DOI: 10.1002/chem.200701511

Linear Uranium Complexes X_2UL_5 with L = Cyanide, Isocyanate: DFT Evidence for Similarities between Uranyl (X = O) and Uranocene (X = Cp) Derivatives

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Abstract: A DFT study of the isostructural compounds $[UO_2L_5]^{n-}$ with $n = 3$–5 and linear $[Cp_2UL_5]^{m-}$ with $m = 1$–3 has been carried out for two different anionic ligands. Structurally stable structures are obtained for all systems. The coordination competition between cyanide (CN^-) and isocyanide (NC^-) as well as between cyanate (OCN^-) and isocyanate (NCO^-) has been studied in the uranyl case. A clear preference for cyanide and isocyanate complexes is reported. The coordination of five ligands in the equatorial plane is rationalised by the analysis of the MO diagram of both systems. Moreover, the qualitative comparison of the two MO diagrams shows a high similarity in agreement with the isolobality concept. The existence of linear $[Cp_2UL_5]^-$ organometallic U(VI) complexes is thus proposed, as well as the possibility of obtaining complexes of both types for U(VI) and U(V) with OCN^- ligands. In addition, the U(IV) linear metallocene is calculated to be stable for the latter ligand.

Keywords: density functional calculations · isolobal relationship · metallocene · uranium

Introduction

The development of actinide chemistry has been increased over the last decade, mainly supported by the problem of nuclear waste storage. This problem is still challenging for both theoretical and experimental chemists. From the experimental point of view, the manipulation of radioactive species requires special facilities, and results reported in the literature are generally limited to early actinides up to uranium. In particular, the case of the uranyl ion UO_2^{2+} has been extensively investigated, both experimentally and theoretically.[1–7] The nature of the bonding in such a dication has been unequivocally determined, and the role of the 5f orbitals in the bonding demonstrated.[1–7] Adopting an ionic picture, the U–O bond can be described as a sigma bond with two strong donor–acceptor (with strong electrostatic character) interactions between the p_x and p_y lone pairs on oxygen and empty d/f orbitals on uranium. However, other kind of mesomeric forms can be drawn (Figure 1).

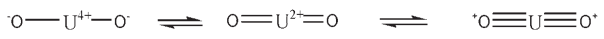

Figure 1. Different bonding models for the uranyl ion.

These different bonding models can be drawn, because in U(VI) both the 5f or 6d orbitals are unoccupied and can be used for establishing the bond with the oxo ligand. It should be kept in mind that the third model in Figure 1, which looks rather inappropriate with a plus charge on the oxygen, is the one obtained from a pure covalent bonding model. Indeed, the MO diagram (Figure 2) clearly indicates that the uranium atom has enough symmetry-adapted orbitals to establish three bonds with each oxygen atom. The analysis of such an MO diagram shows that seven non-bonding orbitals are still accessible, so such a dication can coordinate more ligands. In particular, the remaining orbitals are primarily oriented in the equatorial plane (five orbitals), whereas the other two are more out-of-plane. The coordina-

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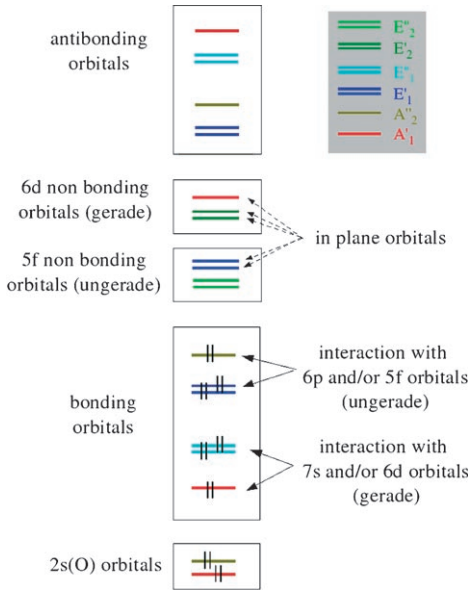

Figure 2. Qualitative MO diagram of the uranyl ion in D_{nh} symmetry.

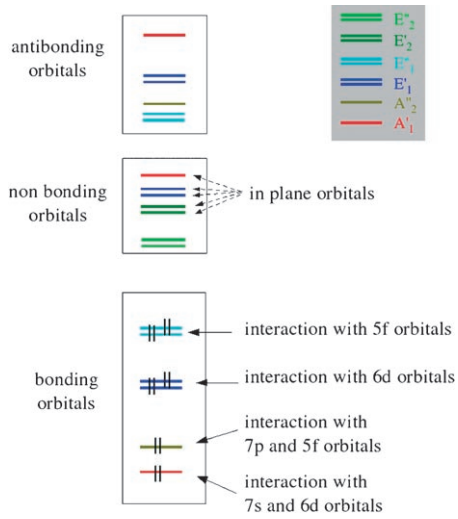

Figure 3. Qualitative MO diagrams for the Cp_2U fragment.

tion in the equatorial plane has been experimentally widely studied for a variety of ligands such as chlorides,[8] hydroxides,[9–10] carbonate,[11] iodates,[12] and very recently cyanides[13] and isocyanates.[14] The understanding of the metal–ligand interaction is a key question that has been investigated by different groups by means of theoretical methods.[1–7]

In parallel to the experimental studies on uranyl-ligand interaction, the group of Ephritikhine has also been working on organometallic uranium complexes such as Cp_2U. This group has recently reported the synthesis of linear uranocene compounds of U(IV) and U(V) that exhibit either five cyanides or five acetonitrile molecules in the equatorial plane:[15–17] in this context, a "linear" complex is one that contains a five-fold axis that passes through the U atom. This result seems puzzling, since the Cp_2M fragment is bent for transition metals or lanthanides, owing to the use of the d orbitals. This kind of compound was obtained for U(III). These experimental facts were explained by DFT calculations[17] and rationalised by the analysis of the MO diagram (Figure 3). A linear structure can be obtained for U(IV) and U(V), because seven or six non-bonding orbitals are occupied, respectively (as seen in Figure 3), but in the case of U(III) an additional antibonding orbital has to be occupied. Therefore, the latter appears not to be structurally stable and a bent structure is obtained by means of second-order Jahn–Teller effect. Notice that the MO diagrams of uranyl (Figure 2) and of linear uranocene (Figure 3) seem rather similar and thus, a parallel between the two systems seems plausible.

When combined with U (or other actinides), this observation clearly defines the isolobality between the oxo and cyclopentadienyl ligands, as proposed by Hoffmann.[18] The interaction between the oxo-ligand and the actinide centre is, however, slightly different than the interaction between the Cp and the metallic centre. Indeed, in the uranyl-type complexes, the interaction involves the 6p orbital (through the 6p-hole that was found at the NBO level), whereas the 7p is involved in the metallocene complex. This is clearly a result of the longer M–Cp distance ($\approx$2.45 Å) compared to that of U–O ($\approx$1.78 Å). However, the notion of isolability is valid, as the frontier orbitals are similar. Therefore, in this paper, the isolobality between the uranyl and uranocene systems has been investigated by a theoretical approach.

Seven-coordinated U(IV), U(V) and U(VI) complexes of both types (X_2UL_5 with X = O or Cp) have been investigated and found to be structurally stable. Test calculations on the choice of the core size of the uranium effective core potential (ECP) have been carried out on $[UO_2L_5]^{3-}$. For that purpose, the possibility of obtaining either cyanide or isocyanide compounds as well as cyanate or isocyanate complexes has been explored. These calculations are related to the different results obtained by Clavaguerra-Sarrio et al.[19] and Sonnenberg et al.[20] In the case of UO_2L_2, the isocyanide compound was found to be more energetically stable, whereas $[UO_2L_5]^{3-}$ was found to be more stable for the cyanide compound. The results are compared with the experimental structures, when known, and the structure of a linear $Cp_2U(VI)$ complex is proposed. Moreover, structurally stable linear uranocene structures are proposed in the case of isocyanate auxiliary ligands.

Computational Details

Uranium has been represented by either a very small core relativistic effective core potential (RECP)[21] (32 valence electrons) or a small-core RECP[22] (14 valence electrons) extracted by the Stuttgart–Dresden–Bonn group in combination with the corresponding basis set (up to g functions). Carbon, nitrogen, oxygen and hydrogen have been represented by either an all-electron, double-ζ quality, 6–31G(d,p) basis set[23] or an ECP for carbon, nitrogen, oxygen in combination with the appropriate basis set.[24] Calculations have been carried out at the DFT(B3LYP and B3PW91) levels[25,26,27] of theory with Gaussian 03.[28] The nature of the

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extrema has been established with analytical vibrational frequency calculations. The reaction enthalpy has been calculated at 298 K using the harmonic approximation.

Results and Discussion

Test calculations on $[UO_2L_5]^{3-}$ with L = CN^-, NC^-, OCN^-, NCO^-: In order to perform calculations on the Cp_2U system, the possibility of performing the calculations with the small core ECP (14 valence electrons) was tested. Geometry optimizations were carried out on $[UO_2L_5]^{3-}$ (L = CN^- and NCO^-) with use of both small core and very small core ECPs. These two compounds were considered, as the experimental data are available.[13,14] The geometries of the optimised complexes are presented in the Supporting Information (Figure S1 and Figure S2). The key geometrical and experimental parameters are reported in Table 1. The geometries obtained are in very good agreement with each other, as well as with the experimental results. Indeed, for the $[UO_2(CN)_5]^{3-}$ complex (optimised at the two levels of theory) the U–O distance differs by 0.02 Å and the U···C distances by only 0.04 Å. In comparison with the experimental structure, the major discrepancies are found to be 0.01 Å for the U–O and U···C distances and ≈0.02 Å for C–N. A similar result is obtained for the isocyanate complex. Indeed, the differences obtained from the two RECP are in the same range as the cyanide complex: 0.02–0.03 Å for the U–O and U···N distances. The comparison with the experimental structure is more complicated here, as only two isocyanates and two phosphane oxides are coordinated. Thus, the optimised U···N distances are found to be overestimated by 0.2 Å. In order to confirm the validity of the DFT approach in reproducing geometries of uranium complexes, the experimental isocyanate complex has also been optimised (the methyl groups on the nitrogen were replaced by hydrogen atoms). The U···N and U···O distances are found to be in excellent agreement with the experiment (U···N: B3LYP 2.379 Å, B3PW91 2.351 Å, exp 2.336 Å and U···O: B3LYP 2.367 Å, B3PW91 2.354 Å, exp 2.277 Å). The geometries were optimised either with the B3LYP or B3PW91 functionals and the results are almost identical. These two functionals were compared, as it has been reported that the B3PW91 functional is better at representing soft interactions.[29] Moreover, since generalised gradient approximation (GGA) functionals can lead to either very good or rather poor results depending on the system. In addition, Vallet et al.[2,3] have mentioned that Hartree–Fock exchange has to be accounted for to get reliable geometrical and energetical values, so that no GGA or local density approximation (LDA) optimizations were carried out. The energetic difference between a cyanate and an isocyanate complex has also been investigated for the experimental complex. Experimentally, only the isocyanate complex has been reported. The calculation finds the cyanate complex to be 22.5 kcal mol^{-1} higher in energy than the corresponding isocyanate complex. This is consistent with the experimental data, as no cyanate complex has been reported and thus the validity of the theoretical approach used hereafter has been demonstrated.

Table 1. Key geometrical parameters of the optimised structures as well as the experimental ones.

	U–O [Å]	U···L [Å]	N–C [Å]
$[UO_2(CN)_5]^{3-}$ (32e ECP)	1.789	2.653	1.180
$[UO_2(CN)_5]^{3-}$ (14e ECP)	1.761	2.691	1.180
$[UO_2(CN)_5]^{3-}$ exp.	1.772	2.549–2.579	1.156–1.166
$[UO_2(NCO)_5]^{3-}$ (32e ECP)	1.791	2.506	1.190
$[UO_2(NCO)_5]^{3-}$ (14e ECP)	1.763	2.526	1.191
$UO_2(NCO)_2(OP(NR_2)_3)_2$ exp.	1.765	2.336	1.145

The difference between both types of calculation (small core ECPs and very small core ECPs) can be explained by a slightly better treatment of core-valence interaction with the very small core ECP since the whole 5th shell is explicitly included in the calculation which is not the case with the small core one.

From an energetic point of view, the coordination of the anionic auxiliary ligand in the equatorial plane is calculated to be very favourable. Indeed, the total binding energy is calculated to be −447.0 kcal mol^{-1} and −438.0 kcal mol^{-1} for the isocyanate and cyanide ligands, respectively, by using the very small core RECP. For comparison, the binding energies are found to be −433.0 kcal mol^{-1} and −420.0 kcal mol^{-1} , respectively, using the small core ECP. These results are found to be in fair agreement with each other. The binding energy is obtained by computing the free energy of reaction in the gas phase of the reaction [Eq. (1)]:

$$UO_2^{2+} + 5L^- \rightarrow [UO_2L_5]^{3-} \quad (1)$$

It should be kept in mind at this stage that the absolute value is clearly overestimated, as no solvent effects have been considered; they should favour the left-hand side of Equation (1). However, this favourable coordination can be explained by the important electrostatic interaction between the cationic uranium centre and the anionic ligand. Clearly this would not be overcome by solvation effects. This interaction overcomes both the electrostatic repulsion between the auxiliary ligands and the entropic loss due to coordination.

To ensure the comparison between the two RECP values, as well as to study the possibility of both type of coordination proposed in the literature,[19,20] the geometries of isocyanide and cyanate complexes have been optimised (see the Supporting Information, Figure S1 and Figure S2). For the latter, a similar study has already been undertaken for the experimental system reported by Crawford et al. [19] and, in the present work, a preference for the isocyanate complex by more than 20 kcal mol^{-1} is found. In the isocyanide case, both structures have been optimised and shown to be a minima on the potential energy surface. This is in agreement with the earlier work by Clavaguerra-Sarrio et al.[19] and

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Sonnenberg et al.[20] From the geometrical point of view, as expected, the U···N distance is found to be smaller than the U···C distance by roughly 0.1 Å. This can be explained by two facts. First, the nitrogen lone pair is found to be more localised than the carbon lone pair in the cyanide ligand. This might be expected, given that the higher effective nuclear charge for N than for C, so the interaction between the lone pair on the ligand and an empty orbital on the uranium centre should be at shorter distance. Secondly, the interaction in the isocyanide complex should overcome the attractive charge-dipole interaction present in the cyanide case. From the energetic point of view, the cyanide complex is found to be more stable than the isocyanide one by 17 kcal mol^{-1}. This result is in agreement with the work of Sonnenberg et al. who reported that the more stable structure in pentacoordination is found with a cyanide ligand and the change in stability between the cyanide and the isocyanide was found for a tetracoordination.

Concerning the cyanate/isocyanate coordination problem, the situation is somewhat different. Using both RECP, the cyanate complex is not found to be a minimum. The structure presented in Figure S2 in the Supporting Information exhibits 5 or 6 imaginary vibrational frequencies. Thus, only the isocyanate compound is structurally stable, in agreement with the work of Crawford et al.[14]

To conclude, the use of a small core RECP leads to satisfactory results for the uranyl complexes so that such an ECP will be used in the following, in particular, for the Cp_2U complexes. Moreover, test calculations on the choice of the functional (B3LYP or B3PW91) have given results in good agreement with each other. The results are, as expected, not strongly dependent on the choice of the functional. Thus, in the following, the calculations will be performed either using one or the other functional.

Calculations on $[UO_2L_5]^{q-}$ $q=3$–5 with L=CN$^-$, NCO$^-$: Here, the structures obtained for U(IV), U(V) and U(VI) derivatives of the uranyl ion will be presented. For the discussion on the stability by comparison with the Cp_2U linear system, see below. Geometry optimizations have been performed at the DFT level for $[UO_2L_5]^{5-}$, $[UO_2L_5]^{4-}$ and $[UO_2L_5]^{3-}$ with the cyanide and the isocyanate ligands. The optimised structures are presented in Figure 4 (cyanide) and Figure 5 (isocyanate) and the key geometrical parameters in Table 2.

It should be noted at this stage that the complexes are highly negatively charged, so geometry optimization was difficult. In particular, in the U(IV) case (charge of −5), it was not possible to optimise the structures satisfactorily. From an experimental point of view, the UO_2 moiety is difficult to dissolve so that such a structure would certainly never be observed.

For the U(VI) complexes, the coordination of the ligand leads to an appreciable elongation of the U–O bond by 0.08 Å. Thus, the coordination of a strong anionic σ donor in the equatorial plane results in a weakening of the strong -yl bond, so the U–O bond would be more reactive.

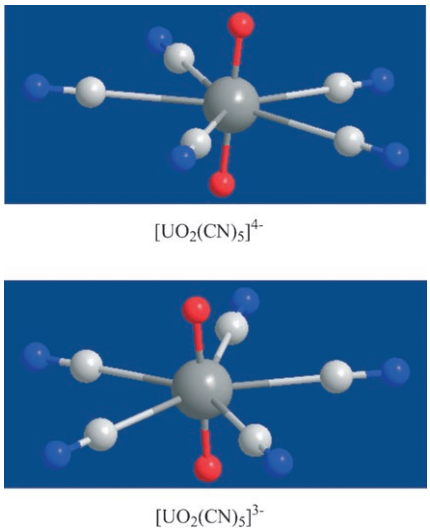

Figure 4. Optimised structures of the U(V) and U(VI) cyanide complexes.

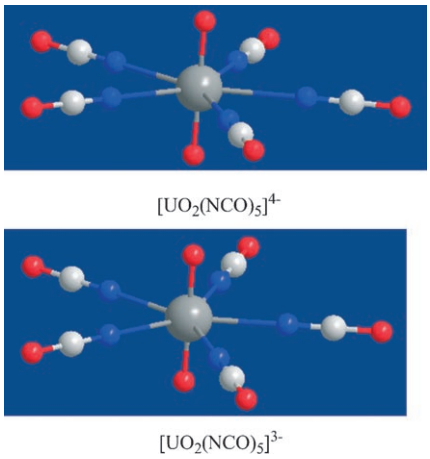

Figure 5. Optimised structures of the U(V) and U(VI) cyanide complexes.

Table 2. Key geometrical parameters of the optimised structures.

	U–O [Å]	U···L [Å]	N–C [Å]
$[UO_2(CN)_5]^{4-}$	1.803	3.029	1.186
$[UO_2(CN)_5]^{3-}$	1.761	2.691	1.180
$[UO_2(NCO)_5]^{4-}$	1.808	2.783	1.190
$[UO_2(NCO)_5]^{3-}$	1.763	2.526	1.191

A similar result is obtained in the U(V) case. Strictly, this complex cannot possess a five-fold axis, as a result of Jahn–Teller distortions created by the unpaired electron (the HOMO is of e_1' symmetry). However, optimisations of this complex in C_1 symmetry lead to a C_{2v} structure in which the angular deviations from D_{5h} symmetry are trivial, never exceeding 0.1°. The ligand coordination weakens the U–O bond since the bond is elongated by 0.06 Å with respect to

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the bare uranyl ion. From the energetic point of view, the coordination according to Equation (1) is calculated to be endergonic by 83.2 and 67.7 kcal mol^{-1} for the isocyanate and the cyanide complexes, respectively. These results have to be compared with the coordination energies for the U(VI), which were highly exergonic (around −440 kcal mol^{-1}). The difference between the two results can be attributed to the longer U···L distances found and a lower positive charge of the uranium centre, leading to a lower electrostatic interaction. Moreover, in the U(V) case, there is an unpaired electron that leads to an electronic repulsion with the ligand lone pairs. However, such a structure is found to be a minimum on the potential energy surface and, under specific experimental conditions, U(V) complexes may be isolable. A similar argument, the U(IV) complexes should be even less thermodynamically stable than the U(V) complexes, in agreement with the fact that the geometry optimisation was not possible.

Comparing the two ligands, it should be noted that the U···L distances are found to be systematically lower for the isocyanate ligand than for the cyanide ligand. This can be explained by the difference of dipole moment between the two ligands. The calculated dipole moments are found to be equal to 0.0173 D for the cyanide and 1.5061 D for the isocyanate ion. Therefore, for the isocyanate ion, a stronger charge-dipole interaction is obtained that leads to a smaller U···L distance. Consequently, isocyanate ligands are found to be slightly more favourable ligands than the cyanide ligands for uranyl complexes, in terms of charge-dipole interaction, and lead to stronger coordination.

A similar study has been performed on the Cp_2UL_5 family.

Calculations on $[Cp_2UL_5]^{q-}$ $q=1$–3 with L = CN^-, NCO^-: Geometry optimizations have been performed on the U(IV), U(V) and U(VI) linear uranocene complexes for both ligands. The optimised geometries are presented in Figure 6 (cyanide complexes) and Figure S4 (isocyanate complexes) in the Supporting Information. The key geometrical parameters are reported in Table 3. Let us start by analyzing the cyanide complexes. The U(IV) and U(V) systems are known experimentally.[17] The optimised geometries are in good agreement with the experimental geometries. The U···L distances are well reproduced with a maximum discrepancy of 0.05 Å in the U(IV) case. The U−X distances (X = Cp centroid) are much more complicated to compare, because the experimental structures were obtained with $Cp^*(C_5Me_5)$ ligands and the calculations were performed with $Cp(C_5H_5)$. Thus, for steric reasons, the optimised U−X distances are expected to be shorter than the experimental ones. We have found that the short U−X distances do not influence the cyanide coordination to the uranium centre. This indicates that the cyanide coordination is driven by electronic effects, whereas the U−X distances are primarily affected by the steric influence of the methyl groups. To summarise, the linear structure was found to be possible for pentacoordinated uranium complexes according to the MO diagram (Figure 3). Indeed, the use of the 5f orbitals in the bonding induces the presence of seven nonbonding orbitals for the Cp_2U fragment with five pointing in the equatorial plane and two out of the plane. Thus, from an MO point of view, a pentacoordinated complex with a maximum of two unpaired electrons can adopt a linear structure. Consequently, U(IV), U(V) and U(VI) can adopt such a structure. In the case of U(IV), the presence of the two unpaired electrons on the uranium centre induces an electrostatic repulsion with the lone pairs located on the ligands, so both linear and bent structures can exist. This repulsion becomes smaller on going from U(IV) to U(V), so that the latter is experimentally found to be stable in a linear form.

Table 3. Key geometrical parameters of the optimised structures.

	U−X(Cp centroid) [Å]	U···L [Å]	N−C [Å]
$[UCp_2(CN)_5]^{3-}$	2.547	2.673	1.176
$[UCp_2(CN)_5]^{2-}$	2.485	2.559	1.174
$[UCp_2(CN)_5]^{-}$	2.436	2.477	1.176
$[UCp_2(NCO)_5]^{3-}$	2.573	2.540	1.191
$[UCp_2(NCO)_5]^{2-}$	2.526	2.421	1.195
$[UCp_2(NCO)_5]^{-}$	2.491	2.330	1.200

Following this argument, the repulsion is non-existent in the U(VI) case, so that the linear complex should be structurally the most stable of the series. From a theoretical point of view, such a structure has been optimised. As expected, the U−X and the U···L distances are calculated to be smaller than in the corresponding ones for the U(IV) and U(V) complexes. This can be explained by the increase of the positive charge at the uranium centre and also by the non-existence of the electrostatic repulsion between the lone pair on the ligand and the uranium unpaired electrons. Experimental work is in progress to generate such a complex that would be the first linear organometallic complex of U(VI).

We have shown above that the coordination of five isocyanate ligands to the uranyl moiety has been shown to be even more exergonic than for cyanide. We therefore investigated the possibility of obtaining a structurally stable linear uranocene with five isocyanates in the equatorial plane has been investigated. The optimised structures are presented in Figure 7 in the Supporting Information. As expected, it has been possible to obtain structurally stable structures for U(IV), U(V) and U(VI). This finding is in agreement with the MO diagram (Figure 3) and the argument proposed for the cyanide case.

A similar geometrical variation is observed with respect to the oxidation state of the uranium centre as in the cyanide complexes. The distances decrease as expected, following the argument stated before. For a given oxidation state, it should be noted that the U···L distance as well as the U−X distances are smaller for the isocyanate ligand than for the cyanide. This was observed in the uranyl derivatives case described above and was attributed to a better charge-dipole interaction with the isocyanate ligand.

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As for the U(VI) linear uranocene complex of cyanide, the three isocyanate linear complexes are predicted to be structurally stable.

Comparison of the two types of systems: In comparing the two families of systems, a parallel seems to be drawn, as U(VI) and U(V) linear systems are predicted to be structurally stable from our computational point of view. The validity of the isolobality concept in these examples is thus firmly established. The comparison of the MO diagrams clearly shows that both uranyl and uranocene derivatives should exhibit a similar stability. The same number of non-bonding orbitals is found for both systems, so a system existing for one family should also exist in the other family. This has been verified in the cases of $[UO_2(CN)_5]^{4-}$ where the linear Cp_2-homologue exists and for $[Cp_2U(CN)_5]^-$ where the uranyl equivalent is also structurally stable. Considering this similarity of the MO diagrams, $[UO_2(CN)_5]^{5-}$ would be structurally stable, but here the limit of a pure covalent model applies. Even though the orbital interaction is favourable, the electrostatic repulsion between ligands and the electron–electron repulsion between lone pairs on the ligands and the unpaired uranium electrons have to be taken into account.

On the other hand, the MO diagrams show that every ligand possessing a lone pair can in principle coordinate in the equatorial plane of a uranium complex of both families. Thus, it should be possible to obtain the linear uranocene structures with other kind of ligands. In particular, isocyanate could possibly be used for such a purpose. To overcome the problem of the electrostatic repulsion between ligands in the uranyl case, where it appears to be crucial, the use of neutral ligands can be considered. Work is in progress in that direction: preliminary results show that the U(IV), U(V) and U(VI) uranyl-type pentacoordinated complexes of CO are structurally stable.

Conclusion

In this paper, we have reported a comprehensive study of pentacoordinated cyanide and isocyanate linear complexes of U(IV), U(V) and U(VI) with either two oxo ligands (uranyl-type) or two cyclopentadienyl ligands (Cp-type). The use of small-core RECP (14 electrons) was checked and validated by comparison with either experimental structures or very small-core RECP (32 electrons) results. The possibility of forming either cyanide or isocyanide as well as cyanate or isocyanate complexes has been investigated. It has been shown that cyanide pentacoordination is preferred, although the isocyanide is also a minimum, whereas only the isocyanate complexation leads to a minimum on the PES.

Two structurally stable structures have been predicted with cyanide ligands: $[UO_2(CN)_5]^{4-}$ and $[Cp_2U(CN)_5]^-$. Their existence has been rationalised by analysis of the MO diagrams (Figure 2 and Figure 3) and follows the isolobality concept. In particular, the similarity between the two MO diagrams allows us to draw a parallel between the two families of complexes.

The influence of the electrostatic repulsion between anionic ligands has been considered, to explain the difficulty of characterizing highly negatively charged complexes of uranyl-type. This was verified by test calculations, using the neutral ligand (CO). Work is in progress in that direction and the results will be presented in a forthcoming paper.

Acknowledgement

L. M. is grateful to the Institut Universitaire de France. CalMip (CNRS, Toulouse, France) is acknowledged for calculation facilities.

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Received: September 24, 2007
Published online: January 7, 2008

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