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Review

DFT Investigations of the Magnetic Properties of Actinide Complexes

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Abstract: Over the past 25 years, magnetic actinide complexes have been the object of considerable attention, not only at the experimental level, but also at the theoretical one. Such systems are of great interest, owing to the well-known larger spin–orbit coupling for actinide ions, and could exhibit slow relaxation of the magnetization, arising from a large anisotropy barrier, and magnetic hysteresis of purely molecular origin below a given blocking temperature. Furthermore, more diffuse 5f orbitals than lanthanide 4f ones (more covalency) could lead to stronger magnetic super-exchange. On the other hand, the extraordinary experimental challenges of actinide complexes chemistry, because of their rarity and toxicity, afford computational chemistry a particularly valuable role. However, for such a purpose, the use of a multiconfigurational post-Hartree-Fock approach is required, but such an approach is computationally demanding for polymetallic systems—notably for actinide ones—and usually simplified models are considered instead of the actual systems. Thus, Density Functional Theory (DFT) appears as an alternative tool to compute magnetic exchange coupling and to explore the electronic structure and magnetic properties of actinide-containing molecules, especially when the considered systems are very large. In this paper, relevant achievements regarding DFT investigations of the magnetic properties of actinide complexes are surveyed, with particular emphasis on some representative examples that illustrate the subject, including actinides in Single Molecular Magnets (SMMs) and systems featuring metal-metal super-exchange coupling interactions. Examples are drawn from studies that are either entirely computational or are combined experimental/computational investigations in which the latter play a significant role.

Keywords: actinides; uranium complexes; magnetochemistry; Super-exchange; SMM; DFT

1. Introduction

During recent decades, the magnetochemistry of actinide complexes has gained an important impetus, not only at the experimental level, but also at the theoretical one [1–8]. Indeed, since the first observation early in the 1990s of the antiferromagnetic (AF) coupling between uranium(V) centers in the para-imido [(MeC₅H₄)₃U]₂(μ-1,4-N₂C₆H₄) complex by Rosen et al. [9], this class of binuclear actinide systems has been arousing interest [10–52]. Moreover, the discovery in 2009 of the slow magnetic relaxation for the mononuclear complex U(Ph₂BPz₂)₃ [53], which is a signature of a single-molecule magnet (SMM) behavior, has motivated more research, even though lanthanide SMMs have been described in the literature for a longer time [54,55]. A growing number of uranium-containing systems [56–69]—mononuclear as well as binuclear species—have been

synthesized to develop SMMs; the results have been the subject of recent reviews [70–75]. Such systems are of great interest, owing to the well-known larger spin–orbit coupling for actinide than for lanthanide ions [72], and the more diffuse 5f orbitals (5f covalency) [63,76–78] than the lanthanide 4f ones, which could lead to strong magnetic super-exchange [53]. Therefore, these unique features of actinides relatively to transition metals and lanthanides open the way to the design of new actinide-based SMMs with high blocking temperatures [71,72,75]. Moreover, over the last twenty years, much effort has been devoted to investigating the magnetic properties of actinide complexes by quantum chemical methods [62–65,67,70–76,79–81]. Indeed, investigating the electronic structure of actinide complexes is essential to understanding their magnetic behavior [1,2,71–73]. However, for such a purpose, the use of a multiconfigurational post-Hartree-Fock approach is required, as stated by several authors [63,64,82,83], but such an approach is computationally demanding (vide infra) for polymetallic systems, notably for actinide ones, and usually simplified models are computed instead of the actual systems [63,64]. Thus, Density Functional Theory (DFT) appears as an alternative tool to compute magnetic exchange coupling and to explore the electronic structure and magnetic properties of actinide-containing molecules, especially when the considered systems are very large [6,8,21,37,60,79,80,84,85]. Indeed, DFT emerged in the early 2000s as a powerful technique, particularly when used in combination with the hybrid B3LYP functional [86,87] and the Broken-Symmetry (BS) Noodleman’s approach [88,89], for satisfactory simulations of magnetic properties. This is true not only in the case of d-transition metal systems [82,83,90–104], but also for actinide-containing molecules [105–107]. It is worth noting that actinide-based SMMs are multiconfigurational systems, and the use of the monodeterminantal approach with DFT is a subject of debate [63,108–110].

We present here a review of relevant achievements regarding DFT investigations of the magnetic properties of actinide complexes. This review will also deal with representative examples that illustrate the subject, including actinides in SMMs and systems featuring metal-metal exchange coupling interactions. We focus on studies that are either entirely computational or are combined experimental/computational investigations in which the latter play a significant role.

2. Survey of Molecules Potentially Exhibiting Magnetic Behavior

2.1. Magnetic Coupling Interactions

Actinide complexes exhibiting magnetic exchange properties are rarely mentioned in the literature [1,2], relatively to the rich d-transition metal magnetochemistry. Most documented cases involve diuranium(V) systems [8,23–27,37,49–51,106,111–116], and only a few studies of magnetic coupling in diuranium(III) and (IV) complexes or mixed uranium(IV)–transition metal have been reported [46,52,105,107,117–122]. Among them, remarkable examples of unusual U(V)–U(V) coupling involving a pentavalent bis(imido) uranium dimer [106] and within diuranium(V) dioxo diamond cores [46,49,114–116,123–126] have been reported, which can exhibit Néel temperatures of up to 70 and even 110 K [23,24,27,114,115,127].

Magnetic coupling constants J were estimated in the 1990s for U^V/U^V dinuclear complexes such as the AF $[(MeC_5H_4)_3U]_2(\mu-1,4-N_2C_6H_4)$ species ($J = -19 \text{ cm}^{-1}$) [1,2,9], and later for ferromagnetic U^{IV}/U^{IV} coupling in U_2Co pyrazolate (cyclam)Co $[(\mu-Cl)U(Me_2Pz)_4]_2$ system ($15 \text{ cm}^{-1} \geq J \geq 48 \text{ cm}^{-1}$) [21] and in the arene-bridged uranium(IV) complex $U[HC(SiMe_2Ar)_2(SiMe_2-\mu-N)](\mu-Ar)U(Ts^{Xy})$ ($J = 20 \text{ cm}^{-1}$) [38]. As expected for the more ionic uranium(IV) species, reports of U^{IV}/U^{IV} couplings are rather scarce, being limited to few examples [33,105,107,122,128] discussing couplings which are mediated by either chalcogen bridges or aromatic spacers. Moreover, examples of uranium(IV)–copper(II) and uranium(IV)–nickel(II) couplings have been reported [43–45,117,118]. It is noteworthy that a successful strategy to promote interactions between paramagnetic actinide ions has been the use of covalently-linked bridging ligands [1,2]. Thus, a great variety of spacer ligands bearing two functionalized actinide centers have been tested, showing significant metal-metal communication

and magnetic interaction. For example, the linear bis(imido) (imido = 1,4-diimidobenzene) covalent linkage was the first one used in the diuranium(V) *para*- and *meta*-bridged complexes (Figure 1) [9].

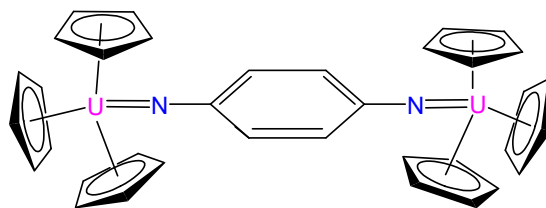


Figure 1. The diuranium(V) imido complex which exhibits AF U...U coupling [9].

More recently, reports of Kiplinger's group [106,112,128] on ketimide actinide-containing assemblies, indicated that the 1,4-phenylenediketimide ligand could lead to diverse and interesting magnetic behavior. In their study, bis(ketimide) $[(C_5Me_4Et)_2(Cl)An]_2(\mu\{-N=CMe-(C_6H_4)-MeC=N\})$ binuclear An^{IV}/An^{IV} (Th, U) complexes⁶² were synthesized (Figure 2). The authors reported that, although evidence for magnetic coupling between metal centers in the bimetallic U^{IV}/U^{IV} ($5f^2-5f^2$) complex is ambiguous, the complex displays appreciable electronic communication between the metal centers through the π system of the dianionic bis(ketimide) dianionic bridging ligand [128].

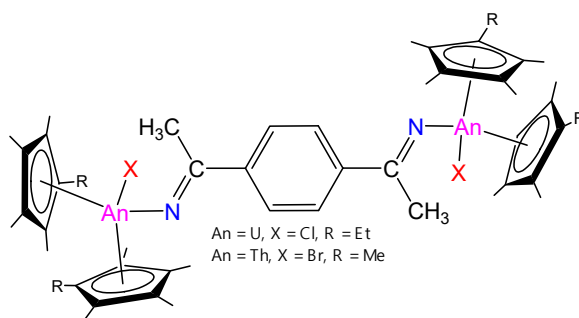


Figure 2. Structure of the bis(ketimide)-bridged $[(C_5Me_4Et)_2(Cl)An]_2(\mu\{-N=CMe-(C_6H_4)-MeC=N\})$ binuclear An^{IV}/An^{IV} (Th, U) complexes (ketimide = 1,4-phenylenediketimide) [128].

Another kind of bridging-spacer system includes inverted-sandwich systems, which contain two uranium atoms bridged by a cyclic aromatic hydrocarbon ligand e.g., benzene, toluene (Figure 3) [9], cycloheptatrienyl ($\eta^7-C_7H_7$) or naphthalene and cyclooctatetraene ($\eta^8-C_8H_8$), as recently reviewed [127]. Indeed, Cummins and Coll. [10] reported in the 2000s the X-ray structure of the first inverted-sandwich structures of different arene spacers, namely the $(\mu\text{-}\eta^6:\eta^6\text{-}C_7H_8)[U(N[R]Ar)_2]_2$ complex ($R = C(CH_3)_3$, $Ar = 3,5\text{-}C_6H_3Me_2$) (Figure 3), in which a toluene molecule bridges two uranium bis-amido fragments in a symmetrical $\eta^6:\eta^6$ mode, involving covalent delta bonds. These aromatic ligands, which could exhibit rich redox chemistry for a range of reducible substrates, have been proposed to promote intra-molecular electronic and magnetic communications between uranium centers [65]. This class of inverted-sandwich structures was enriched in 2011 by the first arene-bridged diuranium(III) $[U\text{-}(BIPM^{TMS}H)(I)]_2(\mu\text{-}\eta^6:\eta^6\text{-}C_6H_5Me)$ system exhibiting SMM behavior [60].

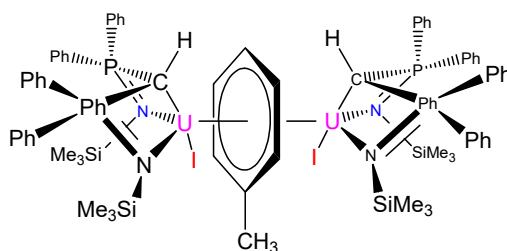


Figure 3. Structure of the arene-bridged uranium(III) $[U\text{-}(BIPM^{TMS}H)(I)]_2(\mu\text{-}\eta^6:\eta^6\text{-}C_6H_5Me)$ SMM [60].

The formulation of the metal oxidation state in this species could either be uranium(II)/neutral arene, uranium(III)/dianionic arene, or uranium(IV)/tetraanionic arene, but spectroscopic characterization and theoretical computations favor uranium(III)/dianionic arene formulation [127]. Cummins and Coll. [11] have extended this inverted-sandwich series of complexes to the naphthalene-bridged $M_2(\mu-\eta^6, \eta^6-C_{10}H_8)[U(NC[{}^tBu]Mes)_3]_2$ ($M = K, Na$; $Mes = 2,4,6-C_6H_2Me_3$) and its cyclooctatetraene ($\mu-\eta^8, \eta^8-C_8H_8$) $U_2(NC[{}^tBu]Mes)_6$ congener. As reported by these authors, the performed DFT computations on the $[(\mu-\eta^8, \eta^8-C_{10}H_8)U_2(NCH_2)_6]^{2-}$ and $(\mu-\eta^8, \eta^8-C_8H_8)U_2(NCH_2)_6$ models in their quintet state ($S = 2$) are consistent with the tetravalent U^{IV} ($5f^2$) oxidation state of the metal centers [11]. The C–C bond lengths of the bridging arene were found to be slightly lengthened compared to those of free toluene, and with the help of theoretical calculations, suggested δ -back-bonding between uranium and the arene ring. In 2004, William J. Evans and Coll. [19] reported the structure, reactivity and DFT analysis of the two arene-bridged diuranium $[(Mes({}^tBu)N)_2U]_2(\mu-\eta^6, \eta^6-C_7H_8)$ and $[(\eta^5-C_5Me_5)_2U]_2(\mu-\eta^6, \eta^6-C_6H_6)$ systems. The latter species was described as two U(III) covalently bonded metals to the arene ligand via δ 'symmetry bonding molecular orbital (MO). Ephritikhine and Coll. [119,120] had previously reported a unique bridged-cycloheptatrienyl diuranium $[U(BH_4)_2(OC_4H_8)_5][(\mu-\eta^7, \eta^7-C_7H_7)[U(BH_4)_3]_2]^-$ anionic complex. It was suggested that the $(C_7H_7)^{3-}$ ring should be described as an aromatic planar group and the metals as U^{IV} ions, with four highest δ 'symmetry bonding MOs. Such covalently bridged systems by δ -bonding should promote $U \cdots U$ electronic and magnetic communications [1,2,35–38,60,65,72,73]. Although to our knowledge no systematic theoretical studies have been reported on the magnetic behavior of the latter complexes, it seems likely that δ -bonding, which dominates the bonding in the inverse sandwich unit, could favor metal-metal exchange coupling as stated by recent reports evidencing arene-bridged diuranium SMM behavior [60,72,73]. Indeed, in their continual efforts to develop new synthetic routes to magnetic actinide systems, S.T. Liddle's group recently (2017) extended their investigations to crystal field and magnetic interactions in diuranium $[U(Tren^{TIPS})]_2(\mu-E)$ ($E = S, Se, Te$) bridged-chalcogenide complexes with $U^{IV}-E-U^{IV}$ cores (Figure 4) [37], which exhibit linearly U–E–U linked cores.

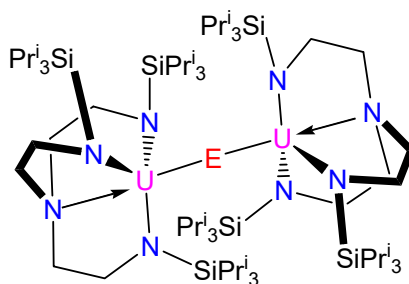


Figure 4. Structure of the diuranium $U^{IV}/U^{IV} [U(Tren^{TIPS})]_2(\mu-E)$ ($E = S, Se, Te$) bridged-chalcogenide systems [37].

Plots of the magnetic susceptibility vs. temperature of these linkages present shoulders that could be interpreted as evidence of uranium–uranium magnetic exchange. However, a detailed study using CASSCF computations of their electronic structures revealed that the magnetic properties of these systems can be simply correlated to single-ion crystal field (CF) effects which vary as the nature of the chalcogen varies.

As reviewed recently [71,72], a successful route to super-exchange effects in actinide-containing multinuclear species is through cation–cation interactions (CCI) [23–33,46–51,59,61,69,114–116,123], mostly between uranyl(V) UO_2^+ of actinyl units. This linkage forms an oxo-bridge between metal centers affording a great number of oxo-bridged systems exhibiting significant coupling between U^V centers [27,49], mixed U^V /transition metal [28–32,111] or lanthanide centers [47,112,123], with the largest actinide-based multinuclear complex affording the unique structure of a wheel-shaped cluster $\{[UO_2(salen)]_2Mn(Py)_3\}_6$ ($Py = pyridine$) which is assembled through UO_2^+ and Mn^{II} interactions [29].

Additionally, CCIs were observed between $\text{Np}^{\text{IV}}/\text{Np}^{\text{V}}$ ions in neptunyl complexes [75]. Beside the great number of synthesized CCI systems, few theoretical studies of their magnetic properties have been carried out [1–4,7,8,37,60,63,64,71,72,80,81].

2.2. SMM Behavior

The first actinide system found to display slow magnetic relaxation was the mononuclear uranium(III) $[\text{U}\{\text{Ph}_2\text{B}(\text{N}_2\text{C}_3\text{H}_3)_2\}_3]$ complex exhibiting clear SMM behavior (Figure 5) [53]. Since then, a wide range of SMMs based on uranium(III, V) have been reported [56–59,62,127,129–131], which are mainly supported by pyrazolylborate ligands as reviewed recently [69–72,127].

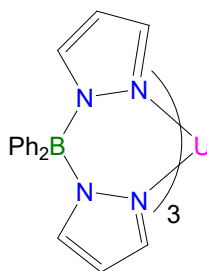


Figure 5. Structure of the uranium(III) $[\text{U}\{\text{Ph}_2\text{B}(\text{N}_2\text{C}_3\text{H}_3)_2\}_3]$ SMM [127].

In 2012, the uranium SMM chemistry was extended to the pentavalent species of U(V) ions, with the report of the nanostructure wheel-shaped $[\{(\text{UO}_2[(\text{CH}_2\text{NCHC}_6\text{H}_4\text{-2-O})_2])_2(\text{Mn}[\text{Py}]_3)\}_6]$ complex [61]. As reported, significant magnetic interactions between the uranyl(V) and manganese(II) ions were studied by susceptibility measurements. In 2013, the synthesis of a terminal uranium(V) mono-oxo complex $\text{U}(\text{Tren}^{\text{TIPS}})(=\text{O})$ (Figure 6) supported by the sterically demanding ligand $\text{N}(\text{CH}_2\text{CH}_2\text{NSiPr}_3)_3$ ($\text{Tren}^{\text{TIPS}}$) ligand was reported by S.T. Liddle and Coll., [127] revealing the first example of an uranium(V) monometallic SMM.

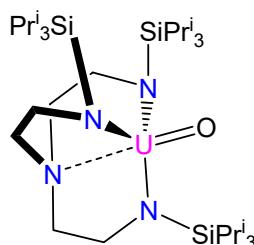


Figure 6. The mononuclear uranium(V) $\text{U}(\text{Tren}^{\text{TIPS}})(=\text{O})$ SMM [127].

3. DFT Investigations of Actinide Complexes Magnetism

3.1. Theoretical Approaches for Computing Exchange Coupling Constants

Magnetic properties of species bearing unpaired electrons are driven by the manifold of states of different spin multiplicities they exhibit, especially if the latter energies are close [82,83]. The calculation of magnetic properties of molecular systems, which necessitates a high accuracy of the computed energies, needs to properly take into account both static and dynamic electron correlation. Static correlation is generally well described by multiconfigurational (MC) treatments like CASSCF, whereas dynamical correlation can be recovered with MR-CI techniques or by perturbation using CASPT2 technique, for instance [132–139]. However, CASSCF computations are drastically limited by the size of the active space, so that such high-level computations can only be applied to relatively small molecules or models [82]. DFT could offer the opportunity to estimate the magnetic properties of large systems at a low computational cost [80–83,90]. The exact wavefunctions which are eigenfunctions of the square spin operator \hat{S}^2 with eigenvalues $S(S + 1)$ can be written as expansion of Slater determinants each

of them being eigenfunction of the spin component \hat{S}_z [83]. Such exact descriptions of the electronic states of a molecule cannot be obtained using DFT, which is a ground state and single determinant theory; therefore, the exact determination of the electronic states energies cannot be obtained.

Regarding magnetic exchange, the used spin Hamiltonian is the Heisenberg–Dirac–van Vleck (HDvV) one, $\hat{H} = -\sum J_{ij} \hat{S}_i \cdot \hat{S}_j$ where \hat{S}_i, \hat{S}_j are the spin operators associated to the magnetic centers i, j and J_{ij} the coupling constants between these centers [82,83,90,91].

Experimentally, the coupling constants J_{ij} are derived from the magnetic susceptibility measurements by fitting the experimental curve. This approach was successfully used by Rinehart and Coll.¹ to model the susceptibility of the diuranium(V) bis(imido)-bridged complex. As shown in Figure 7, the best fit of the susceptibility's curve provides an exchange constant of $J = -19 \text{ cm}^{-1}$ [1,2].

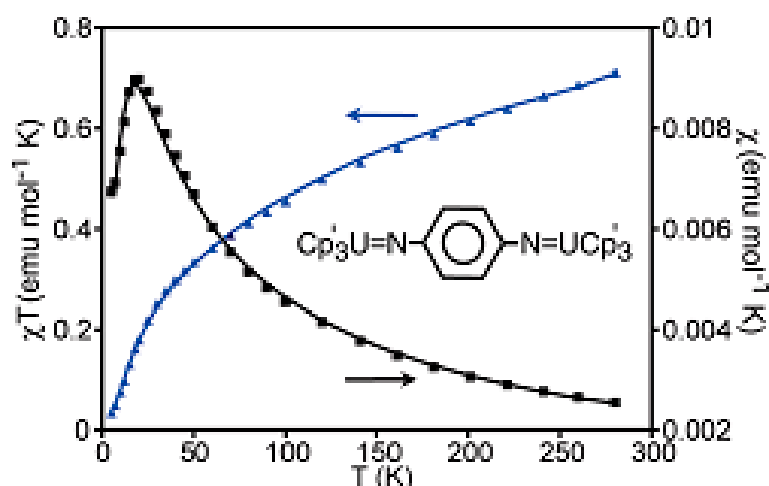


Figure 7. Temperature-dependent magnetic susceptibility χ (black symbols) of $[(\text{MeCp})_3\text{U}]_2$ (μ -1,4- $\text{C}_6\text{H}_4\text{N}_2$) and fits (lines) and the magnetic molar χT versus T (blue) of the magnetically isolated analog $[(\text{MeCp})_3\text{U}]_2$ (μ -1,3- $\text{C}_6\text{H}_4\text{N}_2$). Susceptibility data (reprinted with permission from [2], American Chemical Society, 2010).

Estimating the coupling constant using DFT is made possible using the Broken Symmetry (BS) approach proposed first by Noodleman et al. [88,89], which have been nicely reviewed by Bencini [82] and Neese [83]. In the case of a dinuclear system, it consists of evaluating the magnetic coupling constant J_{ij} from the energy difference between two main configurations, i.e., the high-spin state (HS) of spin $S_{\text{max}} = 1$ (in the case of a $5f^1/5f^1$ configuration) which is generally well described by a single determinant and the BS state determinant which is eigenfunction of \hat{S}_z with eigenvalue $M_s = 0$, but not of \hat{S}^2 . In the latter binuclear case, the HS determinant bears the two highest singly occupied molecular orbitals (SOMOs) with spins α/α , whereas the BS starting determinant, before running the SCF process, is simply produced from the HS determinant by a spinflip of the electron leading to the α/β configuration. Different formulas for the calculation of the coupling constant from the E_{HS} and E_{BS} energies have been proposed;⁴² among them, the Yamaguchi et al. formula [140–142]:

$$J_{12} = (E_{\text{BS}} - E_{\text{HS}}) / (\langle S^2 \rangle_{\text{HS}} - \langle S^2 \rangle_{\text{BS}}) \quad (1)$$

where $\langle S^2 \rangle_{\text{HS}}$ and $\langle S^2 \rangle_{\text{BS}}$ are respectively the mean values of the squared spin operator for the HS and BS states.

The validity of the BS approach has been discussed [143], and the reliability and accuracy of the obtained results have been largely investigated [82,83,93–98,133–139]. It has been shown that computations of the magnetic coupling constants at the B3LYP level [86,87] generally lead to satisfying results and good agreement either with high level post-HF computations or with experimental measurements [89]. For instance, D. Gatteschi and Coll. [144] reported DFT calculations

in 2009 considering a mixed {3d-4f} [Cu(II)Gd(III)] complex [L¹CuGd(O₂CCF₃)₃(C₂H₅OH)₂] (L¹ = N,N'-bis(3-ethoxy-salicylidene)-1,2-diamino-2-methylpropanato), with the aim of assessing a suitable DFT functional to understand the mechanism of magnetic coupling and to develop magneto-structural correlations. Several GGA, meta-GGA and hybrid functional calculations with different percentages of HF exchange have been performed. The coupling J constant using the $\hat{H} = J\hat{S}_{Gd}\cdot\hat{S}_{Cu}$ spin Hamiltonian, was extracted from the difference energy between the HS state (S_T = 4) and the BS one, using the following equation:

$$J = \frac{E_{BS} - E_{HS}}{2S_{Gd}S_{Cu}} \quad (2)$$

The DFT/BS model provides ferromagnetic J constant value of -5.8 cm^{-1} (in the used model, negative J value indicates a ferromagnetic character), which is in excellent agreement with the experimental value of -4.42 cm^{-1} , the B3LYP functional being recommended [144].

3.2. Magnetic Exchange Coupling in Actinide Bimetallic Systems

The DFT/BS approach for computing and modeling the exchange coupling interactions faces situations in actinide systems which are different from the lanthanide ones because of their potential for more covalent metal-ligand interactions especially for uranium [8,21,71–73,75]. Even so, numerous DFT/BS studies aiming at rationalizing the sign and strength of the exchange coupling for various bridged diuranium by drawing magneto-structural correlations have been carried out [105–110,145–147].

The discovery of the first AF coupled $5f^1/5f^1$ bis(imido) diuranium(V) complex [(MeC₅H₄)₃U]₂(μ-1,4-N₂C₆H₄) [9], rationalized later [1,127], was undoubtedly a milestone in the field of actinide molecules likely to exhibit magnetic exchange coupling [1–3,6]. One of the first magnetic systems which was theoretically investigated by DFT/BS computations, is the bis(imido) pentavalent diuranium(V) [U(N^tBu)₂(l)(^tBu₂bpy)]₂ complex reported by Kiplinger's group in 2009 [106]. This system exhibits significant AF coupling between the two metallic $5f^1/5f^1$ spin centers, as shown by the magnetic molar χ versus T, through CCI between [U(NR)₂]⁺ moieties similar to that observed in poly-uranyl [UO₂]⁺ systems [23–32,46–51,59,61,69,114–116]. The authors carried out B3LYP computations, employing the Stuttgart RSC 1997 ECP basis set for uranium. The geometries of the HS and BS states were optimized with no symmetry constraints. DFT calculations show that the axial U=N double bond (2.073 Å) consists of one σ and one π bonds, whereas the bridging equatorial U–N bond (2.384 Å) is a single bond, as depicted in Figure 8.

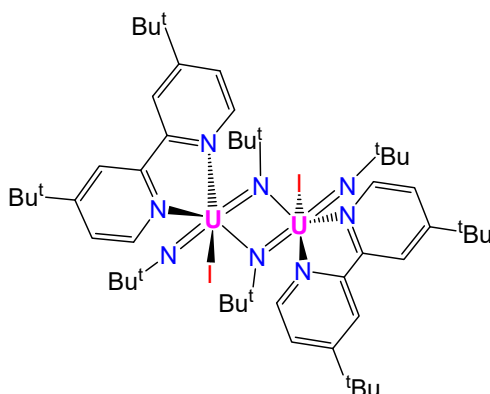


Figure 8. Structure of the U₂N₂ core [106].

Their computations predicted that the BS state is lower in energy than the triplet HS state, leading to an AF exchange coupling constant J of -12 cm^{-1} , which is in good agreement with the experimental fitting of the susceptibility measurements. As reported [106], the weak AF coupling between the two $5f^1$ centers is due not only to the long U–N distance, but also to the fact that half orbitals consist of

antisymmetric combinations which place a node along the U-N bond. Theoretical insights into the AF interaction between metal centers were assessed using the $[\{U(NtBu)_2(I)_2(bpy)\}_2]$ model to investigate molecular orbital interactions in the U_2N_2 core. As reported by the authors [106], the B3LYP natural orbital analysis shows that the two unpaired SOMO and SOMO-1 are localized on the uranium centers corresponding to the $5f^1_\phi/5f^1_\phi$ configuration.

One year later, Newell et al. [107] reported in 2010 on the para and meta dinuclear tetravalent U^{IV}/U^{IV} $[(NN'_3)_2U_2(DEB)]$ and trinuclear $[(NN'_3)_3U_3(TEB)]$ complex ($NN'_3 = [N(CH_2CH_2NSi^tBuMe_2)_3]$) (Figure 9) containing aromatic arylacetylide ligands i.e., diethynylbenzene (DEB) and triethynylbenzene (TEB) ligands as bridging-spacers for two or three metallic $5f^2/5f^2$ and $5f^2/5f^2/5f^2$ spin centers.

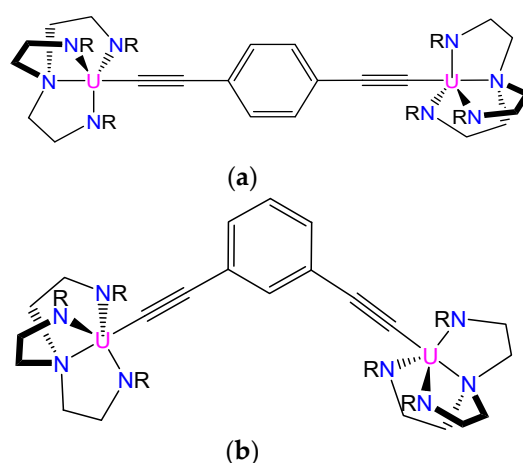


Figure 9. Molecular structures of the para- (a) and meta-diuranium(IV) (b) $[(NN'_3)_2U_2(DEB)]$ [107].

As reported by the authors, the experimental investigations of their magnetic properties show that the di- and tri-nuclear compounds appear to display weak magnetic communication between the uranium centers. This communication is modeled by fitting the direct current (DC) magnetic susceptibility data, using the spin Hamiltonian $\hat{H} = -2J \hat{S}_{z1} \cdot \hat{S}_{z2}$, which leads to a weak ferromagnetic coupling constant i.e., $J = 4.76, 2.75,$ and 1.11 cm^{-1} , respectively for meta-, para-diuranium(IV) and triuranium(IV) complexes. As reported in the same study [107], geometry and nuclearity appear to have an effect on the strength of the coupling between the U(IV) centers. Turning back to the theoretical analysis, geometries of the considered model complexes were optimized using B3LYP computations. In these models, the bulky Si^tBuMe_2 substituting groups in the NN'_3 ligand have been replaced by H atoms and scalar relativistic effects only included in the used uranium effective core potential. For the simplified models derived from the meta- and para-bridged dinuclear species, the BS approach led to computed J values equal to 1.6 and -0.1 cm^{-1} for the meta- and para-bridged complexes, respectively, in fair agreement with experimental trends. As expected, all complexes show only small net spin density (Figure 10) on the ethynylbenzene ligands. As stated by the authors, the computed HS/BS spin densities mapping for meta (a/b) and para (c/d) isomers, both show that the spin density is mostly localized on the two U^{IV} centers, with no contribution from the bridged-DEB ligand, explaining the weak ferromagnetic and AF character of the meta and para species, respectively [107]. The authors concluded that despite the structural difference with the actual meta and para DEB-bridged dinuclear systems, the result shows that coupling in the single wavenumber range is not unexpected.

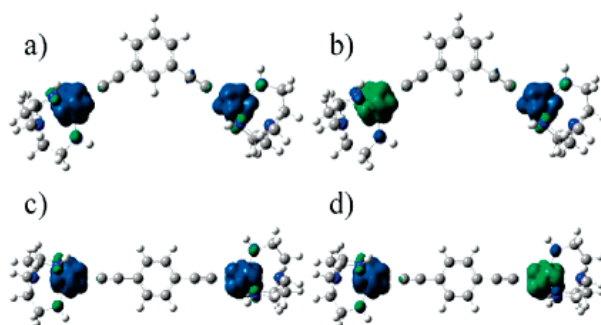


Figure 10. Net spin density plots for HS/BS *meta* (a,b) and *para* (c,d) DEB-bridged dinuclear species. (Reprinted with permission from [107], American Chemical Society, 2010).

Subsequent DFT/BS investigations were carried out in 2012 by R. Arratia-Pérez and Coll. [105] on the magnetic properties of the bis(dicyclooctatetraenyl) diuranium(IV) $[U(\eta^8-C_8H_7)_2]_2$ model system (Figure 11). The authors, who used scalar relativistic computations with the Zeroth Order Regular Approximation (ZORA) and the PBE GGA functional [148,149] in combination with the BS approach, found a strong ferromagnetic coupling between the uranium centers bearing the $5f^2-5f^2$ orbitals, the U...U distance in the $(COT)_2U^{IV}\dots U^{IV}(COT)_2$ complex being equal to 5.320 Å.

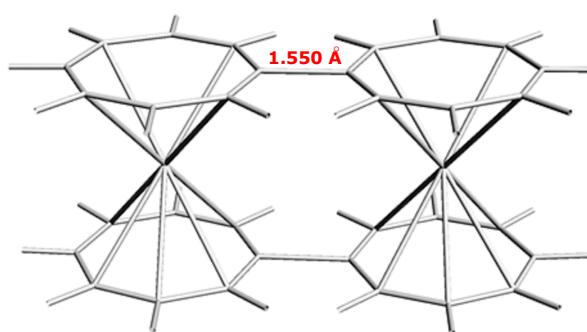


Figure 11. Molecular model for $[U(\eta^8-C_8H_7)_2]_2$ with D_{2h} symmetry [105].

Returning to the $5f^1-5f^1$ bis(imido) diuranium(V) systems [9], the ZORA/B3LYP computations of the coupling constant [146] properly reproduce the AF character of the *para* $[(\{MeC_5H_4\}_3U)_2(\mu-1,4-N_2C_6H_4)]$ diuranium(V) complex and the ferromagnetic one of its *meta* isomer $[(\{MeC_5H_4\}_3U)_2(\mu-1,3-N_2C_6H_4)]$ (Figure 12).

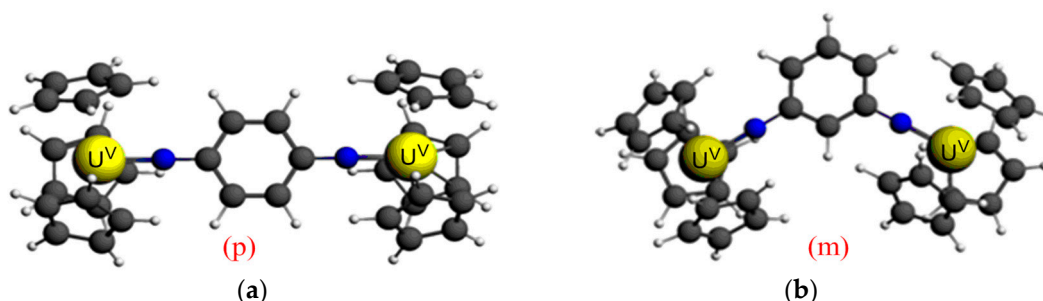


Figure 12. Structures of the *para* (a) and *meta* (b) imido diuranium(V) complexes (reprinted with permission from [146], Elsevier, 2012).

The spin-density plots of the HS/BS states (Figure 13) illustrate that the spin polarization effect is mainly responsible for the observed magnetic character. Considering the *para*- U_2 imido isomer, alternation of the signs of the atomic spin populations along the path is obtained for the BS state and

not for the HS one. In contrast, for the meta-isomer, alternation of these signs is obtained for the HS state, which is lower in energy than BS one, ensuring the ferromagnetic character of the complex.

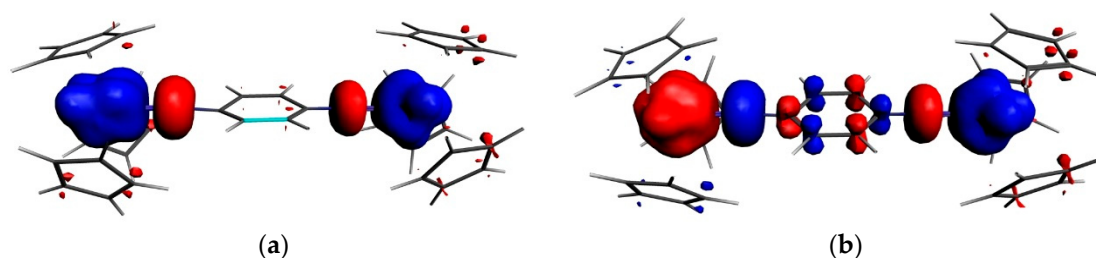


Figure 13. ZORA/B3LYP spin-density (difference of alpha and beta electron densities) distribution plots for the HS (a) triplet and BS (b) states of para-U₂imido (blue color: positive spin density and red color: negative spin density) (reprinted with permission from [146], Elsevier, 2012).

The topology of the path linking the two magnetic of para-U₂imido and meta-U₂imido complexes plays a crucial role for the electronic communication between the U(V) centers. Furthermore, from the MO point of view, the AF interaction between the two uranium(V) ions mediated by the aromatic imido bridge is mainly due to the effective π -overlap between $5f^1$ orbitals and the nitrogen orbitals of the bridging ligand groups.

As mentioned, the Kiplinger's group [128] reported in 2008 the occurrence of a significant electronic communication between the U^{IV}/U^{IV} ($5f^2/5f^2$) centers within the bis(ketimide) binuclear [(C₅Me₄Et)₂(Cl)An]₂(μ -{N=CMe-(C₆H₄)-MeC=N}) An^{IV}/An^{IV} (Th, U) complexes. However, the magnetic character of the coupling between the metal centers could not be shown unambiguously. Computationally, the exchange coupling constant has been estimated considering the simplified [(C₅H₅)₂(Cl)An]₂(μ -ketimide) model (An/An = U^{IV}/U^{IV} and U^{IV}/Th^{IV}), where C₅Me₄Et is replaced by the Cp = C₅H₅ ring (Figure 14) [147]. Using ZORA/B3LYP computations, the BS ground state of these U^{IV}/U^{IV} $5f^2$ - $5f^2$ complexes has been found of lower energy than the quintet HS state, indicating a weak AF character (estimated coupling constant $|J| < 5 \text{ cm}^{-1}$) which has not yet been confirmed experimentally to our knowledge.

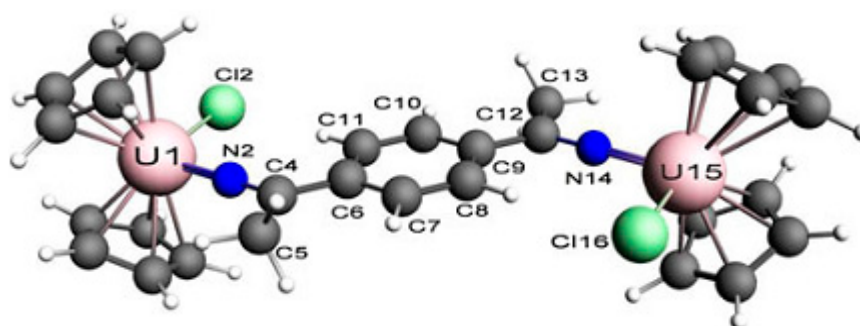


Figure 14. Structures of the bis(ketimide) diuranium(IV) complexes (reprinted with permission from [147], Springer-Verlag, 2012).

The magnetic exchange coupling has been rationalized considering spin density distributions (Figure 15). As obtained for the previous bis(imido) U^V/U^V ($5f^1/5f^1$) system [146], the AF coupling appears through the alternating signs of the atomic spin populations along the path linking the two magnetic metal centers $5f^2$ - $5f^2$ in the BS state, the AF character being mainly explained by spin polarization.

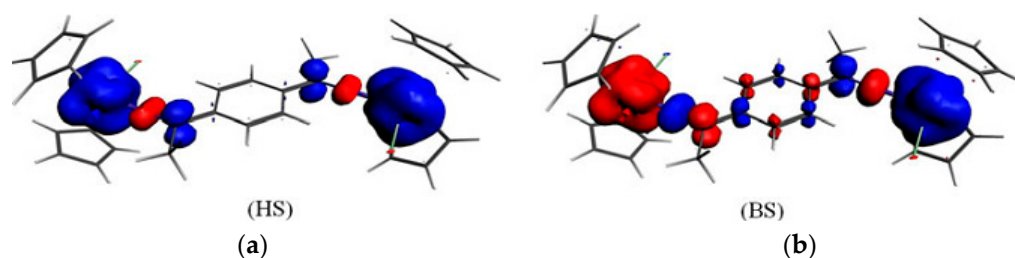


Figure 15. ZORA/B3LYP spin-density (difference of alpha and beta electron densities) distribution plots for the HS (a) triplet and BS states (b) of U₂bis(ketimide) (blue color: positive spin density and red color: negative spin density). (Reprinted with permission from [147], Springer-Verlag, 2012).

The effect of the replacement of one paramagnetic metal U(5f²) by the diamagnetic Th(5f⁰) one in the U^{IV}–(μ-ketimide)–Th^{IV} hypothetical complex drastically affects the spin polarization effect; the spin densities tend to zero beyond the first neighbors of the paramagnetic center. No magnetic exchange interaction occurs in such a system.

C. C. Cummins and Coll. [15,16] reported in 2013 on the electronic structure and magnetic properties analyses of the arene-bridged U^{III}/U^{III} dimer [U₂(N[^tBu]Ar)₄(μ-toluene)] (Ar = 3,5-C₆H₃Me₂) complex (Figure 16).

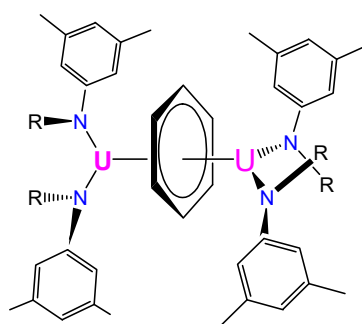


Figure 16. Structure of the (μ-toluene)U₂(N[^tBu]Ar)₄ (Ar = 3,5-C₆H₃Me₂) complex [16].

Computationally, DFT geometry optimizations were performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [148,149] and the dispersion corrected B-97D functional [150] considering a model where the large sized 1-adamantyl and 3,5-C₆H₃Me₂ groups were replaced by *t*butyl and phenyl moieties, respectively. With reference to the results of DFT and CASSCF/CASPT2 calculations relativistic effects being included with the Douglas-Kroll-Hess (DKH) Hamiltonian (spin-orbit not included), all possible spin states of the model compounds, including singlet, triplet, quintet, and septet spin states, were explored. The DFT electronic structure analysis showed that the highest four SOMOs are 5f orbitals of the two uranium centers, followed energetically by two covalent δ MOs, as presented in Figure 17. These latter MOs corresponding to the U-arene-U bonding contain contributions from uranium 5f orbitals overlapping with π antibonding orbitals of the tolyl group.

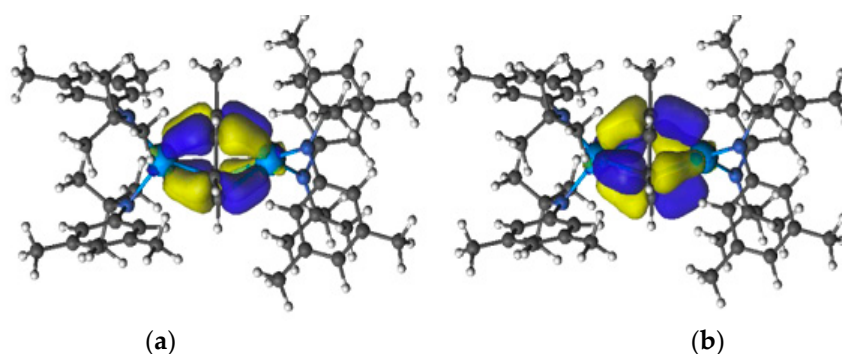


Figure 17. Singly occupied δ bonding natural MOs from the $(\mu\text{-toluene})\text{U}_2(\text{N}^{\text{tBu}}\text{Ar})_4$ complex in its quintet state. (a) SOMO-4 and (b) SOMO-5 (reprinted with permission from [16], American Chemical Society, 2013).

The ground state at the CASPT2 level is the singlet; however, the triplet and quintet are respectively 0.7 and 2.5 kcal/mol higher in energy than the singlet state, whereas the septet is much higher, at 34.5 kcal/mol. As reported by the authors [16], solid-state magnetic susceptibility measurements of the dinuclear system showed complicated features. Indeed, although paramagnetic behavior is observed over the temperature intervals 5–300 K, the $1/\chi$ versus T graph showed minimum values between 95 and 125 K, which is characteristic of a transition to AF state. However, the optical and magnetic properties of $\text{U}^{\text{III}}\text{-}(\mu\text{-toluene})\text{-U}^{\text{III}}$ were difficult to relate to reported examples of mononuclear uranium organometallic complexes. The authors did not estimate the coupling constants.

As indicated above, remarkable classes of diuranium(V) bridged-oxo complexes exhibiting $\text{U}^{\text{V}}\text{O}_2^+ \dots \text{U}^{\text{V}}\text{O}_2^+$ CCIs and strong AF exchange coupling were reported by various authors [23–32,46–51, 61,69,114–116], motivating theoretical investigations [7,8,63–65,71,72,74,75,79]. Among them, strongly coupled binuclear complexes $[\text{UO}_2\{\text{N}(\text{SiR}_3)_2\}_2(\text{py})_2]$ forming a butterfly-shaped Si–OUO₂UO–Si uranium(V)-oxo motif (Figure 18) have been synthesized (2012), X-ray characterized and their electronic and magnetic properties investigated with the support of DFT computations [49]. A variable-temperature measurement of susceptibility shows a clear signature of AF coupling between the $5f^1\text{-}5f^1$ centers.

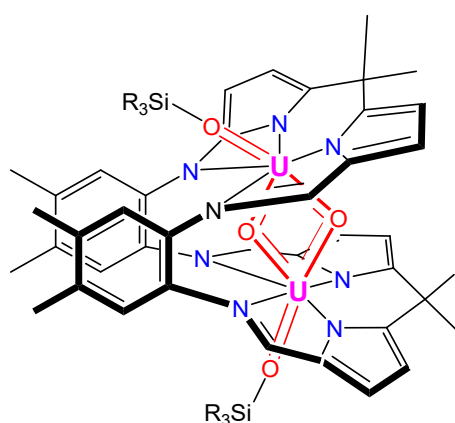


Figure 18. Structure of the butterfly-shaped diuranium(V) $[\text{UO}_2\{\text{N}(\text{SiR}_3)_2\}_2(\text{py})_2]$ complex [49].

The geometries of the $5f^1\text{-}5f^1$ structures were optimized in the gas phase using B3LYP calculations, considering the ferromagnetic triplet ($f^\alpha f^\alpha$), the BS ($f^\alpha f^\beta$) and the spin restricted singlet ($f^\alpha f^\beta$) states. A striking structural feature of the U_2O_2 core is its C_{2v} -symmetrical diamond shape and an average U–O distance of 2.094 Å, with a very short $\text{U}\cdots\text{U}$ separation of 3.3557(5) Å. As reported by the authors using B3LYP calculations [49], the BS state was calculated to be more stable than the triplet and restricted singlet states by 1.4 and 42.7 kcal/mol, respectively, which is in agreement with the

observed AF character of the complex. The U...U separation was calculated to be equal to 3.366 and 3.379 Å in the BS and triplet states, respectively, within 0.01 Å deviations from the experimental values. NBO analysis of the bonding in the U₂O₂ core for both states, based on the calculated Mayer and Wiberg bond orders, reveals formally U–O single and partially double-bond character, which is in agreement with the structural features. The MO analysis shows that the two α and β components of HOMO-27 and HOMO-28, obtained with the B3LYP functional for the BS state, are related to the σ and π bonding interactions, respectively, within the U₂O₂ core. The π -type orbitals, which are dominated by 2p-contributions from the oxo-bridged atoms, appear to stabilize the diamond U₂O₂ core. The B3LYP calculated spin density in the AF BS state shows the $f^\alpha f^\beta$ configuration with electrons of different spins localized on each uranium atom.

As reported in the same study [49], the calculated U...U separation of 3.366 Å is much shorter than twice the covalent radius of the uranium atom (3.92 Å), which may indicate some metal-metal bonding interaction, as predicted by theory [145,151–154]. However, the structural analogy with Mo^V(μ -O)₂Mo^V complexes which exhibit single Mo–Mo bonds was faced to the paramagnetic state of the U^V(μ -O)₂U^V complex, and no reported examples exist of molecular bonds between two f-block ions in such structures. The authors conclude that the extremely short U...U separation exhibited by the diuranium(V) oxo-bridged system indicates strong electronic communication between the two 5f¹ centers. However, it was postulated that the geometry of the oxo-group interaction within the diamond-shaped U₂O₂ core, and not the shortened U...U separation, was the primary mediator of the super-exchange. Indeed, as reported by the authors,^{20d} the AF coupling due to super-exchange across the two oxo groups, modeled by a spin Hamiltonian, led to a particularly large fitted value $J_{exp} = -33 \text{ cm}^{-1}$, suggesting that the butterfly geometry could be of interest for the building more complex magnetic structures.

Other diuranium bis(μ -oxo) systems, synthesized by K. Meyer and Coll. [115], (in 2014) exhibit diamond-core shaped [U(μ -O)₂U] structural motifs and remarkably different magnetic behaviors depending on the uranium oxidation state. Indeed, the magnetic data show for pentavalent [U(^{nP,Me}ArO)₃(tacn)U^V]₂(μ -O)₂ (tacn = triazacyclononane, nP = neopentyl) structure a U^V/U^V AF coupled system, while its reduced species, the dianionic U^{IV}/U^{IV} K₂[U(^{nP,Me}ArO)₃(tacn)U^{IV}]₂(μ -O)₂ tetravalent complex, revealed itself to be non-magnetic [115]. These two complexes (Figure 19), have been investigated computationally using B3LYP coupled to the BS approach; scalar relativistic effects were accounted for by using the ZORA Hamiltonian [155].

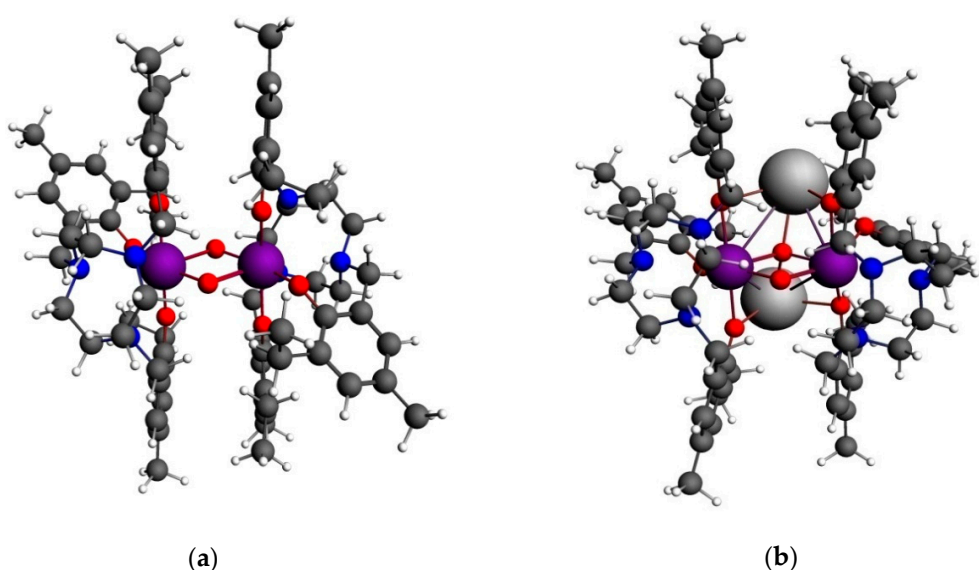


Figure 19. Optimized molecular structures of the (a) [U^V(μ -O)₂U^V] and (b) K₂[U^{IV}(μ -O)₂U^{IV}] complexes (reprinted with permission from [155], American Chemical Society, 2016).

The computations reveal the BS ground state of the pentavalent $[\text{U}^{\text{V}}(\mu\text{-O})_2\text{U}^{\text{V}}] 5f^1\text{-}5f^1$ complex lower in energy than the high spin (HS) triplet state, indicating a AF character in agreement with experimental magnetic susceptibility measurements. The non-magnetic character observed for the tetravalent $\text{K}_2[\text{U}^{\text{IV}}(\mu\text{-O})_2\text{U}^{\text{IV}}] 5f^2/5f^2$ species is also predicted by ZORA/B3LYP calculations which led practically to the same energy for the HS and BS states [115]. As previously reported for related dioxo diuranium(V) systems [49], super-exchange is likely to be responsible for the AF coupling through the π -network orbital pathway within the $(\mu\text{-O})_2$ bridge, with the dissymmetrical structure of the U_2O_2 core playing a determining role. Spin densities in HS and BS states were computed for the $\text{U}^{\text{V}}(\mu\text{-O})_2\text{U}^{\text{V}}$ complex in order to understand and rationalize their AF character. The obtained spin density surfaces (Figure 20) showed that both HS and BS states exhibit localized spin densities on the two magnetic diuranium(V) centers, with significant values on their nearest O_{oxo} and non-negligible ones on the O_{Ar} neighbors.

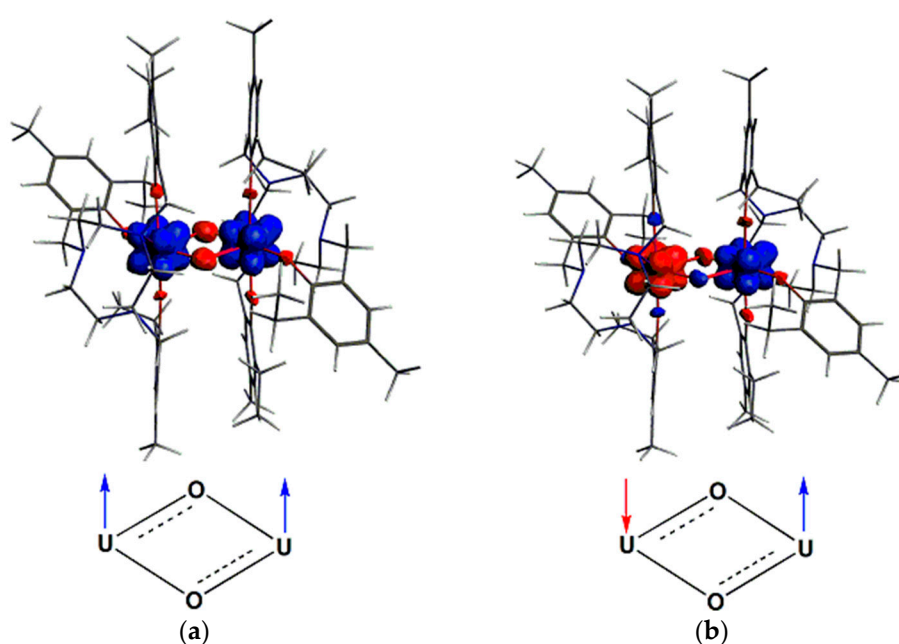


Figure 20. ZORA/B3LYP spin density surfaces for the HS (triplet) in left and BS states in right of $\text{U}^{\text{V}}(\mu\text{-O})_2\text{U}^{\text{V}}$ complex (blue color: positive and red color: negative spin density). The plotted isodensity surfaces (a) HS and (b) BS states corresponds to a value of $\pm 0.0025 \text{ e bohr}^{-3}$. (reprinted with permission from [155], American Chemical Society, 2016).

Interestingly, the spin density maps show that the difference between the HS and BS states is the sign alternation of the spin populations around the dioxo $(\mu\text{-O})_2$ path-linking the two magnetic $\text{U}^{\text{V}}(5f_{xyz}^1)$ centers in its BS state. For the HS state, the spin of the bridging $(\mu\text{-O})_2$ ligands is symmetrically polarized by the two U^{V} spin carriers. In contrast, for the BS state, the two oxygen atoms are differently polarized with sign alternation of positive and negative spin densities.

The magnetic properties of di- and triuranium(V) $[\text{UO}_2(\text{dbm})_2\text{K}(\text{18C6})]_2$ (dbm: dibenzoylmethanate) and $[\text{UO}_2(\text{L})_3]$ ($\text{L} = 2(4\text{-Tolyl})\text{-}1,3\text{-bis}(\text{quinolyl})\text{malondiiminat}$) complexes (Figure 21), exhibiting diamond-shape U_2O_2 and triangular-shape U_3O_3 cores with $5f^1\text{-}5f^1$ and $5f^1\text{-}5f^1\text{-}5f^1$ configurations, have been studied experimentally [23–25]. The ZORA/B3LYP calculations (unpublished results) which have been carried out confirm the AF character of these complexes. The estimated J values have been respectively found equal to -24.1 and -7.2 cm^{-1} for the dioxo and the trioxo species, the used geometries of the magnetic cores being those of the X-ray structures.

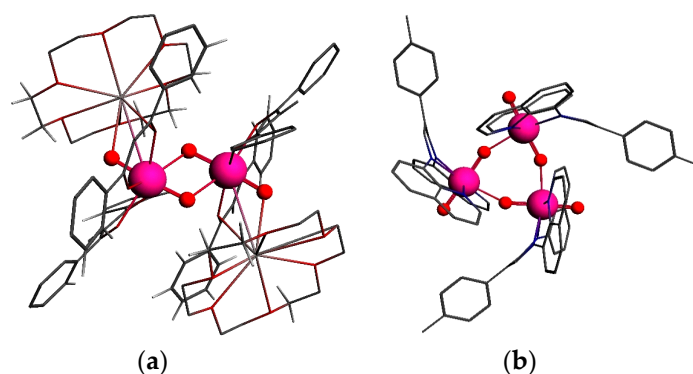


Figure 21. Optimized molecular structures of dioxo (a) $[\text{UO}_2(\text{dbm})_2\text{K}(18\text{C}6)]_2$ and trioxo (b). $[\text{UO}_2(\text{L})]_3$ ($\text{L} = 2(4\text{-Tolyl})\text{-}1,3\text{-bis}(\text{quinoly})\text{malondiiminate}$) Sticks used to depict C, N and K atoms; H atoms have been omitted for clarity. Pink and red colors respectively for uranium and oxygen atoms. (Unpublished results).

The obtained spin density maps (difference between the α and β electron densities) of the HS and BS states of the diuranium species are displayed in Figure 22. They are rather similar to those of the $\text{U}^{\text{V}}(\mu\text{-O})_2\text{U}^{\text{V}}$ complex (Figure 20).

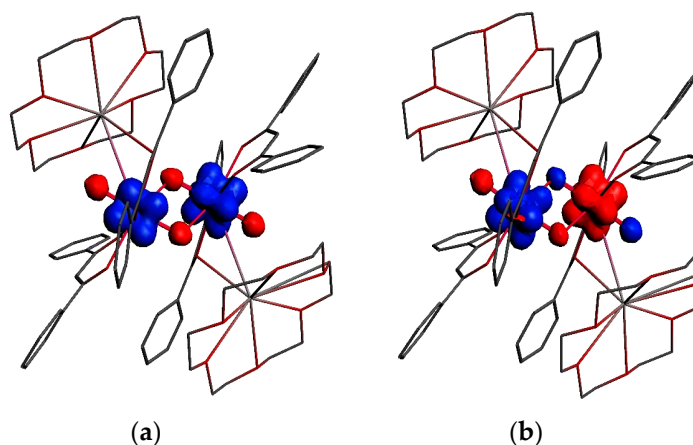


Figure 22. ZORA/B3LYP spin density distributions for the HS (triplet) and BS states of the dioxo $[\text{UO}_2(\text{dbm})_2\text{K}(18\text{C}6)]_2$ system (blue color: positive and red color: negative spin density). The isodensity surface corresponds to a value of $0.0025 \text{ e bohr}^{-3}$. (Unpublished results). (a) (HS); (b) (BS).

More recently (2017), the first benzoquinonoid-bridged dinuclear actinide complexes were reported by S. Hohloch et al. [156] The target dinuclear systems with different structures, i.e., $\text{U}(\text{L})_2$, $[\text{Th}(\text{L})]_2\text{Q}^{\text{Dipp}}$, $[\text{Th}(\text{THF})(\text{L})]_2\text{Q}^{\text{OMe}}$ and $[\text{U}(\text{L})]_2\text{Q}^{\text{OMe}}$ associated with the tripodal tris[2-amido(2-pyridyl)ethyl]amine ligand L, have been synthesized from the dianionic 2,5-bis[2,6-(diisopropyl)anilide]-1,4-benzoquinone (Q^{Dipp}) and 2,5-bis[2-(methoxy)anilide]-1,4-benzoquinone (Q^{OMe}) ligands, as depicted for the quinoid-bridged $\text{U}^{\text{IV}}/\text{U}^{\text{IV}}$ diuranium system in Figure 23.

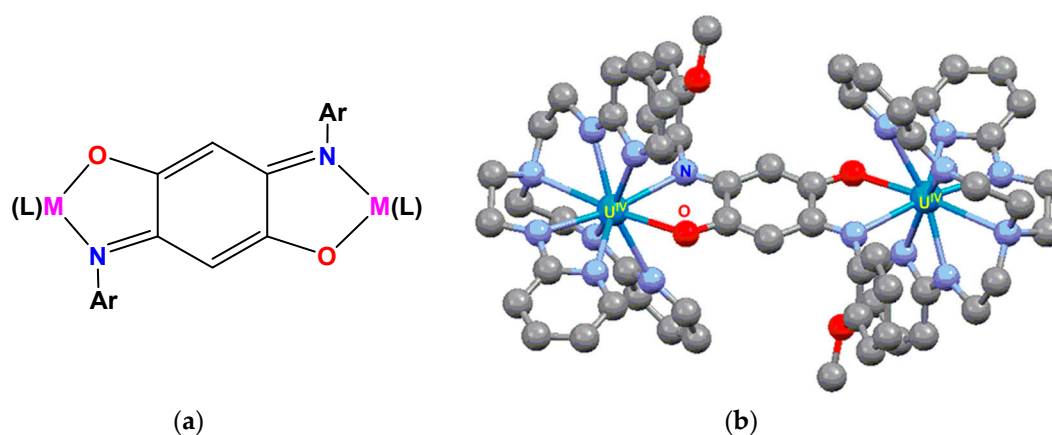


Figure 23. Schematic depiction (a) and molecular structure (b) of the imino-alkoxy quinoid diuranium(IV) $[U(L)_2Q^{OMe}]$ system. (reprinted with permission from [156], the Royal Society of Chemistry, 2017).

As reported by the authors, magnetic measurements of the uranium(IV) iodide $[UI(L)_2]$ and quinoid $[U(L)_2Q^{OMe}]$ bridged species, which exhibit long intermetallic $U^{IV} \dots U^{IV}$ distances i.e., 5.125(1) Å and 8.904(1) Å respectively, indicate that there is weak magnetic exchange between the two uranium(IV) ions which was not quantified from the DC susceptibility measurements. Furthermore, as reported in the study, the low-temperature susceptibility data indicate that the ground states for the two U^{IV}/U^{IV} dimer should be non-magnetic singlets. With the support of DFT calculations, using a hybrid B3PW91 functional [157] and a core pseudopotential for uranium, the electronic structure analysis of the U^{IV}/U^{IV} diuranium $[U(L)_2Q^{OMe}]$ system shows that the four unpaired electrons occupying SOMOs, are mainly of mixed uranium/quinoid character as illustrated by the SOMO-2 (Figure 24), except the SOMO-1, which is purely metal-based.

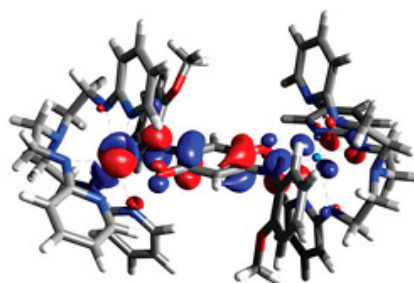


Figure 24. SOMO-2 of the $[U(L)_2Q^{OMe}]$ quintet state system. Plot surfaces displayed with an iso-value of 0.02 au (reprinted with permission from [156], the Royal Society of Chemistry, 2017).

The unpaired spin-density plot (Figure 25) shows that there is significant spin-delocalisation from uranium to the quinoid bridge.

Importantly, the quinoid ligand of the diuranium(IV) $[U(L)_2Q^{OMe}]$ complex could undergo a reversible reduction to form a radical anion. However, the chemical redox reaction leads to an unstable and sensitive anionic complex, despite the fact that X-ray crystallography indicates that the product contains a radical bridge. However, the magnetometry of the anionic species has not been investigated, and the impact of the radical bridge on the intermetallic exchange interaction could not be evaluated.

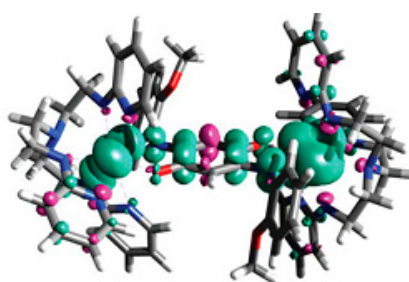


Figure 25. spin-density plot of the $[U(L)_2]_2Q^{OMe}$. Plot surfaces displayed with an iso-value of 0.02 au (reprinted with permission from [156], the Royal Society of Chemistry, 2017).

3.3. Mononuclear Actinide Complexes

Several uranium-radical systems emerged in the mid-2000s as mononuclear complexes exhibiting magnetic properties [62,66,74,129–131,158–170]. Structural, spectroscopic and magnetic properties of various mononuclear uranium(IV)-benzophenone radical complexes; e.g., the ketyl $[(t^{\text{Bu}}\text{ArO})_3\text{tacn}]U^{\text{IV}}(\text{OC}\cdot t^{\text{Bu}}\text{Ph}_2)$ complex (**2**) (Figure 26), were investigated by O.P. Lam et al. (2008) [164] with the support of DFT calculations. The temperature dependence of the magnetic susceptibility data for this ketyl radical complex shows a similar trend to that of a previous CO_2 η^1 -bound uranium $[(^{\text{Ad}}\text{ArO})_3\text{tacn}]U^{\text{IV}}(\text{CO}_2^{\bullet-})$ complex [165].

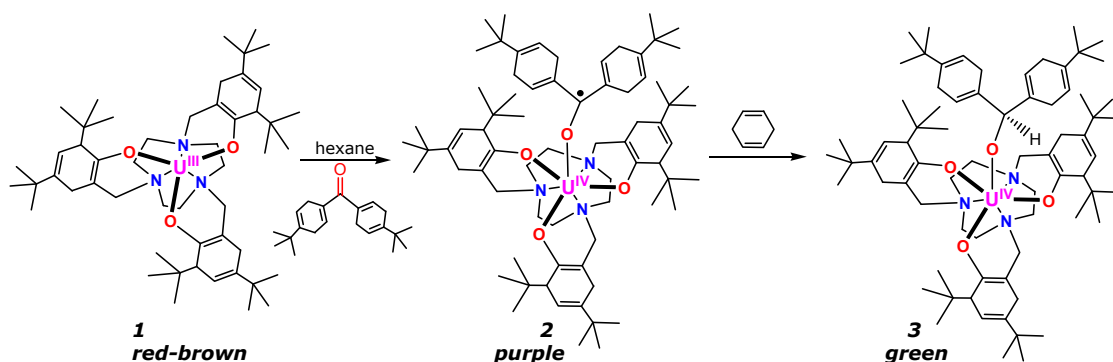


Figure 26. Formation of U(IV) benzophenone ketyl radical complex **2** through a one-electron reduction of 4,4'-Di-tert-butylbenzophenone by U(III) precursor complex $[(t\text{-BuArO})_3\text{tacn}]U^{\text{III}}$ (**1**) followed by H abstraction to form a U(IV) diphenyl methoxide complex **3** [164].

The ketyl radical complex **2** was modeled to have three unpaired electrons, computing it as a U(III) complex. However, the resulting orbitals and spin density plots (Figure 27) suggest a more complex representation.

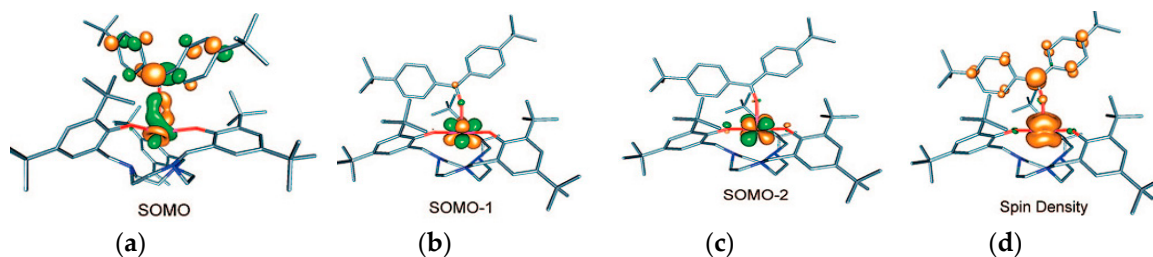


Figure 27. DFT isosurface contour plots featuring frontier SOMOs and spin density of the ketyl $[(t^{\text{Bu}}\text{ArO})_3\text{tacn}]U^{\text{IV}}(\text{OC}\cdot t^{\text{Bu}}\text{Ph}_2)$ complex (**2**). (a) SOMO; (b) SOMO-1; (c) SOMO-2; (d) Spin density. (Reprinted with permission from [164], American Chemical Society, 2008.)

As reported by the authors, while SOMO-2 and SOMO-1 (Figure 27) are of δ -type f_{xyz} and $f_{z(x^2-y^2)}$ pure uranium 5f orbitals, the highest energy SOMO exhibits a metal/ligand character. The resulting spin density of the U(IV) $5f^2$ complex (2) confirms that the f_{xyz} and $f_{z(x^2-y^2)}$ orbitals carry the main part of the spin, with a small spin polarization on the coordinated ligand. Variable temperature magnetization data were measured for two independently synthesized samples. The data of complex (2) show a steady drop in μ_{eff} as the temperature is lowered, decreasing from $3.48 \mu_B$ at 300 K to $1.61 \mu_B$ at 5 K which is unusual compared to common U(IV) ($5f^2$) complexes and is likely due to magnetic contributions from the unpaired electron residing on the disubstituted benzophenone fragment, as well as from the U(III) resonance structure (Figure 28, 2d). This is consistent with the DFT calculations, in which one third of the single radical electron is localized on the uranium, hence, increasing the magnetic moment.

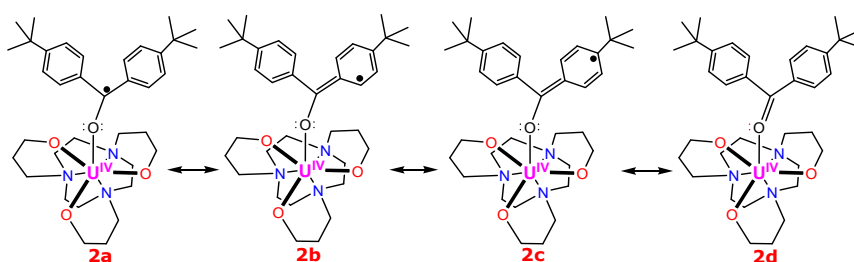


Figure 28. Resonance structures of complex 2 (labelled 2a–2d) [164].

The authors concluded that regarding the magnetic data of complex (2) revealing an unusual U(IV) $5f^2$ complex which should be considered as a charge-separated U(III)–L \leftrightarrow U(IV)–L $^{\bullet-}$ ($5f^3$) \leftrightarrow ($5f^2$) species. DFT calculations suggest that coupling between the U^{IV} center and the ketyl radical L $^{\bullet-}$ ligand is at least physically reasonable because the computed frontier SOMO of the molecule possesses both metal and ligand contribution.

3.4. Mixed Actinide/Transition Metal (5f-3d) and Actinide/Lanthanide (5f-4f) Complexes

To date, only scarce examples of mixed (5f-3d) actinide/transition metal complexes exhibiting magnetic exchange interactions are found in the literature [1,43–45,114,115,118–121]. Moderate ferromagnetic exchange coupling was measured by J. D. Rinehart et al. (2007) [1,122] for the linear chloride-bridged 5f–3d heterometallic mixed trinuclear U^{IV}/M^{II}/U^{IV} dimethylpyrazolate (cyclam)M^{II}[(μ -Cl)U^{IV}(Me₂Pz)₄]₂ (M^{II} = Ni, Cu, Co, Zn) cluster shown in Figure 29.

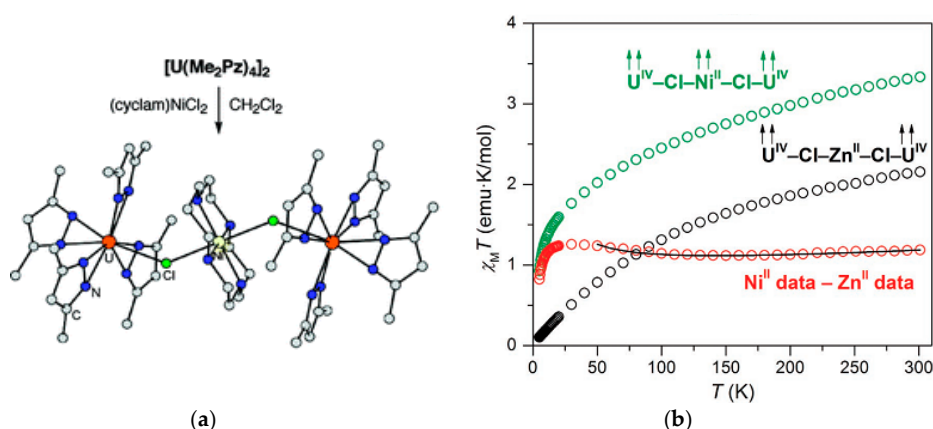


Figure 29. (a) Structure of the linear cluster (cyclam)Co^{II}[(μ -Cl)U^{IV}(Me₂Pz)₄]₂ and (b) Variable-temperature magnetic susceptibility plot. Orange, purple, green, gray, and blue spheres represent U, Co, Cl, C, and N atoms, respectively. H atoms are omitted for clarity (reprinted with permission from [122], American Chemical Society, 2007).

The measured exchange constant J lies in the range $15\text{--}48\text{ cm}^{-1}$ for the CoU_2 cluster core and $2.8\text{--}19\text{ cm}^{-1}$ for the NiU_2 congener. To understand the origin of this ferromagnetic coupling within the MU_2 core, the authors considered a spin Hamiltonian of the following form: $\hat{H} = -2J[\hat{S}_{\text{Co}} \cdot (\hat{S}_{\text{U1}} + \hat{S}_{\text{U2}})]$.

DFT/PBE calculations which were performed [58] on a $[(\text{Me}_2\text{Pz})_4\text{UCl}]^-$ anionic fragment of the cluster revealed the unpaired electrons of the U^{IV} center to reside in the $5f_{xyz}$ and $5f_{z(x^2-y^2)}$ orbitals, as shown in Figure 30 [122].

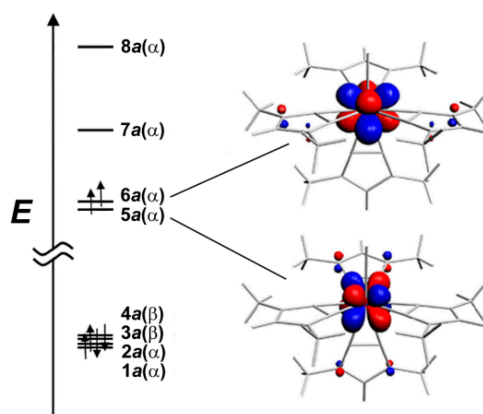


Figure 30. DFT frontier energy level diagram and MOs for $[(\text{Me}_2\text{Pz})_4\text{UCl}]^-$. The Me_2Pz -ligands are shown as skeletal representations, and the $\text{U}\text{--}\text{Cl}$ axis is oriented vertically (reprinted with permission from [122], American Chemical Society, 2007).

As reported, these orbitals have δ symmetry with respect to the $\text{U}\text{--}\text{Cl}$ z -axis bond, such that the overlap with σ and π orbitals of the chloride bridge will be zero. Any of the spin from the Co^{II} $3d_{z^2}$ orbital feeding through the chloride bridging ligands will therefore engage rigorously orthogonal orbitals, leading to a ferromagnetic exchange interaction. Consistently, ferromagnetic exchange is also observed for the NiU_2 cluster, which features a Ni^{II} ($S = 1$) center with unpaired electrons in the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals. However, despite the presence of a large axial zero-field splitting for NiU_2 , no indication of the slow magnetic relaxation is reported, as is typically observed for SMM behavior [1].

During the same year (2007) there has been a report suggesting that coupling may occur through direct metal-metal orbital overlap in the mixed-valence linear trinuclear cluster $\text{U}(\text{fc}[\text{NSiMe}_3]_2)_2$ ($\text{fc} = 1,1'$ -ferrocenylene) and its $[\text{Fe}^{\text{II}}\text{U}^{\text{IV}}\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{NSi}(\text{tBu})\text{Me}_2)_4]\text{BPh}_4$ cationic congener which is depicted in Figures 31 and 32. [18] The latter molecule exhibits a rigid coordination to ferrocenylamido moieties and $\text{U}\cdots\text{Fe}$ distances of $2.9556(5)$ and $2.9686(5)$ Å.

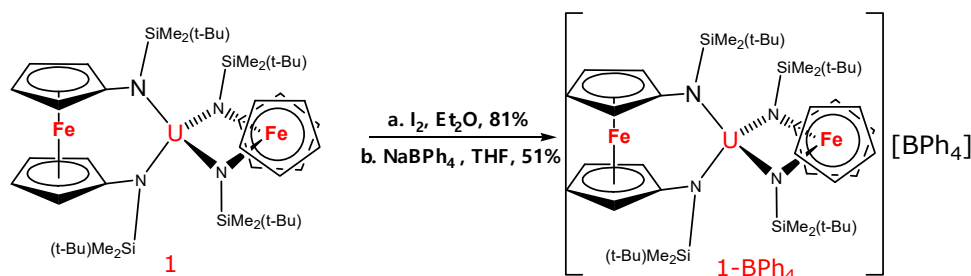


Figure 31. The transformation reaction of **1** $\text{U}(\text{fc}[\text{NSiMe}_3]_2)_2$ into $[\text{Fe}^{\text{II}}\text{U}^{\text{IV}}\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{NSi}(\text{tBu})\text{Me}_2)_4]\text{BPh}_4$: **1-BPh4** [18].

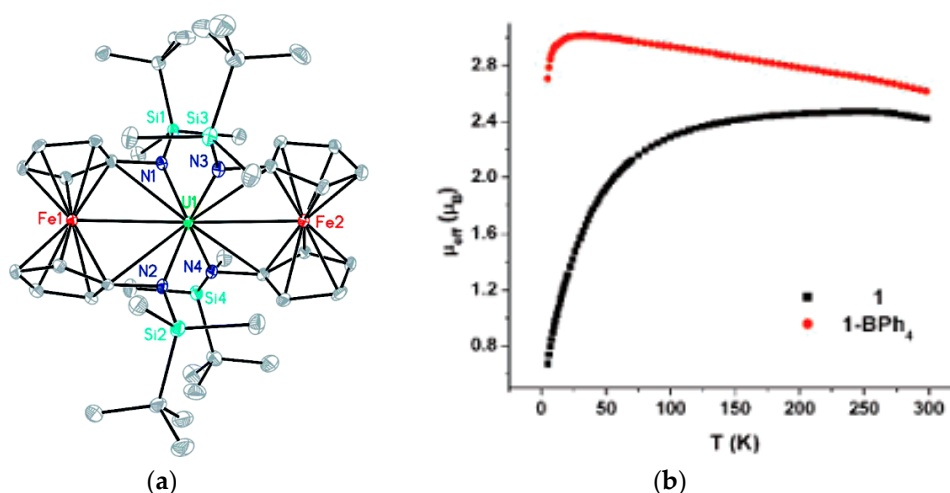


Figure 32. (a) X-ray Structure of $[\text{Fe}^{\text{II}}\text{U}^{\text{IV}}\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{NSi}(\text{tBu})\text{Me}_2)_4]$ cation (1^+) complex. H atoms are omitted for clarity. (b) Variable-temperature magnetic data for UFe^{II}_2 (1, black squares) and $\text{Fe}^{\text{II}}\text{U}^{\text{IV}}\text{Fe}^{\text{III}}$ (1-BPh_4 , red circles). (Reprinted with permission from [18], American Chemical Society, 2007).

This mixed-valent bisferrocenyl complexes have been studied in order to understand the dependence of the electronic coupling between the two iron centers relative to the linker connecting them. When uranium is used as a linker, 5f orbitals make this actinide a better mediator than the zirconium d-transition metal for the electronic communication between iron centers. Indeed, as noted by the authors [1,18], the observed behavior is indicative of an extremely strong ferromagnetic exchange $\text{U}^{\text{IV}}-\text{Fe}^{\text{III}}$ interaction, mediated by direct orbital overlap between the metals orbitals. DFT calculations were performed on the thorium and zirconium bisferrocene trinuclear $\text{Th}(\text{fc}[\text{NH}]_2)_2$ cation models related to the actual $\text{U}(\text{fc}[\text{NSiMe}_3]_2)_2$ system. For the thorium bisferrocene cation model, additionally, the HOMO and HOMO-5 (Figure 33) consist of a uranium 5f orbital interacting with orbitals of both iron atoms at the same time, which might explain the occurrence of strong electronic communication mediated by actinide-transition metal orbital overlap.

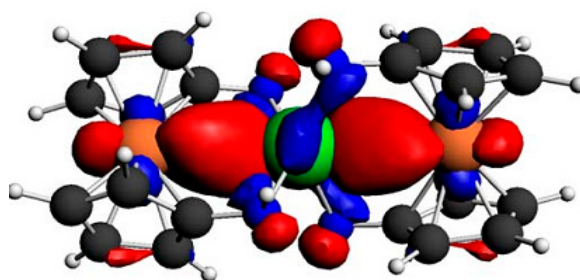


Figure 33. HOMO-5 of the $\text{Th}(\text{fc}[\text{NH}]_2)_2$ model cation. Green and magenta color for Th and Zr metals, respectively (reprinted with permission from [18], American Chemical Society, 2007).

Finally, magnetic coupling was also reported in 2006 for 5f-4f trinuclear UYb_2 cluster $\text{Cp}^*_2\text{U}[(\text{NC}(\text{CH}_2\text{C}_6\text{H}_5)\text{tpy})\text{YbCp}^*_2]_2$ (tpy = terpyridyl) [108].

3.5. Magnetic Susceptibility and EPR/NMR Spectra of Actinide Complexes

New developments in the computational transuranium chemistry were surveyed recently (2018) by N. Katsoyannis [8], with emphasis on the assessment of the magnetic properties of transuranic elements. As reported in this review, the magnetic susceptibility and the electronic structure of borate materials, in particular those of Californium (Cf) and Berkelium (Bk) metals, e.g., $\text{An}[\text{B}_6\text{O}_8(\text{OH})_5]$

(An = Cf^{III} and Bk^{III}) [171,172], have been studied using both GGA and hybrid functionals in conjunction with NBO analysis [8].

The electronic structures and magnetic properties of Ar₃U^{IV}–L complexes, with Ar = C₅(CH₃)₄H[–] or C₅H₅[–] and L = CH₃, NO, and Cl have been investigated recently (2014) [67]. The study aimed to provide *ab initio* data for the magnetic susceptibilities, assignments of the low-energy parts of the electronic spectra, as well as characterizations of selected states based on natural orbitals and their occupations. For the ground states, relativistic CASSCF and CASPT2 calculations were compared to scalar relativistic DFT using the ZORA Hamiltonian. As concluded by the authors, for the nitrosyl complex, the ground state is a closed-shell spin-singlet i.e., a nonmagnetic ground state. For the other L = Cl and CH₃ complexes, the ground states are triplets, with no orbital degeneracy for the chloride complexes and an orbital-doublet for the methyl complex. Furthermore, the nature of the electronic ground state and low-energy excited states is evidenced by the susceptibility curves displaying linear χT [67]. The computed susceptibilities from *ab initio* calculations agree well with available experimental data; e.g., for the (C₅Me₄H)₃UCl complex, the *ab initio* calculated temperature-independent paramagnetism (TIP) susceptibility χ_{TIP} is 8.52 and 10.44 (units of 10³ cm³mol^{–1}) for the experimental and optimized structure, respectively.

DFT-based calculations have also been reported [168] and proved to correctly reproduce chemical shifts of diamagnetic uranium(VI) compounds. DFT benchmarking calculations of ¹H and ¹³C NMR chemical shifts of closed shell U(VI) systems for which experimental data are available (Figure 34), were reported [79]. Different levels of GGA and hybrid functionals were employed, i.e., B3LYP [86,87], PBE [148], PBE0 [149], LC- ω PBE [173,174], TPSS and TPSSh [175,176] and also including the Grimme's D3 dispersion corrections [150,157]. Overall, it was found that the most robust methodology for obtaining accurate geometries is the PBE functional with Grimme's D3 dispersion corrections, whereas for ¹H and ¹³C NMR chemical shifts, no special recommendation emerges regarding the best choice of density functional, although for spin-spin couplings, the LC- ω PBE functional with solvent corrections is a good approach.

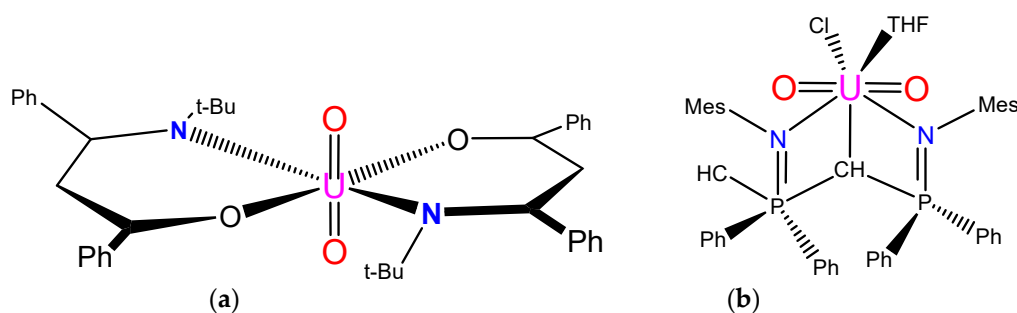


Figure 34. Structures of Uranyl(VI) monomers (a) β -Ketoiminato and (b) Carbenes Complexes [79].

The authors concluded that among the investigated approaches, the disagreement with experiment of the averaged ¹H and ¹³C chemical shifts rarely exceeds 15% deviation for the studied U(VI) compounds. The geometry employed has relatively little effect on the ¹H and ¹³C chemical shifts, and increasing the quality of the basis set to include triple and quadruple polarizations does not bring any improvement. For spin-spin couplings, the inclusion of relativistic effects with ZORA including spin-orbit coupling (SOC) led to a less dispersed set of results for ¹³C NMR signals relatively to scalar ZORA calculations.

Autschbach and Coll. [169,170] have recently (2016) investigated theoretically using DFT calculations combined with two-component ZORA and four-component Dirac–Kohn–Sham (DKS) relativistic frameworks, the SOC effects in a uranium(VI) complex regarding NMR chemical shifts. Gas-phase structures were optimized using def2-TZVP basis sets and the PBE functional [148], as well as with two hybrid PBE0 [149] and B3LYP functionals [86,87]. Bulk solvent effects on the optimized structures and on the computed NMR shieldings were simulated via the conductor-like screening

model (COSMO) [169]. Their study aimed to reassess the giant spin–orbit effects on NMR shifts observed for closed shell uranium(VI) complexes, investigating the role of the exchange–correlation response kernel. As reported by the authors [169], the considered exchange–correlation kernel in two-component ZORA/DFT calculations is crucial to properly predict the giant ^1H NMR shifts in closed-shell uranium(VI) hydride complexes, and also of the extremely large SOC induced ^{13}C shifts for uranium(VI)-bound carbon atoms. The range for unknown shifts with the revised approach was successfully predicted, and further predictions have been made for complexes that are synthetically known.

Finally, the magnetic susceptibility of actinide(III) cations has been intensively investigated by synergetic experimental and theoretical study, as reported by H. Bolvin and Coll. [177]. Through DFT and SO-CASPT2 calculations, the authors aimed to rationalize the experimental magnetic susceptibilities of $[\text{An}(\text{H}_2\text{O})_9](\text{CF}_3\text{SO}_3)$ actinide(III) aqua complexes ($\text{An} = \text{Pu}, \text{Am}$ and Cm). The geometry optimizations were performed using the B3LYP functional and an implicit solvation model. Once magnetic susceptibility measurements of An(III) cations were corrected from radioactivity effects, SOC-CASPT2 calculations have been used on free ions and aquo complexes to calculate the electronic structure explaining the magnetic properties of Pu(III), Am(III) and Cm(III). EPR is a useful tool to probe molecular magnetic properties. This tool was used to study U(V) nitride complexes [178]. The relative importance of the investigated spin–orbit and crystal field interactions explains the different ground states of the nitride complexes relative to oxo isoelectronic species. In addition, U(V)-U(V) super-exchange coupling in dimers of these complexes has been studied in relation with EPR experiments [178]. Through EPR and magnetic susceptibility measurements, another U(V)-U(V) system, namely $\text{U}[\text{ArOSeOAr}]_2(\text{THF})_2(\mu_2\text{-OC}_6\text{H}_4\text{O})$, which is found to exhibit unusual magnetic properties, also deserves to be highlighted [179].

4. Conclusions

The DFT computation of magnetic coupling constants of polynuclear actinide complexes, mainly of uranium, is now well documented. Several magnetic dinuclear or trinuclear uranium complexes have been successfully investigated; the tried and tested methodology makes use of the broken symmetry approach and a hybrid DFT functional, mainly the B3LYP one. A variety of bridging ligands between the uranium centers have been considered either experimentally or theoretically; among them, imido or ketimide phenyl and benzoquinonoid-based conjugated bridges, but also oxo, nitrido and chalcogeno bridges. Bis- and tris-uranyl-based complexes have also been investigated, as well as inverted-sandwich uranium species. Complexes containing uranium in different oxidation states, U(V), U(IV) and U(III) leading to magnetic electron configurations, $5f^1\text{-}5f^1$, $5f^2\text{-}5f^2$ and $5f^3\text{-}5f^3$ have been studied; the ferromagnetic or antiferromagnetic character of the coupling is generally correctly predicted by DFT computations. The magnetic properties of such complexes arise from spin polarization and super-exchange, which are rationalized thanks to frontier MO and spin density analyses. DFT studies regarding mononuclear uranium complexes, SMMs and mixed $5f\text{-}3d$ or $5f\text{-}4f$ actinide-transition metal and actinide-lanthanide species, are very scarce in the literature.

Encouraging results have been obtained over recent decades by applying DFT calculations to investigate and rationalize magnetic exchange coupling within actinide polynuclear systems. The generally good agreement between DFT results and the experimental findings gives us confidence that this computationally-cheap approach will remain useful, even if more sophisticated and accurate post-Hartree-Fock treatments will be more developed in the future, thanks to the increasing power of computers.

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