on this species,[100] the latter structure was found to be more stable by −7.9 kJ mol^{-1} than ([$UO_2(OAc)_3$]$^-$−1). It is also worth pointing out that the noncoordinating oxygen atoms apparently interact with the methyl groups of the other acetate ions, forming a weak hydrogen bond (Figure 8). Although this arrangement has most likely some contribution to the stability of these structures in the present gas phase calculations, in the solution the surrounding imidazolium cations overcome the hydrogen bond donating potential of the acetate methyl group. Thus, the energy difference between [$UO_2(OAc)_3$]$^-$−1 and [$UO_2(OAc)_3$]$^-$−2 should be, in fact, further increased[60,61] in solution by the strong hydrogen bonds donated by the imidazolium cations to the acetate ligands, as has also been observed in the classical MD simulations discussed above.

The 7.9 kJ mol^{-1} energy difference between [$UO_2(OAc)_3$]$^-$−1 and [$UO_2(OAc)_3$]$^-$−2 is roughly in the same range as the 19 kJ mol^{-1} value between the bidentate [$UO_2(OAc)(H_2O)_3$]$^+$ and monodentate [$UO_2(OAc)(H_2O)_4$]$^+$,[51] which shows that the monodentate coordination is, in general, stronger than the bidentate,[51] as long as the 5-fold coordination is retained. The dissociation of a further O→U bond (yielding [$UO_2(OAc)_3$]$^-$−3) is endothermic by 18.0 kJ mol^{-1}. Thus, the relative energies show a clear order of 5 > 6 > 4 in the preference of the different coordination numbers, which is in a very good qualitative agreement with the MD results above (Figure 7), and also fits to previous computational[47,60,93] and experimental[50] results on different uranyl complexes in, e.g., aqueous media.

The obtained O→U and U═O bond lengths for [$UO_2(OAc)_3$]$^-$−1 are also about the same as in previous theoretical[51,97] and experimental[98] studies. The O→U bond distances for all [$UO_2(OAc)_3$]$^-$ are also in the same range as indicated for the liquid phase by the AIMD and classical MD simulations above (Figure 4), supporting the validity of the MD results. In agreement with the HSAB principle, the bonds between the acetate ions and the uranyl unit are rather ionic than covalent, as shown by the relatively low shared electron numbers for the corresponding O→U atom pairs (SEN = 0.119−0.446). The lower directionality of these ionic interactions allows a more flexible arrangement around the central uranium atom in the case of the monodentate complexes; therefore, the repulsion between the ligands can be minimized by turning the nonbonding oxygen atom out of the center via increasing the C−O−U bond angles to 140−145°, whereas the interaction between the ligand and the metal atom can be maximized by the possible closer approach of the coordinating oxygen atom to the metal atom. These effects can be clearly observed via the average length of O→U and U═O bonds, and also the obtained electrostatic potential-fitted charges at the uranium atom (Figure 10). While the O→U distances decrease, showing directly the more efficient bonding in each O→U atom pair, the U═O bond lengthens, due to Coulombic repulsion along the O═U═O axis, as has been reported earlier.[63−65]

The formation of a C→U bond between a carbene molecule and the most stable [$UO_2(OAc)_3$]$^-$ isomer is favorable energetically, as shown by the low relative energy of the corresponding derivative (−42.7 kJ mol^{-1}) with respect to [$UO_2(OAc)_3$]$^-$−2 and the free isolated NHC. The coordination of the carbene allows the further unwrapping of the complex by the rupture of another O→U bond (Figure 8), providing 36.7 kJ mol^{-1} extra stabilization due to the considerations above in terms of ligand−ligand repulsion, and to the recovery of the preferred 5-fold coordination. This again releases a coordination site around the uranium atom, allowing another carbene to bind to the complex. Similarly to the case of [$UO_2(OAc)_3$]$^-$ derivatives above, the average lengths of the C→U, O→U, and U═O bonds show again that each metal−ligand interaction becomes stronger upon decoordination (Figure 10). However, structure [$UO_2(OAc)_3(NHC)$]$^-$−3 with four ligand-uranium bonds is again slightly less stable than that with five coordinating atoms. From the data it can also be observed that the coordination of the carbene results in a significant drop in the charge at the uranium atom, showing that on one hand the soft NHC ligand donates electrons very effectively to the metal (cf. data for [$UO_2(OAc)_3$]$^-$−2 vs [$UO_2(OAc)_3(NHC)$]$^-$−1 or [$UO_2(OAc)_3$]$^-$−3 vs [$UO_2(OAc)_3(NHC)$]$^-$−2), while on the other hand it facilitates the more flexible monodentate arrangement of the acetate ligands, having the same effect as discussed above.

Interestingly, in the case of the [$UO_2(OAc)_3(NHC)_2$]$^-$ system, the isomer with 6-fold coordination could not be optimized: the calculations always converged into structures with all three acetate ions attached as monodentate ligands to the uranium atom. Among the two obtained structures with 5-fold coordination (see Figure 9), the *trans* isomer ([$UO_2(OAc)_3(NHC)_2$]$^-$−1) is more stable by 22.3 kJ mol^{-1}, in which the two carbenes are at the opposite sides of the complex. The preference of this *trans* structure can be rationalized as in this isomer the bulky NHC ligands are separated from each other, as well as the anionic acetates, reducing the steric and Coulombic repulsion compared to the *cis* isomer ([$UO_2(OAc)_3(NHC)_2$]$^-$−2), where each kind of ligand is at the same side. The continuously increasing C→U bond lengths support this idea (Figure 10), showing that due to steric effects the carbenes cannot approach the uranium atom that close in the *cis* isomer, which is (partly) compensated by the stronger, and hence shorter O→U bonds. Also, the UO_2^{2+} moiety is significantly bent in the *cis* structure (171.2°, Figure 9), pointing the metal atom toward the acetates. The relative energy of the corresponding most stable structure compared to [$UO_2(OAc)_3$]$^-$−1 and the free NHC ligands is again very low (−161.4 kJ mol^{-1}, Figure 8), indicating that the complexation of

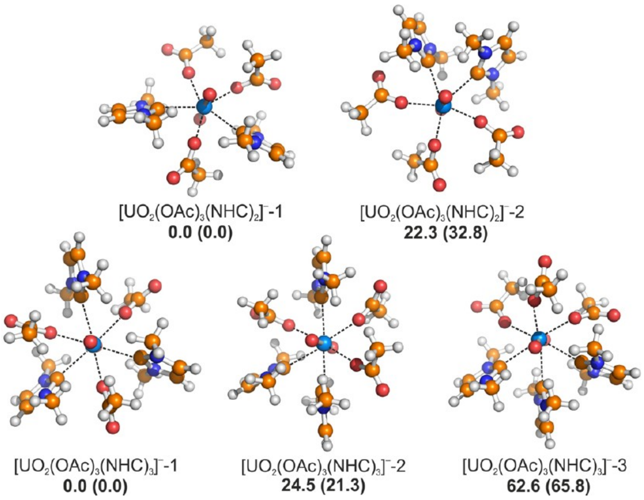

Figure 9. Orientation of the ligands around the uranium atom in structures [$UO_2(OAc)_3(NHC)_2$]$^-$ (with 5-fold coordination, above) and [$UO_2(OAc)_3(NHC)_3$]$^-$ (with 6-fold coordination, below). Relative energies and Gibbs free energies (in parentheses) are shown compared to the most stable isomers, in kJ mol^{-1}.

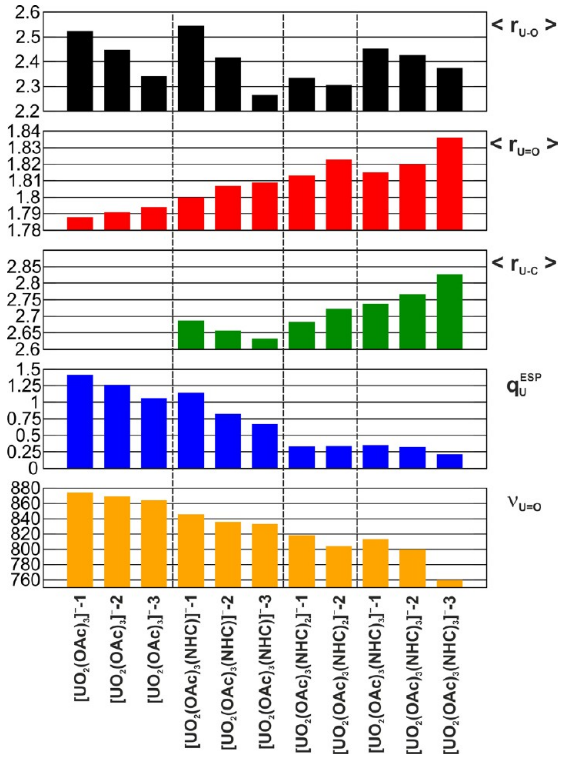

Figure 10. Structural data for the complexes shown in Figures 8 and 9: $\langle r_{U-O} \rangle$, average O(OAc)→U(UO_2^{2+}) bond distances; $\langle r_{U=O} \rangle$, average U═O bond distances; $\langle r_{U-C} \rangle$, average C(NHC)→U(UO_2^{2+}) bond distances; q_U^{ESP}, electrostatic potential-fitted charges at the uranium atom; $\nu_{UO_2^{2+}}$, asymmetric bond stretching vibrational frequency within the UO_2^{2+} moiety. For numerical data, see Supporting Information.

$[UO_2(OAc)_3(NHC)]^-$ by the second carbene molecule is feasible as well, having a reaction energy of −74.1 kJ mol^{-1}.

The attachment of a further carbene ligand to this structure is conceivable, forming structures $[UO_2(OAc)_3(NHC)_3]^-$, with 6-fold coordination (Figure 8). Similarly to the previous case, among the possible three regioisomers that one is the most stable, in which each acetate−acetate and NHC−NHC pairs are separated (Figure 9), and hence minimizing the steric and Coulombic repulsion, as described above. The structure of these complexes also shows similar trends among these three structures as in case of the $[UO_2(OAc)_3(NHC)_2]^-$: while the C→U bonds become longer, the O→U bonds become shorter upon the separation of the alike ligands, while the UO_2^{2+} unit is even more bent (162.8°, Figure 9). Interestingly, the $[UO_2(OAc)_3(NHC)_2]^- + NHC \rightarrow [UO_2(OAc)_3(NHC)_3]^-$ reaction is exothermic by only −6.4 kJ mol^{-1} (Figure 8, note the corresponding positive Gibbs free energy value), showing that after reaching 5-fold coordination with fully monodentate anions the attachment of further carbenes is not favorable energetically. In agreement, the charges at the uranium atom do not decrease significantly upon the coordination of the third carbene ligand, which indicates the lack of further stabilizing electron donation to the metal.

The obtained lengths of the C→U bonds (2.633−2.871 Å at the (RI)B97-D/def-TZVPP level, Figure 10) are similar to those observed experimentally for the hitherto synthesized NHC complexes **1**−**6** of the uranyl cation (2.609−2.640 Å for those in Figure 1). The slight differences arise because those structures had four ligands, which should result in shorter ligand−metal bonds, as shown in Figure 10. Accordingly, a comparison of the calculated and experimental values for structures **1**−**6** indicated a reasonable match in C→U bond distances (see Supporting Information). The shared electron numbers show for the C→U bond somewhat higher covalency than for the O→U pairs, but the obtained maximal SEN = 0.586 value (for $[(UO_2)(OAc)_3(NHC)]^-$−1) is still low for a strong covalent bond.

According to the MD and DFT results, in such systems the 5-fold coordination yields the most stable structures, while the acetate anions prefer the monodentate orientation in all structures, including those with carbene ligands. Since according to the MD simulations above only four anions can approach the uranyl cation (presumably due to Coulombic repulsion), these two requirements cannot be completely fulfilled at the same time, and at least one ligand is attached bidentately to the metal atom (see Figure 7). The attachment of the carbene to these complexes can assist cleaving one of the O→U bonds of the bidentate acetate ligand, while the 5-fold coordination is retained. Since the carbene introduces no further significant Coulombic repulsion, the formation of these complexes can result in significant stabilization. Accordingly, on the basis of this mutual assessment of the MD and DFT results it seems reasonable to assume that the NHC complexes of the uranyl cation can be formed in imidazolium acetate ionic liquids upon simply dissolving the uranyl salt.

However, in the data above neither the reaction energy of the carbene's formation from the IL itself, nor the effect of solvation, has been considered. Since these complexes should form specific and directional interactions (hydrogen bonding) with the solvent, a continuum model, such as PCM, is difficult to interpret. Furthermore, the solvation shell is rather big (see the MD simulations above), and hence has many conformations, which makes a cluster approach with DFT methods very demanding for these systems. It is, nevertheless, possible to deduce some valuable information from the previously performed experimental investigations[28−30] on the carbene-like reactions of imidazolium acetate ionic liquids. Since the possible formation and activity of the NHC in these experiments was already clearly presented experimentally,[28−30] the most intriguing open question is in this regard if the proton that has been removed from the imidazolium cation can have any influence on the formation of the present carbene complexes. In these reactions, the carbene's formation has been observed to be accompanied by that of $[(OAc)_2H]^-$ structures as well,[28,30] and the high stability of this hydrogen bonded species has been suggested to contribute to the IL's intrinsic property of forming carbenes.[28] The AIMD simulations of system **IV** (Figure 3), in clear agreement, reveal that the proton stays relatively far (ca. 6−8 Å) from the hypovalent center of the carbene throughout the whole simulation, while it is equally shared between two acetate molecules. This strong interaction can be represented by the combined distribution function of the two shortest O−H distances (Figure 11), showing that the proton is continuously transferred back and forth between the two acetate molecules within a remarkably short (and therefore very strong) O···H−O hydrogen bonding system. Accordingly, these results, together with the aforementioned experimental findings, show that the proton interacts with the solvent very strongly, and hence should not prohibit the reaction, until the formation of the carbene complexes occurs in such quantities that the proton is available in large excess in the solution. This concept has been proven experimentally for other trapping reactions, which showed that the reaction stopped only after ca. 50% conversion, when all basic acetates are occupied by the formation of $[(OAc)_2H]^-$.[28,30] In

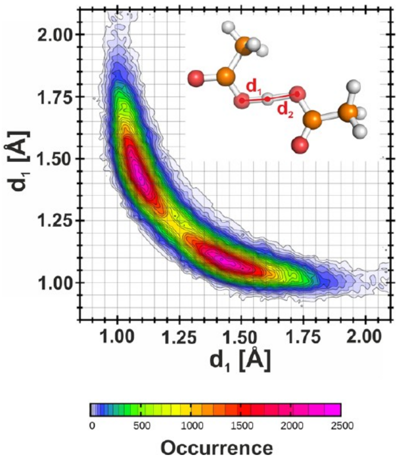

Figure 11. Solvation of the proton in imidazolium acetate-based ionic liquids.

fact, this strong binding could, in principle, locally even attenuate the available acetate anions for complexation, assisting the carbene's coordination to the uranyl cation. Furthermore, regarding the evaluation of the carbene's availability for complexation it is also important to note that in our previous study it has been reported that the acetate anions are occupying the strongest hydrogen bond donating sites of the imidazolium ring at the cation, which leaves the strong hydrogen bond acceptor carbene relatively free and active in the solution.[101]

The reaction of the uranyl cation with the carbene is very similar to that of CO_2 (Figure 12), since the formation of the carbene from the IL should be similar in both cases, while the carbene is competing with the anion for the CO_2[55] just as for the uranyl cation. Also, the solvation of UO_2^{2+} discussed above in the MD section is analogous to that of the CO_2,[99] although the number of coordinating anions is different. Since the reaction of such ILs with CO_2 is known to occur reversibly,[30] according to the considerations above this reaction can be used as a reasonable benchmark to inspect the formation of uranyl-NHC complexes from the IL. The binding energy between the carbene and the CO_2 is -43.3 kJ mol^{-1} at the (RI)B97-D/def-TZVPP level, while the Gibbs free energy is a very low -3.5 kJ mol^{-1}, in agreement with the reversibility of the reaction.[30] The binding energy of CO_2 is actually *less*, ca. half of that with $[(UO_2)(OAc)_3]^-$ (-79.4 kJ mol^{-1} at the same level, Figure 12), while the enthalpy and Gibbs free energy values also indicate a more exothermic and exergonic complex formation with $[(UO_2)(OAc)_3]^-$. This strongly suggests that the latter reaction should also occur, and should be even less reversible.

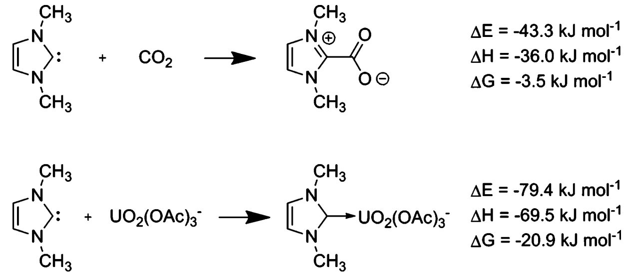

Figure 12. Energy, enthalpy, and Gibbs free energy (298 K, 1 bar) of the carbene's reaction with CO_2 and with $[(UO_2)(OAc)_3]^-$ (at the (RI)B97-D/def-TZVPP level).

After preparing the carbene complex of the uranyl cation, it is an important practical task to distinguish them from the acetate complexes. The changes in the U═O vibrational modes should, however, provide a possible way to do so, since the apparently very efficient electron donor carbene weakens the U═O bond, resulting in a presumably clearly observable ca. 30 cm^{-1} red shift in the corresponding IR bands (Figure 10).

3.3. Part III. Competitive Complex Formation with Water as Impurity.

As we have seen above, the formation of carbene complexes with uranyl(VI) is very likely in the investigated systems. However, it has to be stressed that beyond the formation of a strong C→U bond there are further influental factors that can determine the success of a synthetic approach. Since the reaction involves the formation of the carbene, which is highly sensitive to the basicity of the solution,[27] impurities can have a major effect on this initial step of the reaction as well. Impurities with coordinating ability can also compete with the NHC for the complexation, which in case of oxygen containing substances may completely inhibit the desired reaction, especially considering the assumingly low concentration (or low availability[55]) of the carbene. If the given competing ligand is neutral, then neither the Coulombic repulsion with the acetate anions can prohibit the formation of the corresponding complex, which results in an even more competitive side reaction.

Since water is often very difficult to remove completely from ILs, the presence of moisture can be a potential hindering factor for the formation of the desired carbene complexes of uranyl(VI). In the presence of considerable amounts of water, the accessibility of the carbene is significantly decreased,[31] as shown by AIMD simulations[56] and experiments[28] as well. Moreover, it has been shown by Bühl and co-workers that water can bind to the uranium atom of the uranyl cation with significant strength,[51,60] which may also easily exclude the formation of the carbene complex. Thus, classical MD simulations on system **II** were performed, to see the effect of water on the solvation of the uranyl cation, and the reaction.

MD simulations on system **II** (Figure 3) revealed that the water is mainly interacting with the acetate anions, as has been presented by AIMD simulations before.[56] Interestingly, one of the water molecules forms hydrogen bonds with the coordinating acetate anions in the first half of the simulation, and shortly after its dissociation from the solvent shell of the uranyl, another water molecule arrives and attaches to these acetate ligands (Figure 13). This hydrogen bond, interestingly, influences the coordination of the uranium to a notable extent by competing with the O→U bond, resulting in decoordination of the acetate anions, hence the more frequent "undressing" of the metal atom in the solution (Figure 13). However, despite the occurring surprisingly low coordination numbers (note the occurring 4-fold coordination!), the 5-fold coordination remains dominant, while the nearby water molecule does not form a coordinative bond with the uranium atom. Also, the rest of the above-described, relevant RDFs remain practically unchanged by the presence of the water molecules.

To obtain a direct comparison between the coordination of water and the carbene, also the aqua analogues of the $[(UO_2)(OAc)_3(NHC)_{1-2}]^-$ complexes shown in Figure 8 were investigated by DFT methods. The optimized structures are gathered in Figure 14. Notably, even if in the resulting $[(UO_2)(OAc)_3(H_2O)_{1-2}]^-$ structures there are stabilizing hydrogen bonds between the ligands, the formation of these complexes is significantly less exothermic than that of the corresponding $[(UO_2)(OAc)_3(NHC)_{1-2}]^-$ derivatives. Also,

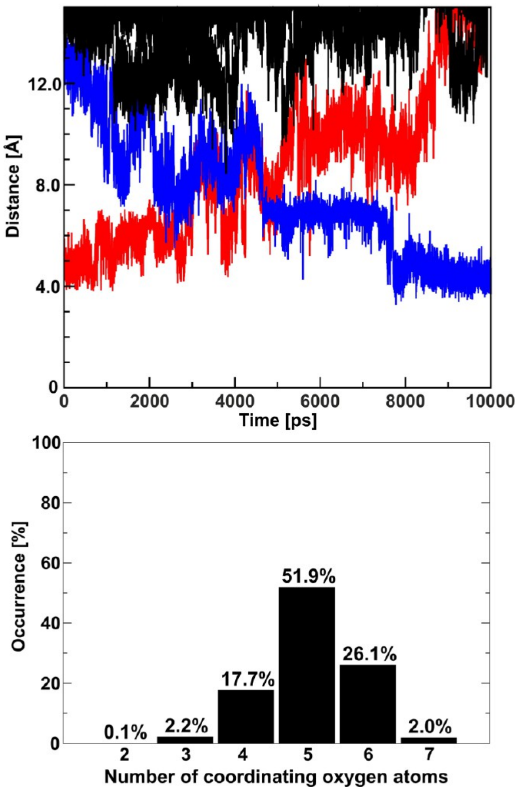

Figure 13. Molecular dynamics simulation of system **II**. Above: development of the $U(UO_2^{2+})-O(H_2O)$ distances throughout the simulation, with the curves for the two water molecules that have close approaches shown in red and blue. Below: distribution of coordination numbers around the uranyl cation in system **II** (cf. Figure 7 for system **I**).

remarkably, the clusters, in which the water is not coordinating to the uranyl cation, instead merely forming hydrogen bonds with the acetate ligands, exhibit significant stabilities, showing that the exchange of the acetate ligands to water is not as beneficial energetically, as in case of the nonbasic, and, hence, noncoordinating bis(trifluoromethylsulfonyl)imide anion.[47] Moreover, the strong interactions between the water and the solvent[56] should also hinder the formation of the aqua complexes, while the carbene forms only weak hydrogen bonds with the methyl groups of the cations,[101] which leaves it free, and available for complexation.

Thus, apparently, traces, or even low amounts of water should not prohibit the reaction via complex formation, if the carbene is available in a considerable amount. However, according to the changes in the coordination shell, the amount of moisture available in the reaction mixture seems to be an interesting parameter to consider in a corresponding experimental study, which might aid in the decoordination of the acetate anions.

Since in the considered reactions a carbene ligand is involved, its decomposition via hydrolysis should also be considered here. Interestingly, although the reaction[102,103] seems feasible, it was recently shown by a combined computational and experimental study on reaction mixtures with carbene/water ratios between 2:1 and 1:100 that this process is either surprisingly slow (in the presence of water traces) or reversible (in excesses of water).[103] Moreover, since the carbene is available from pure imidazolium acetate solvents in general,[27−30,56] its sensitivity against hydrolysis should trigger a slow decay of the neat IL itself under air, which has not been observed experimentally even in the corresponding industrial applications.

4. SUMMARY AND CONCLUSION

In 1,3-dialkylimidazolium acetate ionic liquids (ILs) carbenes are accessible via a single proton transfer from the cation to the anion, which results in carbene-like reactivity.[27−31,56] In this Article the possible application of this intrinsic property is suggested by theoretical methods as a general, potent, mild, and convenient synthetic route toward NHC complexes of various metals. As a critical example, the uranyl(VI) cation was chosen, since in the corresponding scarce complexes the NHC ligand binds very weakly to this metal center, requiring a novel, effective approach for their synthesis, and also providing a careful underestimation for the applicability of the suggested process for other metals in general.

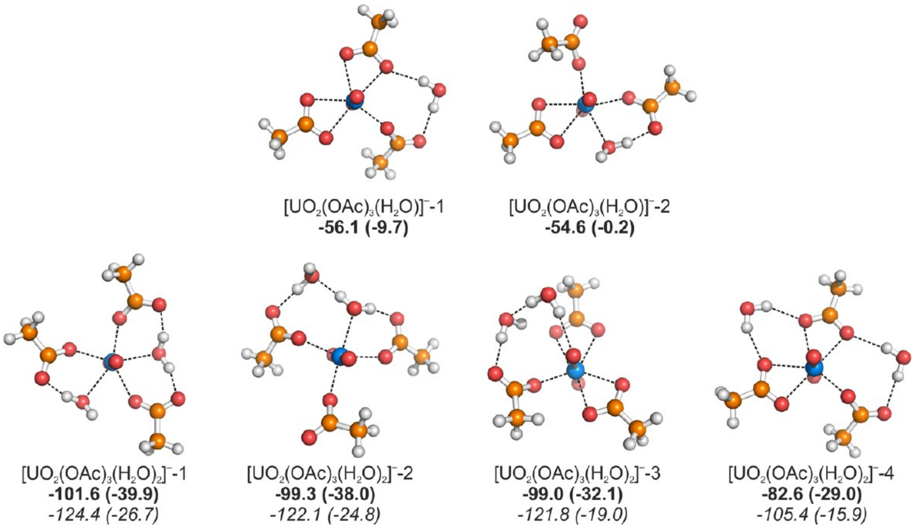

Figure 14. Complexes of $[(UO_2)(OAc)_3]^-$ with one (above) and two (below) water molecules. Relative energies and Gibbs free energies (in parentheses) are given according to the $[(UO_2)(OAc)_3]^- {-2} + (H_2O)_n \rightarrow [(UO_2)(OAc)_3(H_2O)_n]^-$, and the $[(UO_2)(OAc)_3]^- {-2} + nH_2O \rightarrow [(UO_2)(OAc)_3(H_2O)_n]^-$, reactions (in italics), kJ mol^{-1} units (cf. the values for the $[(UO_2)(OAc)_3(NHC)_{1-2}]^-$ in Figure 8).

Both the MD and DFT calculations showed that the coordinating acetate anions prefer a monodentate binding to the metal, which can be explained by the Coulombic repulsion between the ligands, and also by the interactions of the noncoordinating acetate oxygen atoms with the IL cations. Since achieving the most stable 5-fold coordination around the uranium atom requires that at least one of the four coordinating anions should be bidentating at a time, this results in a certain destabilization of the complex. This strain can be released by the coordination of the neutral carbene molecule, which promotes the dissociation of an O→U bond of the bidentating ligand via the forming C→U bond, contributing to the stability of the complex. The NHC, therefore, can be attached to the considered uranyl complexes with significant energy benefit (ca. −79.4 kJ mol^{-1}), showing that the coordination of this species is not only possible in terms of accessible sites, but also thermodynamically favorable. The comparison in energetics with the analogous, and experimentally confirmed[30] reaction of the carbene with CO_2 shows that the coordination energy above should be high enough for the binding to occur. Also, competitive complexation with water ligands was excluded, showing that traces of moisture should not have significant effect on the reaction via complex formation, but the induced changes in the solvation shell may hold interesting possibilities for influencing, or even tuning such reactions.

As discussed above, expectedly the reaction is even more likely in case of those many metals that have more stable NHC complexes and less stable acetate complexes, which shows that this approach should be rather general for preparing such derivatives in a very convenient way: by simply dissolving the metal salt in the appropriate IL.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Graphs corresponding to the MD simulations at 600 K, analogous to those in Figures 4−7. Comparison of the results obtained by the force fields of Wipff[78] and Maginn.[72] Results of the performed test calculations on the application of the RI-B97-D/def-TZVPP method, and the connected discussion. Geometry of all optimized $[(UO_2)(OAc)_N(NHC)_{1-6}]^{2-N}$ ($N = 0-3$) structures. Numerical data for Figure 10. XYZ coordinates and total energies of all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: holloczki@gmail.com.

Notes

The authors declare no competing financial interest.

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