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REGULAR ARTICLE

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Prediction of new inorganic molecules with quantum chemical methods

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Abstract Quantum chemistry can today be employed to invent new molecules and explore unknown molecular bonding. An overview of novel species containing metals bound to polynitrogen clusters is presented. The prediction of metal polyhydrides is discussed. Finally, some species containing gold that behaves as a halogen are described, together with recent advances in actinide chemistry and exploration of the nature of the actinide–actinide chemical bonding.

Keywords Metal-polynitrogen clusters · Metal polyhydrides · Gold · Actinides · CASPT2

1 Introduction

In 1998 quantum chemistry was recognized through the award of the Nobel Prize in Chemistry to W. A. Kohn and J. A. Pople jointly. This recognition was not only based on the ability to solve the quantum-mechanical equations to a good degree of approximation for molecules, but also on the fact that the field can now perform theoretical simulations of real benefit to the community.

Ab initio quantum chemistry has made so many advances in the last 40 years that it now allows the study of molecular systems containing any of the atoms in the periodic system. Transition metal- and actinide compounds can be treated routinely, provided that electron correlation [1] and relativistic effects [2] are properly taken into account.

We start by outlining how quantum chemistry has reached a level where transition metal, actinide, and other heavy atom compounds can be routinely studied. An incomplete historical survey of work which has stood the test of time would, for example, include the following:

1. The hydrogen molecule by Heitler and London [3] in the 1930s.
2. Molecular orbital theory due largely to Mulliken [4] and Slater [5].
3. Self-consistent field (SCF) theory due to Hartree [6] and Fock [7].
4. The introduction of Gaussian basis functions by Boys[8].
5. The presentation in 1965 by Nieuwpoort [9] of the first ab initio calculation on transition metal carbonyls.

By the middle 1960s, some computational chemists were using the SCF method [10] to study molecules which contained atoms beyond the first two rows of the periodic table. The following years were a period where difficult problems could start to be addressed because it became possible to program in FORTRAN and computers became reliable and available. The problem of the evaluation of the two-electron four-center Gaussian integrals was solved [10, 11] and open- and closed-shell systems were studied using restricted and unrestricted methodologies [12, 13]. The basis function problem was handled through the introduction of contracted combinations of Gaussian functions [14–16]. Pople and coworkers announced their Gaussian program, which contained many of these ideas. By 1970, computational quantum chemistry as we know it today had been born. Most of the work in quantum chemistry over the next 20 years consisted in including that part of the energy which was missing from the Hartree–Fock calculations, namely the electron correlation energy [1]. Although a small contribution, it is nevertheless vitally important in molecular processes (The correlation contribution to the bond energy of the nitrogen molecule is 100 kcal mol^{-1}). Fundamental developments were represented by the configuration interaction method [8], the multiconfigurational self-consistent field approach [17], Møller–Plesset theory [18] and coupled cluster theory [19]. Combinations of these approaches such as the complete active space (CASSCF) and perturbational treatment (CASPT2) by Roos [20–22] are also widely used and applications of this approach will be presented here. All these methods have the valuable property that there is a "straightforward" route improvement. They produce the highest-quality results, but their downside is that they are all in principle much more expensive than SCF.

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An alternative route is represented by density functional theory (DFT) [23]. Baerends was working with DFT already in 1970s [24]. Ziegler et al. [25] were producing qualitative results for transition-metal complexes. The reason that people did not enter the DFT field earlier was probably that the molecules were overbound by this theory. The breakthrough came in 1988: Becke [26] in his first classical paper showed that the predictions were remarkably improved if the exchange-correlation functional went beyond the local-density approximation (LDA) and included some dependence on the gradient of the electron density. His second paper [27] told us how to evaluate accurately the matrix elements of these DFT functionals. Becke's results were impressive and Pople introduced Kohn–Sham DFT into GAUSSIAN. The attraction of DFT is its cost. In an elementary implementation it is not more costly than an Hartree–Fock calculation. Electron correlation effects are included through the functional, and not through the basis set. It is possible to use an orbital model, which all chemists like and programming is relatively simple. Not only does it give quality predictions for first- and second-row molecules, but it also often works well for transition metal and actinide complexes, at least when the wave function is dominated by a single configuration. Many calculations using the Amsterdam density functional code (ADF) and Turbomole[28] show the success of DFT. For all these reasons, computational chemistry became a DFT field and, by 1995, the sceptical quantum chemistry community was progressively moved into the DFT field.

With all these tools available, what can we use quantum chemistry for? It can be used in combination with experiment, to confirm or eventually refine experimental results. This use is also a way to benchmark methods against experiment. Computational quantum chemical methods can also be employed for the prediction of the existence of new species, which will eventually be made by experimentalists in a second stage. This use of computational quantum chemistry is especially important when one wants to consider systems, which are not easy to handle in a laboratory. We refer, for example, to explosive or radioactive species. It is clear that a good understanding of the chemistry of these species can be useful in a number of areas. Quantum chemistry can model molecular properties and transformations, and in combination with experiment, it can lead to an improved understanding of processes like, for example, nuclear waste extraction and storage procedures.

We have developed some experience over the years in *inventing* new molecules by quantum chemical methods, which in some cases have afterwards been studied by experimentalists. The general philosophy followed in the prediction of new molecules is based on the principle of *isoelectronic thinking*. One explores the periodic system and tries to understand the analogies between the behavior of different elements. It is known that for first row atoms chemical bonding usually follows the octet rule. In transition metals, this rule is replaced by the 18-electron rule. When going to lanthanides and actinides, the valence f shells play a role. In lanthanide chemistry the $4f$ shell is contracted and does not intervene into the bonding. In actinide chemistry, on the other hand, the $5f$ shell is more diffuse and participates actively in the bonding. How can we use this general chemical knowledge to predict new molecules?

In the following, we shall focus on four main areas of new molecules containing either transition metals or actinides. We shall start by discussing metal-polynitrogen species. In recent years some polynitrogen species like N_5^+ and N_5^- have been synthesized [29,30]. This has posed the challenge whether other stable polynitrogen species may exist and we have explored the possibility of metal centers binding to clusters of nitrogen atoms. We shall then describe some recent work on metal-polyhydride compounds, which are of considerable interest as potential hydrogen storage systems. Finally, we will focus on systems containing heavier atoms like gold and uranium. Gold compounds where gold behaves as a halogen will be described and the unique bond pattern in the U_2 molecule will be discussed.

For some of the species here discussed, we shall illustrate possible formation/dissociation reactions from/to the original elements and present energy balances, using enthalpies instead of free energies. In one case we will discuss also free energies (see the discussion about ScN_7 in Sect. 3). However, we do not think that using enthalpies instead of free energies will make much of a difference, because the synthesis of the compounds here described will not in any case be based on the original elements.

2 Methods

As already mentioned, when studying systems containing transition metals and/or actinides, one needs a method that describes properly electron correlation effects [1] as well as relativistic effects [2]. We do not believe in the use of a unique quantum chemistry method. Here we shall follow a pragmatic approach and, according to the nature of the problem under study, we chose what we believe to be the most appropriate method. The method has to be able to describe all the physics of the system at a reasonable cost.

The strategy is to perform single-configurational calculations in a preliminary step. This is usually done in a DFT framework, using in most cases the B3LYP exchange correlation functional [31]. If we verify that the system is a closed shell, we usually trust the DFT results. However, the wave function for many metal compounds has a multiconfigurational nature. The electronic structure of heavy atom compounds is characterized by a high density of electronic states. Near degeneracies between different electronic configurations and strong configurational mixing will often occur when chemical bonds are formed. A simple molecule like UO_2 has 25 electronic states below 2 eV, which split into 60 levels when spin-orbit coupling is added [32,33]. It is clear that such structures are not easily handled using a single configurational approach. In these cases multiconfigurational methods are used. The CASSCF method [34] is used to generate molecular orbitals and reference functions for subsequent multiconfigurational second order perturbation calculations of the dynamic correlation energy (CASPT2) [21,22,35]. The choice of the active space is crucial for the method. We will show examples of active space choices in the actinide Sect. 6.

Relativistic effect become important quite early in the periodic table. They have non-negligible effects on molecular properties already from the third row in the periodic system (larger than 0.01 Å for bond distances and 0.1 eV for bond energies). The importance of relativistic effects on molecular properties was shown even 30 years ago, primarily in the work of Pyykkö [2] and Roos et al. [2,36]. A large amount of work has since then performed by different research groups and today we know in detail the role of relativity in the properties of molecules in their ground state [37]. The effects of relativity on excited state properties and chemical reactions has also been investigated [38].

Here, relativity is included following two approaches. When we study the ground state of closed shell molecules in a DFT framework, relativistic effects are included by using effective core potentials (ECPs). The energy-adjusted ECPs of Küchle et al. derived from high accuracy calculations on the atom, are used for this purpose [39]. This approach allows to account for the scalar relativistic effects. It is reasonable to suppose that spin–orbit coupling will not affect the structure of the ground state of closed shell species.

When we perform multiconfigurational calculations, within the CASSCF/CASPT2 framework, we usually include both scalar relativistic effects and spin–orbit (SO) coupling. Relativistic all electron atomic basis sets of atomic natural orbital (ANO) type are used. The scalar relativistic effects are taken into account using the second-order Douglas–Kroll–Hess Hamiltonian. The scalar part of this Hamiltonian is used in the generation of the CASSCF wave function. SO coupling is then included by allowing the CASSCF wave functions to mix under the influence of the SO Hamiltonian. The method has been described in details in a recent article [38] and it has been used to study the actinide compounds. For the details of the basis sets, functionals and active spaces chosen in the various examples here presented, we refer to the original papers.

The quantum chemical calculations described here were performed using various quantum chemical packages. The DFT calculations were performed using the Gaussian98 and Turbomole software, while the CASSCF and CASPT2 calculations were performed using the MOLCAS-6.0 quantum chemical package [40].

3 Metal-polynitrogen compounds

The isolation of stable salts of the N_5^+ cation, the first new all-nitrogen species to be made in a century[29,30] has put the spotlight on the search for other stable polynitrogen species.

In recent years we have explored the idea that a nitrogen cluster may be stabilized by the presence of a metal atom and various metal polynitrogen compounds have been examined. First, we predicted the possible existence of the ScN_7 molecule (Fig. 1), which contains a new structural group, the η^7-N_7^{3-} 10-π-electron ring, isoelectronic with the experimentally known η^7-$(C_7H_7)^{3-}$ ligand, and has a relatively low energy of formation of 36 kcal/mol per N_2 unit, above an Sc atom and N_2 [41]. The energy of formation was estimated by using enthalpies. If one instead uses free energies, a value of ca 40 kcal/mol is obtained.

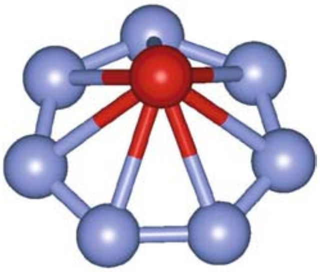

Fig. 1 The structure of the ScN_7 molecule. For the values of the bond distances and angles see Table 1

The idea behind this study is that a 10π system like N_7^{-3} has occupied σ, π and δ shells capable of donation to the metal. The interaction between the metal (M) and the polynitrogen cluster should thus stabilize the compound with respect to a all-nitrogen only molecule. Typical bond distances and angles for ScN_7, obtained at the B3LYP and MP2 level of theory, with split valence (6-31g*) and split valence plus polarization (6-31G($3df$, $3pd$)) basis sets are reported in Table 1.

This initial work has been followed by several studies by other groups. Some recent calculations on nitrogen-rich phosphorus nitrides compounds have been performed showing that species with the general formula $P(N_n)_m$ (n=3,4; m=1–4; with linear N_3, tetrahedral N_4, and square N_4) correspond to local energy minima[42]. Zhao and Li [43] have studied some MN_5^+ species (M=Be, Mg, Ca, Sr and Ba) and shown that these species are kinetically stable.

We have also considered the further complexation of a MN_7 moiety to a 6-π-electron, η^5-N_5^- pentazole ring [44]. This gives rise to sandwich compounds with the general formula N_5MN_7 (Fig. 2). We have investigated the compounds containing a Group 4 element, M=Ti, Zr, Hf. Along row 4, the species containing Sc, Ti, V, with a total charge of −1, 0, +1 respectively were also investigated. It turned out that the energies of formation of this class of molecules were comparable with the previous ScN_7 case, even at the high N-to-M ratio of 12. Furthermore, the M atom in these new species is

Table 1 Bond distances (Å) and angles (degrees) for ScN_7 (Fig. 1), calculated with various methods

	B3LYP/6-31G*	B3LYP/6-31+G(3df.3pd)	MP2/6-31G*
R_{Sc-N}	2.142	2.134	2.163
R_{N-N}	1.374	1.368	1.399
∠NScN	37.4	37.4	35.6
∠NNN	128.6	128.6	128.6

sterically shielded while that of ScN_7 was open (unless the ScN_7 compound would crystallize as chains). Typical bond distances and angles for the N_5MN_7 species, obtained at the B3LYP level of theory, using a split valence plus polarization basis sets, are reported in Table 2.

We have then studied some inverse sandwich compounds with general formula MN_7M', where M is an alkali metal (K,Rb,Cs), N_7 is a 10 π electron ring, and M′ is an alkaline earth metal (Ca, Sr, Ba) [45]. They turned out to be local minima. Among these systems, the CsN_7Ba molecule is the most stable of all and it presents a barrier of 35 kcal/mol to dissociation towards CsNBa and three N_2 molecules. CsNBa is stable and has a multiple nitrogen–barium bond [46].

The same stoichiometry of the N_5MN_7 molecules leads to a tetra-azide structure, $M(N_3)_4$, still binding 12 nitrogen atoms to 7 metal atom. Although azides are known for most groups of the Periodic table [47–49], the Group 4 ones seem to be so far unknown. Therefore their heats of formation and properties would be potentially interesting. If such molecules could be made and could turn out to have suitable stabilities and volatilities, they might be interesting precursor molecules in material science, in view of the need to deposit either the metal M or its nitrides MN and M_3N_4, when making electronic circuits. It should be noted that these MN_n compounds could in principle disintegrate to deposit the desired M, MN or M_3N_4, plus gaseous N_2. The metal nitrides TiN, ZrN, and HfN are also used as thin layers on high-speed cutting tools [50] and the proposed compounds might be a useful way of depositing the layer. Other applications for metal azides are also known.

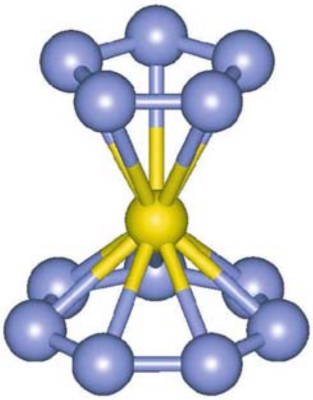

Fig. 2 The structure of the N_5TiN_7 molecule. The other N_5MN_7 molecules have a similar structure

Table 2 B3LYP bond lengths (Å) and angles (degrees) for the N_5MN_7 species (Fig. 2), with M=Ti, Zr, Hf, and Sc

	N_5TiN_7	N_5ZrN_7	N_5HfN_7	$N_5ScN_7^-$
$R_{M–N7}$	2.090 (2.109)	2.254	2.244 (2.228)	2.190
$R_{M–N5}$	2.342 (2.317)	2.540	2.520 (2.492)	2.573
$R_{N7–N7}$	1.370 (1.392)	1.375	1.378 (1.406)	1.370
$R_{N5–N5}$	1.344 (1.362)	1.342	1.342 (1.360)	1.337
$\angle_{N7MN7}$	38.3 (38.5)	35.5	35.8 (36.8)	36.5
$\angle_{N5MN5}$	33.4 (34.2)	30.6	30.9 (31.7)	30.1

MP2 values in parenthesis for N_5TiN_7 and N_5HfN_7. N5 is a nitrogen atom lying on the N_5 ring and N7 on the N_7 ring

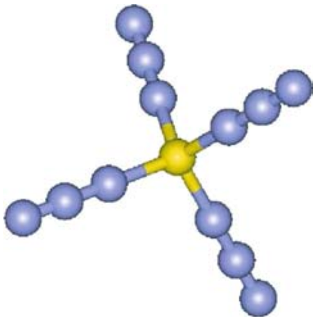

Fig. 3 The structure of the $M(N_3)_4$ molecules

We reported the results of a theoretical study of the metal tetra-azides $M(N_3)_4$, where M=Ti, Zr, Hf, Th [51]. The molecules turned out to be stable with all frequencies real and they present a unique feature, namely the M–N–N–N structure is linear, giving the tetra-azides a tetrahedral shape (see Fig. 3). All the azide species, characterized previously, have bent M–N–N–N angles. Previous to our work, the hexaazidosilicate (IV) ion had been synthesized and characterized [52]. The analogous hexa-azidostannate (IV) was made much earlier [53]. Diazides of certain Group-4 metals were already known. The crystal structure of bis (η^5-cyclopentadienyl) titanium diazide has been determined [54]. The M–N distance is 2.03(1) Å and the M–NNN angle is bent. No earlier information has been found for the present tetra-azides. Typical bond distances and angles for the $M(N_3)_4$, obtained at the B3LYP level of theory, using a split valence plus polarization basis sets, are reported in Table 3.

Based on our prediction, the group of Christe has recently synthesized, isolated and characterized the first binary group 4 azide species $Ti(N_3)_4$, $Ti(N_3)_5^-$ and $Ti(N_3)_6^{2-}$ and provided explanations for the observed and predicted Ti–N–NN bond angles [55]. They have also synthesized and characterized the first binary group 6 azides, $Mo(N_3)_6$, $W(N_3)_6$, $Mo(N_3)_7^-$ and $W(N_3)_7^-$ [56].

4 Metal hydrides

Metal hydrides are of considerable interest as potential hydrogen storage systems [57]. A design target of 6.5 weight (wt) % has been regarded as adequate. Species of MH_n type, with n=9 occurring in ReH_9^{2-} were known. The literature on M–H and M–H_2 bonds has been reviewed by Kubas [58] and Maseras et al. [59]. We have recently predicted the existence of MH_{12} molecules, where M is a group 6 atom, Cr, Mo, and W [60]. The isoelectronic ions VH_{12}^-, TiH_{12}^{2-}, and MnH_{12}^+ also turned out to be stable. In a hypothetical solid $Li(VH_{12})$, the wt percentage would be 17.

Our starting point was the the Au/H analogy [61,62] and the recent discovery of the icosahedral, 18-valence-electron species WAu_{12} [63]. Its hydrogen analogues turned our to

Table 3 Bond lengths (Å) and angles (degrees) for the $M(N_3)_4$ species, with M=Ti, Zr, Hf, Th

	$Ti(N_3)_4$	$Zr(N_3)_4$	$Hf(N_3)_4$	$Th(N_3)_4$
$R_{M\text{-}N1}$	1.879	2.030	2.023	2.259
$R_{N1\text{-}N2}$	1.203	1.204	1.204	1.219
$R_{N2\text{-}N3}$	1.135	1.131	1.131	1.143

In free N_3^-: N–N=1.18 Å
All structures are tetrahedral (Figure 3)

Table 4 B3LYP bond distances (Å) for the MH_{12} species

	CrH_{12}	MoH_{12}	WH_{12}	TiH_{12}^{2-}	VH_{12}^-	MnH_{12}^{2+}
M-H1(σ)		1.713	1.738	1.877	1.686	
M-H2(H_2)	1.707 1.713	1.853	1.861	1.898	1.760	1.756 1.761
H-H(H_2)	0.841	0.828	0.838	0.825	0.838	0.791

H–H is the distance in the H_2 moiety. M–H1(σ) is the distance between M and a nonbound H atom. M–H2(H_2) is the distance between M and H forming a H_2 molecule (See Figs. 4 and 5)

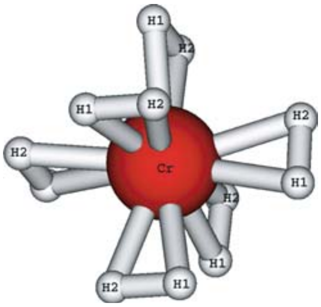

Fig. 4 The structure of the CrH_{12} molecule

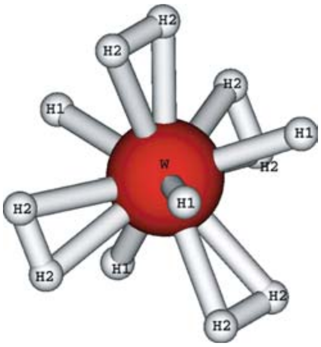

Fig. 5 The structure of the WH_{12} molecule. The MoH_{12} molecule has a similar structure

exist as stable minima and have either a mixture of M–H and M(η_2-H_2) bonds or only dihydrogen bonds. All species were studied using DFT. Single point energy CASPT2 calculations were performed at the DFT optimized geometries in order to investigate the electronic structure of these species. They all turned out to be singlet closed shell in their ground state, with the first triplet well separated from the ground state (60 kcal/mol above in the CrH_{12} case).

The CrH_{12} species has D_3 symmetry with six H_2 moieties (Fig. 4), while MoH_{12} and WH_{12} have D_{2d} symmetry, with four H_2 moieties and four M–H σ bonds (Fig. 5). The H–H distance in the H_2 moieties is larger than 0.8 Å in all species, while a calculation on isolated H_2 gives a H–H bond distance of 0.74 Å. These values for the H-H bond distances can be considered a fingerprint of the fact that the H_2 moieties are really bound to the central metal. The typical B3LYP bond distances are reported in Table 4.

To investigate the stability and chance of formation of these species, we considered the formation/dissociation reaction for the various species: $6H_2+M \rightarrow MH_{12}$. This reaction is 15.8 kcal/mol endothermic for CrH_{12}, while it is 55.0 and 89.0 kcal/mol exothermic for MoH_{12} and WH_{12}, respectively (including the zero-point energy correction). We also compared the stability of different clusters by considering the $3H_2+MH_6 \rightarrow MH_{12}$ and $4H_2+MH_4 \rightarrow MH_{12}$ reactions. The H_{12} clusters are in all cases lower in energy than the corresponding MH_6 and MH_4 analogues.

This study suggested that the number of hydrogen atoms, bound to a metal atom, could be increased from the previously known n=9 to n=12. The four side-on bonded H_2 units can be detached more easily than the remaining four classical M-H hydrides. The neutral molecules could be observed spectroscopically in solid hydrogen matrices. The ionic species could form crystalline compounds.

We are currently investigating the existence of MH_n species with n larger than 12. Preliminary results indicate that species with 14 and 15 hydrogen atoms like TiH_{14} and ScH_{15} may also be stable as single molecules. It also seems possible that these species could be further stabilized if made inside a fullerene cage [64].

5 Gold as a halogen

Gold is an element whose unique properties are strongly influenced by relativistic effects. Stable gold clusters are the subject of both experimental and theoretical studies, because of their potential use as building blocks of new materials and catalytic properties [63,65,67]. A large number of calculations has been performed on various gold compounds, which have been described in details in two recent reviews by Pyykkö [68,69]. We have predicted the existence of metal tetra-auride molecules, MAu_4, where M=Ti, Zr, Hf, Th, and U [61]. In these species, gold carries a formal charge of (−1) and acts as a ligand to the metallic center. The molecules are tetrahedral. Only a few gold (−1) compounds were known in bulk and in the gas phase before this study. Cesium auride in bulk was discussed in a mini-review by Pyykkö [70]. Goodman [71] mentioned other auride species like RbAu. The idea of gold forming tetrahedral compounds was totally unexplored. Quantum chemical calculations using DFT and CASPT2 showed that these molecules are stable, with all real frequencies and some covalent bond character. The clusters are stable with respect to dissociation to M and two Au_2 molecules and also to M and Au_4. All species are closed shell in their ground state, with the exception of UAu_4 which has a triplet ground state, in analogy with the uranium tetrahalide series. From the bond length point of view, the U–Au bond, 2.75 Å, is in between the U–Br bond, 2.68 Å, in UBr_4 and the U–I bond, 2.90 Å, in UI_4 The energy required to break a U–Au bond in UAu_4 is ca 37 kcal/mol (calculated as the energy difference between UAu_4 and U + 4 Au atoms and divided by four). In UBr_4 and UI_4, the energy required to break a U–Br and U–I bond is 74 and 63 kcal/mol, respectively.

A successive study [62] of some MAu_6 molecules, where M=Cr, Mo, W has shown that the hexagold compounds have a structure analogous to the corresponding MH_6 compounds (Fig. 6), while they differ from the MX_6 compounds, where X is a halogen. A transition from a halogenolike, in the MAu_4 compounds, to a hydrogenolike behavior, in the MAu_6 compounds, has thus been suggested. In Table 5, some typical M–Au bond distances are reported.

The dimers $(MAu_4)2$, M=Ti,Zr have been recently proposed theoretically by Ghanty *et al.* [72]. They have a strongly distorted structure from a pair of tetrahedra. These systems are a real challenge for quantum chemistry because the aurophilic interactions [65] require treatment of dispersion type effects, thus precluding DFT. Moreover, the presence of ten metal atoms introduces large dynamic correlation effects. It would be desirable to run Coupled Cluster calculations, but this is not currently feasible.

Wang and Coworkers [73] has produced the aurosilane $SiAu_4$ after the theoretical prediction of the MAu_4 species, and has now shown experimentally using photoelectron spectroscopy, that Si_2Au_n (n=2,4) and its anion resemble the hydrogen analogs [74].

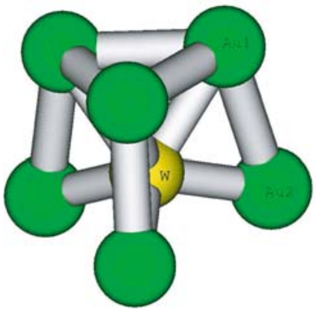

Fig. 6 The structure of the WAu_6 molecule. The Cr and Mo molecules have a similar structure

Table 5 B3LYP bond distances (Å) for the MAu_6 species (See Fig. 6)

	$Cr(Au)_6$	$Mo(Au)_6$	$W(Au)_6$
M–Au1	2.79	2.75	2.67
M–Au2	2.58	2.56	2.54
Au1–Au1	2.77	2.86	2.98
Au2–Au2	4.44	4.34	4.13
Au1–Au2	2.71	2.85	2.99

6 A quintuple bond in the U_2 molecule

The study of actinide chemistry poses a formidable theoretical challenge. The large number of electrons, open f- and d-shells, and strong relativistic effects must be taken into account. Development of the necessary theoretical tools is hampered by the fact that there are few spectroscopic observations for actinide compounds that are suitable for direct comparison with properties calculated for isolated molecules. Ideally gas phase data are required for such comparisons.

We have studied a series of actinide compounds over the years and compared our theoretical predictions with available experimental information. Specifically, we have determined ground state properties and electronic spectra of uranium oxides, UO_2 [32,33] and UO [75], uranium triatomic compounds with the general formula XUY, where X,Y=C,N,O, and U is the uranium atom [76–78] and thorium tetrahalides [79]. We have also studied the coordination of actinyl ions in the presence of counterions in water, like, for example, tricarbonatodioxouranate [80] and the neptunyl ion with carbonate ions [81].

We have recently asked ourselves how two uranium atoms would react when placed together and decided to study the U_2 molecule. The result is a complex and unconventional chemical bond. We shall discuss in the following the outcome of this study [82,83]. The uranium atom with atomic number 92 has six valence electrons in the ground state electronic configuration $(5f)^3(6d)^1(7s)^2$. Four of these electrons are unpaired, giving rise to a quintet ground state. It does not cost much energy to unpair also the $7s$ electrons by forming hybrids with, for example, 6d or 7p orbitals. Thus uranium has in principle six electrons available for chemical bonding. How are these electrons used to form a bond to another uranium atom?

Covalent bonding is commonly described by Lewis's theory [84], with an electron pair shared between two atoms constituting one full bond. Beginning with the valence bond description for the hydrogen molecule, quantum chemists have further explored the fundamental nature of the chemical bond for atoms, throughout the periodic table, confirming that most molecules are indeed held together by one electron pair for each bond. More complex binding may occur when large numbers of atomic orbitals can participate in bond formation. Such behavior is common with transition metals [85]. In the chromium molecule, Cr_2, for example, where the six valence electrons residing in the $3d$ and $4s$ orbitals, all are involved in the bonding to another chromium atom. There is exactly one valence electron per valence orbital.

When involving heavy actinide elements, metal–metal bonds might prove particularly complicated. To date evidence for actinide–actinide bonds is restricted to the matrix-isolation of uranium hydrides, including H_2UUH_2 [86] and the gas phase detection [87] and a preliminary theoretical study [88] of the uranium molecule U_2. We have performed quantum chemical calculations on U_2 showing that, although the strength of the U_2 bond is comparable to that of other multiple bonds between transition metals, the bonding pattern is

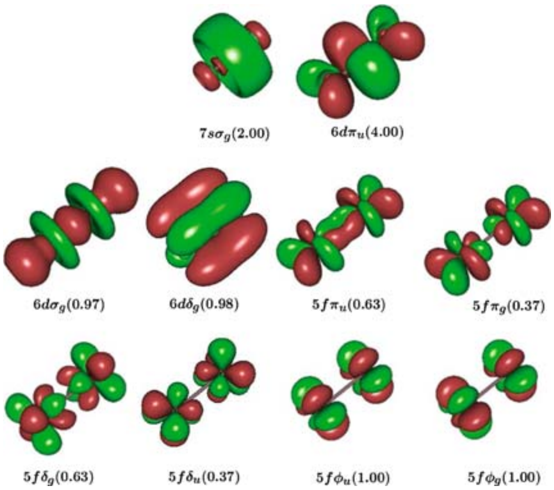

Fig. 7 The molecular orbitals forming the chemical bond between two uranium atoms in the U_2 molecule. The orbital label is given below each orbital, together with the number of electrons occupying this orbital or pair of orbitals in case of degeneracy

unique. The molecule contains three electron-pair bonds and four one-electron bonds, that is 10 bonding electrons, corresponding to a quintuple bond, and two ferromagnetically coupled electrons localized on one U atom each. All known covalent bonding types are contributing. The concept of multiple bonding which is well known among transition metals (see for the work of Cotton on the $Re_2Cl_8^{2-}$ species [89]) has here been extended to the case of two actinide atoms.

We shall give in this section an example of how the active space has been chosen. Trial studies including different sets of valence orbitals in the active space showed that three normal electron-pair bonds are formed by hybrid atomic orbitals dominated by $7s$ and $6d$. Double occupation of these three orbitals was thus enforced in subsequent calculations. The remaining six valence electrons were then allowed to occupy the remaining $5f$ and $6d$ orbitals while searching for the occupation resulting in the lowest energy. The most stable electronic state was found to be a septet state and to have a total orbital angular momentum equal to 11 atomic units.

The molecular orbitals involved in forming U_2 are reported in Fig. 7 together with the occupation number of each orbital (or pair of orbitals). The lowest-energy doubly occupied orbital is of $7s\sigma_g$ type, corresponding to a typical σ bond. The other two doubly occupied orbitals are degenerate, of covalent π-type and result from the combination of a $6d$ and $5f$ atomic orbitals ($6d\pi_u$ in the figure). Two singly occupied orbitals, of σ-type ($6d\sigma_g$) and δ type ($6d\delta_g$), respectively, give rise to one-electron bonds between the two atoms. Two further singly occupied orbitals, of δ-type ($5f\delta_g$) and π-type ($5f\pi_u$), respectively, give rise to two additional, but weak, one-electron bonds. Finally, two electrons occupy two fully localized $5f\phi$ orbitals. The calculation shows that U_2 has three strong normal electron-pair bonds, two fully developed one-electron bonds, two weak one-electron bonds, and two localized electrons. The singly occupied $5f\phi$ orbitals add up to one $5f$ orbital on each atom with the electron spins parallel. In such a situation, the two electrons usually couple such that the total spin becomes zero, because the antiferromagnetic coupling provides some additional bonding, even if small. In U_2, however, all electrons are predicted to have parallel spin, resulting in a total spin angular momentum of 3, a septet state. This unusual characteristic can be attributed to exchange stabilization: if all open-shell electrons have the same spin, the interaction between the non-bonding $5f$ electrons and the two one-electron bonds is energetically more favourbale than the antiferromagnetic coupling of the $5f$ electrons.

The U_2 chemical bond is thus more complex than any other known diatomic bond, with summation of the bonding electrons suggesting a quintuple bond. Its multi-radical nature may support chemical bonds to a variety of ligands. So far the OU_2O [87] and $H_2U_2H_2$ [86] molecules have been detected. We are currently investigating the possible existence of $Cl_3U_2Cl_3$ and $Cl_4U_2Cl_4^{2-}$ and a number of diuranium carboxylates [90].

7 Conclusions

The purpose of this paper was to highlight how modern quantum chemistry can be used to perform accurate investigations of unconventional molecular systems. The study of transition metal- and actinide chemistry poses a considerable theoretical challenge. The large number of electrons, open f- and d-shells, and strong relativistic effects must be taken into account. The necessary theoretical tools are now available and we have here illustrated how it is possible to describe the electronic structure of molecular systems containing all atoms in the periodic table. Such studies may precede experimental work leading to the prediction of new molecular species or new types of chemical bonding.

Novel metal-polynitrogen species, which may be potential high-energy density materials, have been predicted, together with metal-polyhydride compounds, which are of considerable interest as potential hydrogen storage systems. Species containing heavier atoms like gold and uranium have also been studied and this has lead to the discovery of the unique multiple bond in the U_2 molecule.

We ask ourselves if, by explaining the electronic structure among the heaviest atoms, the actinides, we have reached the end of the road. We would rather think, that we have opened a new road, which will possibly lead to the study of actinide multiple bonding in solution. The field is now mature for applications, and quantum chemists with a good chemical knowledge and intuition may take up new challenges.

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