

Understanding Covalency in Molecular f block Compounds from the Synergy of Spectroscopy and Quantum Chemistry

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Abstract

One of the most intensely studied areas of f block chemistry is the nature of bonds between the f element and another species, and in particular the role played by covalency. Computational quantum chemical methods have been at the forefront of this research for decades, and have a particularly valuable role given the radioactivity of the actinide series. The very strong agreement that has recently emerged between theory and the results of a range of spectroscopic techniques not only facilitates deeper insight into the experimental data, but also provides confidence in the conclusions from the computational studies. These synergies are shining new light on the nature of the f element–other element bond.

[H1] Introduction

The covalent bond is a central concept in chemistry. We are introduced to it early in our chemical journeys, through the ideas of shared electron pair bonding and Lewis structures, and *via* molecular orbital (MO) theory¹. The latter tells us that the constructive mixing of atomic orbitals (AOs) on two (or more) adjacent atoms leads to a build-up of electron density in the internuclear region, and hence to chemical bond formation. This fundamental concept underpins much of our understanding of chemical structure, reactivity and spectroscopy.

Nowhere in the periodic table is covalency more hotly debated than in the f block, and particularly the actinide (5f) series. In part, this is due to the number of valence AOs that are, in principle, available for bonding – 5f, 6p, 6d and 7s for the actinides – but the situation is further complicated by the changing energy and radial extension of these orbitals as the series is traversed. For the lighter actinides (Ac, Th), the 5f orbitals are higher in energy than the 6d, but while the former become more stable and contracted with increasing atomic number, and hence less available for spatial overlap with the AOs of surrounding atoms (typically the valence orbitals of p block-based ligands), the latter remain relatively unaltered. This leads to a change in chemistry from transition metal-like behaviour for the elements up to Pu, for example a pronounced variability of oxidation state, to more lanthanide-like behaviour by the middle of the series (Am, Cm), that is, predominant ionic bonding and a more limited range of oxidation states². The radial contraction of the 5f orbitals can also lead to the unusual situation in which their mixing with the AOs of surrounding atoms is primarily driven not by spatial overlap but rather by AO energy matching. By contrast to overlap-driven covalency, energy degeneracy-driven covalency does not lead to a significant build-up of electron density in the internuclear region, and much effort has been devoted to untangling the roles of these two types of covalency in a wide range of actinide compounds³⁻⁸. The differences between covalency in the s, p and d blocks, and f-based covalency in the lanthanide and actinide series, are summarised in Table 1. Studies of f element covalency are not only of fundamental interest, but are also important for designing ligands to effect chemical separation of the actinides from lanthanide fission products in spent nuclear fuel⁹⁻¹³, and for designing molecular precursors to new nuclear fuels¹⁴⁻¹⁶.

Computational quantum chemistry¹⁷ plays a key role in furthering our understanding of chemical bonding throughout the periodic table. This is especially true for the 5f series¹⁸⁻²⁰, where the severe radioactivity of most of the actinides limits their experimental study. However, in recent years there has been a substantial growth in the use of spectroscopic techniques to provide experimental data that links holistically with molecular quantum chemical calculations, thereby gaining greater insight than the use of either approach in isolation. Two of these techniques - nuclear magnetic resonance (NMR) and X-ray spectroscopies – form the principal focus of this review, as they provide unique platforms for exploring covalency in diamagnetic and paramagnetic f element systems, respectively. We focus primarily on molecular studies as this is where covalency studies have been best developed. Indeed, it is only in the last 10-15 years that molecular computational quantum chemical tools have developed to the point that they can furnish detailed understanding of f-block bonding *via* their synergy with the spectroscopic techniques. The majority of our examples are from the 5f series, with supporting lanthanide examples where appropriate, as covalency is typically larger in the actinide series. Following an overview of the computational methods employed, developments in NMR and X-ray spectroscopies are discussed. We then touch on two other, emerging spectroscopic techniques used to address f block covalency (electron paramagnetic resonance (EPR)

and magnetic circular dichroism (MCD)), before drawing the review to a close with an outlook on the future of this research area.

[H1] *Electronic Structure Methods and Analysis*

As in a great many areas of chemistry, Density Functional Theory (DFT)^{21,22} and its time-dependent extension (TDDFT)^{23,24} are the mainstays of theoretical efforts in this field. They are employed to provide details of a system's ground state electronic structure and its subsequent response to interactions with electromagnetic radiation. However, in situations where the electronic structure demands a more sophisticated theoretical treatment, for example when single determinantal descriptions are insufficient, post Hartree-Fock (HF) methods such as Coupled Cluster (CC)²⁵, Configuration Interaction (CI)²⁶ and Complete/Restricted Active Space Self-Consistent Field (CASSCF/RASSCF)^{27,28} approaches are more appropriate. An alternative is to derive the details of the complex electronic structure associated with the f element centre *via* multiplet theory (see reference 29 for a detailed discussion), with parameters increasingly derived from *ab initio* Ligand Field Theory (AILFT)³⁰⁻³².

The quantum chemical methods outlined above yield electronic structures in terms of sets of MOs. These MOs, however, are physically unobservable and do not provide a unique description of electronic structure, so care should be taken when using them in interpretation, analysis and property determination³³. A number of more robust analysis approaches have been developed to better characterise bonding and covalency, and these typically make use of the electron density ρ (an observable which, in principle, is experimentally accessible). Löwdin demonstrated that the electron density can be decomposed into a set of unique Natural Orbitals (NOs)²⁶, derived from the density matrix. This concept was extended by Weinhold³⁴ to generate orbitals emphasising characteristics of chemical interest. It is now common to discuss covalency and bonding in terms of these Natural Bond Orbitals (NBOs) and Natural Localised Molecular Orbitals (NLMOs)³⁵. A similar approach can be used to determine the nature of electronic transitions, *via* Martin's Natural Transition Orbitals (NTOs)³⁶, derived from the transition density matrix. The density matrix can also be used directly to provide a measure of bond order, with the two most well-known approaches being the Wiberg³⁷ and Mayer³⁸ bond orders; the latter can be interpreted as a generalization of the former. Finally, the spatial properties of the electron density are increasingly employed in chemical analysis, *via* Bader's Quantum Theory of Atoms in Molecules (QTAIM)³⁹⁻⁴¹. Here, the topological characteristics of the scalar field associated with the electron density are exploited to determine contiguous atomic volumes, or basins. Each basin is a proper open quantum system, allowing molecular properties to be unambiguously determined in terms of atomic contributions. Of most relevance to bonding and covalency are the magnitude of the electron density at the bond critical point (BCP) ρ_{BCP} which lies on the interatomic surface between two bonded atoms, and the delocalisation index (DI), which measures the degree of electron sharing between atoms and also serves as a measure of bond order. The QTAIM has also been extended to provide a rigorous energy decomposition scheme, the Interacting Quantum Atoms (IQA) approach⁴². A brief glossary summarising the key computational analysis tools, and some of the experimental methods covered herein, is provided at the end of this review.

[H1] NMR Spectroscopy

The use of NMR spectroscopy to study f block compounds is a growing area of research, and many different NMR active nuclei have been probed. Here, we focus on solution NMR studies (or solution in combination with solid state NMR) of covalency in closed-shell, diamagnetic molecular f block compounds, while acknowledging the use of ^{17}O solid state NMR to study $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ and UO_2CO_3 ⁴³ and AnO_2 (An = Th, U-Am)⁴⁴, and ^{19}F solid state NMR to investigate ThF_4 ⁴⁵ and UO_2F_2 ⁴⁶.

Although paramagnetic compounds are more typical of the 4f and 5f series than diamagnetic f block compounds, the quantum chemical computation of their NMR properties is substantially more challenging, and studies of such systems have lagged well behind. Nevertheless, there are sufficient examples of the latter to furnish much useful insight, as we now set out in an approximately chronological approach, following the development of the field over the last decade or so. The theoretical methodology which underpins much of this section has very recently been summarised elsewhere⁴⁷. A noteworthy feature of the studies described below is how the accuracy and reliability of experimentally-determined chemical shifts has allowed computational chemists to benchmark their methodology. For example, hybrid density functionals, which generally provide improved descriptions of electronic structure vs the pure (generalised gradient corrected) functionals by incorporating a certain percentage of the exact exchange from Hartree-Fock theory, are the mainstay of work in this area, and the percentage of Hartree-Fock exchange required to achieve best agreement with experiment is often explored computationally. The typically excellent agreement between computed and experimental chemical shifts that results from this process gives confidence in the subsequent computational analyses of covalency.

The effects of spin-orbit coupling (SOC) are known to play a role in the NMR of transition metal hydrides, and it has been argued that such effects would be larger in the early 5f series on account of f orbital involvement in the M–H σ bonding⁴⁸. To explore this, the ^1H chemical shifts δ were computed for a series of d^0f^0 metal-bound hydrides, featuring examples drawn from the early actinide series (An = Th, Pa, U) and also several Hf, Ta and W compounds. As illustrative examples, we consider two pairs: $[\text{HMF}_5]^{2-}$ (M = Hf, Th) and HMF_5 (M = W, U). The computed ^1H chemical shifts in the former pair are rather similar, 9.6 ppm vs 16.5 ppm, respectively. By contrast, while HWF_5 has a ^1H chemical shift of 30.7 ppm, that of the U analogue is 254.8 ppm. Breaking down these values into scalar and SO components shows that it is the latter which is very much the driver of these differences, which can be rationalised on the basis of the metal orbital contributions to the M–H bond. NLMO analysis of this in HMF_5 (M = W, U) shows that, while both have 47.2% metal character, for W this is 83.9% d with only 0.2% f contribution, but U has a 66.8:22.4 f:d ratio. Analogous NLMO data for $[\text{HThF}_5]^{2-}$ indicate the metal contribution to the M–H bond is less than a third of that in HUF_5 , and with much less f character, in agreement with its significantly smaller ^1H deshielding. These detailed molecular orbital composition data therefore support the initial hypothesis by showing that large 5f contributions to the M–H σ bonding are linked with substantial SOC-driven deshielding.

Further support for the important role played by SOC came from study of the uranyl(VI)–alkyl complex $[\text{Li}(\text{DME})_{1.5}]_2[\text{UO}_2(\text{CH}_2\text{SiMe}_3)_4]$ ⁴⁹. The methylene ^{13}C resonance of this species was determined to be so downfield (242.9 ppm) that it prompted re-evaluation of the analogous

resonance in the related homoleptic hexaalkyl complex $[\text{U}(\text{CH}_2\text{SiMe}_3)_6]^{50}$. This led to a dramatic re-assignment of its methylene ^{13}C chemical shift from 34.0 ppm to 434.4 ppm. The calculated chemical shifts in both uranium complexes are close to experiment, particularly for $[\text{UO}_2(\text{CH}_2\text{SiMe}_3)_4]^{2-}$, and the origin of the very large deshieldings was once again traced to SOC arising from the U f contribution to the U-C σ NLMOs. Moving to the lanthanide series, similar conclusions were reached from an NMR and DFT study of a pair of Ce(IV)-C_{aryl} compounds⁵¹. Agreement between the experimental and calculated $^{13}\text{C}_{\text{aryl}}$ chemical shift is excellent only at the SOC level, and the SOC-driven deshielding is a consequence of the Ce 4f and 5d contributions to the Ce-C_{aryl} σ bond.

The chemical shift δ is obtained from the computed shielding σ by comparison with the shielding of a chosen reference compound. σ can be broken down into three components, the diamagnetic term σ^d , the paramagnetic term σ^p and the SO term σ^{so} . Deeper insight into the nature of the f-element–other element bond can be obtained by evaluating the contributions from each of these terms. Combined experimental and computational determination of ^{77}Se and ^{125}Te NMR chemical shifts in a series of thorium (IV) chalcogenide systems $[\text{Th}(\text{E})\{\text{N}(\text{SiMe}_3)_2\}_3]^-$ (E = Se, Te), and their oxo-U(VI) congeners, revealed excellent agreement between measurement and calculation⁵². Furthermore, trends in the ^{77}Se and ^{125}Te NMR data across a range of systems, assembled by supplementing these Th and U targets with other isoelectronic early actinide compounds, were dominated by the σ^p term. Ramsey's formula⁵³ states that σ^p is proportional to the overlap of the magnetically coupled orbitals (which is related to bond covalency), inversely proportional to the cube of the radial expansion of the shielding electrons from the nucleus in question, and also inversely proportional to the energy separation between the corresponding occupied and virtual orbitals. In the early actinide (An) systems⁵², the key magnetic orbitals are the An-E σ and π bonding MOs, the former coupling to vacant An-E π^* MOs and the latter to σ^* . A larger An-E covalency will enhance the overlap of the magnetically coupled bonding orbitals with vacant, mainly metal-centred orbitals and hence cause larger deshieldings. Figure 1 shows the correlation between computed ^{77}Se chemical shifts and the QTAIM DI covalency metric for the early actinide and transition metal systems⁵², and features excellent linear relationships within the Th family, the Pa/U family and the transition metal series. Separate linear fits are required for the Th vs the Pa/U compounds owing to the specific metal contributions to the key MOs; the Th systems have almost no f character (as is also the case, of course, for the transition metal systems) whereas the Pa and U compounds show appreciable f-based covalency. The strong relationship between NMR chemical shift and QTAIM DI was further supported by study of Th(IV)-bound carbon atoms in structurally-related alkyl and carbene systems⁵⁴, where an R^2 value of 0.956 was determined across nine compounds. By contrast to the previous ^{77}Se and ^{125}Te data, however, the changes in the total ^{13}C shifts are determined not only by the σ^p term, but also σ^{so} , which is in general more pronounced for systems with larger $\sigma(\text{Th-C})$ bond covalency.

Computationally replacing the I ligands in the experimentally known $(\text{py})_6\text{Th}_2\text{I}_4(\mu_2\text{-Se}_2)_2$ complex by Br and Cl leads to increases in the Th–Se distances, upfield ^{77}Se chemical shifts and reductions in the Th-Se DI. The data were rationalised in terms of the π donor ability of the halide ions; replacing I⁻ by Br⁻ or Cl⁻, which are better π donors, reduces the Th-Se bond covalency⁵⁵. The effects of ligand

modification have also been explored using ^{13}C NMR, in an elegant study of uranium(VI)-acetylide complexes of the general formula $\text{U}(\text{O})(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{R})[\text{N}(\text{SiMe}_3)_2]_3$, where the para substituent $\text{R} = \text{NMe}_2, \text{OMe}, \text{Me}, \text{Ph}, \text{H}$ or Cl experimentally, with CN and NO_2 also being studied computationally⁵⁶. Almost perfect linear correlations were found between experimental ^{13}C δ values for the uranium-bound C atom and U-C DIs and WBIs, as well as between these bond order metrics and calculated ^{13}C data. Higher frequency ^{13}C shifts correlate with greater U-C covalency, which occur with more electron donating R groups, which also generate shorter computed U-C distances. Analysis of the calculated shieldings shows that σ^d is largely unaltered across the series of molecules. Instead, the overall value of δ is dictated by changes in σ^p and σ^{s0} , both of which become less negative as the electron donating ability of R decreases. Invoking Ramsey's formula, the calculated ^{13}C chemical shifts correlate strongly with the reciprocal of the energy of the LUMO, which is a U-based f orbital in all cases.

The degree of covalency and its link to SOC was further explored in a solution ^{15}N NMR study of two Th nitride systems, the bridging $[(\text{R}_2\text{N})_3\text{Th}(\mu\text{-N})(\text{Th}(\text{NR}_2)_3)]^-$ ($\text{R} = \text{SiMe}_3$) and the terminal parent amide $[\text{Th}(\text{NR}_2)_3(\text{NH}_2)]^{57}$. The experimentally determined ^{15}N chemical shifts in both systems were well-reproduced computationally only when SOC was included, but the downfield shift induced by SOC is significantly larger in the bridging system than the terminal. This was linked to greater Th-N covalency in the former, evidenced by larger Wiberg Bond Indices (WBIs, 0.94 vs 0.65) and NLMO composition data. These same two systems were also studied by solid state ^{15}N NMR spectroscopy⁵⁸. Such measurements can yield the principal components of the chemical shift tensors, that is δ_{xx} , δ_{yy} and δ_{zz} , and the tensor span $\Omega = \delta_{xx} - \delta_{zz}$ can give information on chemical bonding. The experimentally measured Ω for the bridging system is significantly larger than the terminal (847 ppm vs 237 ppm), which computational analysis traced to larger covalency in the $\sigma(\text{Th-N})$ bonds of the former and larger SOC due to significant Th 5f contribution to those bonds.

Comparisons of covalency in f and d block compounds are frequently made, with transition metal systems generally featuring more covalent linkages than f block equivalents. It was therefore striking that computational analysis of the $\text{U}\equiv\text{N}$ $\sigma + 2\pi$ triple bond in the terminal uranium(VI)-nitride¹⁵ $[\text{U}(\text{N})(\text{Tren}^{\text{TIPS}})]$ ($\text{Tren}^{\text{TIPS}} = \{\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3\}^{3-}$) showed it to be similarly covalent to analogous transition metal nitrides. The development of NMR spectroscopy as a tool for probing covalency allowed the further exploration of this rather surprising result, and a combined solution and solid-state ^{15}N NMR study, linked with DFT calculations, was reported⁵⁹. By contrast to several other studies, σ^{s0} was found to be small, which was traced to the small N 2s character in the U-N σ bond, small Fermi contact term, and hence little SO-induced spin-polarisation transfer to the ^{15}N nucleus. σ^p was identified as the principal factor in determining the ^{15}N δ and, given that σ^p is a direct reporter of covalency, correlations were sought between δ and several computational measures of bond order across a range of d^0f^0 transition metal and actinide nitrides. The best such correlation was found with the Mayer Bond Order (MBO), for which $R^2 = 0.862$. This analysis revealed that the $\text{U}\equiv\text{N}$ linkage is, remarkably, even more covalent than transition metal analogues, supporting the computational predictions from a decade earlier.

Bond order metrics such as the QTAIM DI and the WBI are not the only indicators of covalency to correlate well with NMR chemical shifts. V_{xc} , the exchange-correlation contribution to the interatomic interaction energy from IQA theory, is a covalency metric which has recently been introduced to the f block⁶⁰. It was used in a study which combined ²⁹Si NMR experiments with DFT calculations to probe the covalency in M(II)-silanide bonds for a range of s and f block metals⁶¹. Agreement between measured and computed ²⁹Si chemical shifts was excellent, and good correlations were observed not only between ²⁹Si δ and M-Si DIs, but also between ²⁹Si δ and M-Si V_{xc} data. A series of 20 molecules was studied computationally, involving five different silanide ligand environments and four different metals in the +2 oxidation state; Mg, Ca, Yb and No. The ²⁹Si chemical shifts were found to depend primarily on the σ^p term when the metal is held constant and the ligand varied, but on σ^{so} when the metal is varied for a given ligand set. The latter variation was traced to the metal d contribution to the M-Si bonding NLMO, which transmits metal d-based SO shielding to the ²⁹Si nucleus *via* Si 3s character. Ramsey's formula was invoked to link the changes in σ^p to variations in orbital overlap-driven covalency, with a covalency ordering of No(II) > Yb(II) > Ca(II) \approx Mg(II).

The most recent addition to the field featured the introduction of a new NMR-active nucleus to probe f block covalency. Solution and solid state ³¹P NMR experiments were used to study the bonding in a series of Th-P compounds, all based on the TREN^{TIPS} ligand, and spanning Th-PH₂, Th=P, Th-P(H)-Th and Th=P=Th linkages⁶². NLMO analysis revealed unusually large Th s contributions to the Th-P σ bonding. For example, the Th-PH₂ linkage has 12% Th character overall, with a 26:54:19 7s:6d:5f breakdown. Correlations of ³¹P chemical shifts with MBO data for the Th targets, plus a further 57 transition metal-phosphorus compounds drawn from groups 3-10 and all three transition series, are weaker than typically observed. This is particularly true when compared with the correlations for the N-based TREN^{TIPS} systems discussed in reference 59. It was concluded that the P-ligand environments are more sensitive to the nature of the ancillary ligands than the harder N-based donors.

In summary, the studies discussed in this section have shown that SOC effects can lead to very significant deshieldings in the signals of f element-bound NMR active nuclei, and that this SOC results from both f and d orbital-driven covalency in the metal-ligand bonding. Breaking down the computed shieldings into diamagnetic σ^d , paramagnetic σ^p and spin-orbit σ^{so} contributions shows that the latter two terms, and in particular σ^p , tend to dominate NMR trends. As σ^p is related to covalency through its dependence on the overlap of the magnetically coupled orbitals, very strong correlations are found between NMR chemical shifts and computational covalency metrics such as the WBI and the QTAIM DI and V_{xc} , demonstrating that chemical shift is a sensitive reporter of covalency. The use of NMR chemical shifts to assess covalency in analogous transition metal and f block compounds has shown that in some cases the latter feature metal-ligand bonds which are, remarkably, more covalent than their d block equivalents.

[H1] X-Ray Spectroscopy

The first applications of X-ray absorption spectroscopy (XAS) to the study of f element covalency exploited excitation at the ligand K edge, that is, promotions of ligand 1s electrons. Originally

developed as a means to investigate bonding in transition metal coordination complexes⁶³, this methodology exploits MO orthogonality to infer the covalency in bonding MOs from the absorption intensity of antibonding MOs. Subsequently, researchers have also made use of the metal L₃ and M_{4/5} edges, associated with excitations of metal-based 2p and 3d electrons, respectively, to further develop understanding of bonding and electronic structure in f element complexes. It should be noted, however, that ligand K-edge spectra are typically more feature-rich owing to the accessibility of a broader range of ligand MOs. The calculation of XAS spectra of lanthanide and actinide compounds with relativistic active-space based approaches, in which the exact wavefunction is accurately approximated through the combination of a large number of electronic configurations, has recently been highlighted⁶⁴. Two key advantages of active space simulation methodologies in the interpretation of XAS data lie in their ability to better describe core-relaxation effects and to demonstrate the complexity of the relationship between specific electronic excitations and observed spectral features.

In a landmark study, Cl K edge spectroscopy was applied to actinide-containing systems in an investigation of bonding in thorium and uranium metallocene dichlorides⁶⁵. This built upon previous studies of analogous group (IV) transition metal (M = Ti, Zr, Hf) compounds⁶⁶. Pre-edge features provided direct evidence of covalent M-Cl orbital mixing, an observation qualitatively supported by TDDFT simulations. Combined, these approaches revealed the origin of the observed pre-edge features as Cl 1s → M *nd* transitions for Ti, Zr and Hf, and Cl 1s → M 5f/6d transitions for U and Th. Furthermore, decomposition of MOs into atomic contributions helped determine that Cl 3p contributions to the M-Cl bonds were greater than 20% for the transition metal complexes, reducing to a still non-negligible 9% for the U analogue. This demonstrated that actinide covalency, while less pronounced than that of transition metal analogues, was nonetheless substantial and experimentally observable.

The organometallic chemistry of the f-block is interesting in part due to the elements' large ionic radii, which support ligation by multiple large ligands. The An(IV) oxidation state was also investigated in an early application of C K edge XAS to the prototypical actinide organometallics, AnCOT₂ (An= Th, U; COT = η⁸-C₈H₈)⁶⁷. Here, TDDFT was combined with Configuration Interaction Singles (CIS) calculations to assign observed pre-edge features to transitions into valence MOs with both An 5f_δ and 5f_φ character. While both transitions were found to have substantial intensities in the Th complex, the 5f_φ transition was largely suppressed in the U analogue, attributed to the substantially increased metal character of the MO (Th: 65%, U: 94%). Nonetheless, this study represented, to the best of the authors' knowledge, the first experimental evidence of φ-type orbital mixing. The same approach, complemented by magnetic studies and RASSCF simulations, was taken to explore the related [U(η⁷-C₇H₇)₂]⁻ anion, a rare example of a pentavalent uranium organometallic⁶⁸. The simulated XAS spectrum accurately reproduced experimental features and intensities when blue-shifted by ~20 eV, required to account for the lack of core-hole relaxation in the simulations. Decomposition of the associated NOs showed substantial mixing between U 5f and ligand π orbitals and enhanced U 5f_δ bonding interactions greater than those observed in tetravalent UCOT₂, consistent with previous EPR data⁶⁹. This owed to the better energy match with the frontier ligand orbitals of appropriate symmetry that occurs as the U 5f orbitals decrease in energy with

increasing oxidation state. ϕ -type orbital mixing in the core-excited states, similar to that found in UCOT₂, was also reported. These studies demonstrated the applicability of XAS to organometallic species, as well as the exotic bonding motifs that simulation can characterise.

The only known tetravalent lanthanide analogue of the actinocenes, cerocene (CeCOT₂), has provoked decades of debate – primarily focused on the metal's oxidation state - owing to its complex electronic structure⁷¹⁻⁷⁴. Ce M_{4,5} edge XAS studies identified substantial Ce 4f and 5d mixing with symmetry matched ligand orbitals⁷⁵. To interpret these XAS data, CI simulations found that the Ce(III) contribution to the electronic ground state was in line with that expected for strongly-correlated materials and larger than that found for typical Ce(IV) compounds, with overall covalency similar to that of the uranium analogue⁶⁷. Shortly afterwards, RASSCF studies of the Ce L₃ edge of cerocene⁷⁶ were reported, reproducing the dominant spectroscopic features and providing a 2p → 5d assignment. A careful and detailed analysis of excited state electronic structures was performed using a novel application of NTOs. Experimentally, the Ce L₃ edge spectrum is well-documented as having a two-peak structure and this analysis allowed characterisation of this structure in terms of a clear difference in Ce 4f occupation.

Over the last 15 years, the chemistry of the lanthanides in the +2 oxidation state has grown⁷⁷⁻⁸⁰ and XAS has found application in understanding the electronic structure of these Ln(II) compounds. Studies of the Ln(II)Cp'₃ (Cp' = η^5 -C₅H₄SiMe₃) organometallics⁸¹ employed ground state DFT simulations to estimate the observed L₃ edge core excitations. Although requiring substantial shifts of 421 eV (Sm) and 348 eV (Ho) to align with experiment, these simulations demonstrated that the observed spectral features again corresponded to excitations with primarily Ln 2p → 5d character. Combined spectroscopic and computational data showed a destabilisation of 7-8 eV in the L₃ edge position for compounds exhibiting a "traditional" Ln 4fⁿ⁺¹ configuration, by contrast to those with a 4fⁿ5d¹ configuration. Given the substantial variation in interelectronic repulsion between these two configurations, a commensurate difference in covalent bond character might be expected, although this wasn't reported.

Perhaps the best understood and characterised actinide complex is uranyl (UO₂²⁺, Figure 2a), featuring a key structural motif in high oxidation state actinide chemistry in the linear actinyl unit, O=An=O. Uranyl was, in fact, the subject of a very early application of ligand K edge XAS to the study of actinide bonding^{82/51}. There, the Δ -SCF method, in which excited electronic states are approximated through the restriction of orbital occupation based on symmetry arguments, was employed within a DFT framework to assign the observed pre-edge features and provide qualitative measures of covalent bond character, as well as identifying the role of the pseudocore 6p level in bonding. The results of these somewhat primitive simulations have since been verified with more sophisticated methods^{83,84}. The high symmetry of the actinyls, and specifically the presence of a centre of inversion, has allowed for the recent quantitative differentiation between 5f and 6d contributions to covalency. In the uranyl analogue [U(NR)₂Cl₄]²⁻ (R = ^tBu, Ph), equatorial U–Cl bonding⁸⁵ was investigated, with multiple pre-edge features identified in the 2819 - 2925 eV range and assigned by DFT as ¹A_{1g} → ¹A_{2u} and ¹A_{1g} → ¹E_u transitions. Despite the presence of strongly coordinating axial imido ligands, equatorial U–Cl bond covalency was similar to that reported

previously^{65,86}, with Cl 3p contributions to orbitals with U 6d character approximately 30% higher than those with 5f character.

The Resonant Inelastic X-ray Scattering (RIXS) technique has gained favour in recent years. RIXS provides access to a broader range of spectroscopic data *via* application of the Kramers-Heisenberg expression⁸⁷, which considers both excitation and emission processes to provide a two-dimensional mapping of a complex's interactions with X-ray radiation (Figure 2d). By considering the variation in excitation intensity at maximal emission intensity, RIXS provides the basis for High Energy Resolution Fluorescence Detection (HERFD)-XAS. This exploits the longer intrinsic core-hole interaction lifetime of an intermediate state to provide increased resolution in the absorption process⁸⁸. A simulation of the 3d4f RIXS map of uranyl using RASSCF simulations was recently reported: shifting energies by -13.6 and -21.2 eV for excitation and emission processes, respectively, necessary to reflect the fact that the strong spin-orbit splitting experienced by the U 3d shell is only incorporated in a post-SCF treatment, gave alignment with spectroscopic data and allowed for full assignment of the experimental RIXS map^{70,89}. Very recently, a variational spin-orbit coupled multiconfigurational study in which SOC has been included within the SCF procedure has been conducted⁹⁰. The results suggest that peaks in the uranyl M₄ edge HERFD-XAS spectrum may be partly attributable to “shake-up” features arising from concerted processes involving both core and valence electronic excitations⁹⁰.

For the plutonium analogue, HERFD-XAS was combined with multiplet theory to help interpret the ground state electronic structure from XAS data⁸⁹. By contrast to U and Np, Pu 5f orbital localisation was largely unaffected by changes in oxidation state or chemical environment: a trend of decreasing An-O_{yl} orbital mixing from U to Pu was also identified. Attribution of this to stronger overlap between U 5f/6p and O 2p orbitals showed that the overlap-driven covalent character of An-O bonds in the actinyls decreases across the U-Pu series, while the energy degeneracy-driven covalent character increases without increasing the electron density accumulating in the bond.

When comparing the bonding of Group 4 transition metals with that of uranium in [MCl₆]²⁻ compounds⁸⁶, the U-Cl bonds were experimentally determined to contain greater (18%) Cl 3p character than those of Ti, Zr and Hf. This is in contrast with the bonding characteristics of these elements in metallocene dichlorides⁶⁵. The most pronounced pre-edge features were attributed to Cl 1s → U 6d transitions, with the octahedral symmetry of these species allowing DFT to quantify specific orbital interactions, albeit with TDDFT-predicted intensities contradicting spectroscopic data. Similar covalency was also identified in the lower symmetry [UOCl₅]²⁻ compounds. Extending the study of actinide hexachlorides into the transuranics, greater Cl 3p mixing was demonstrated with An 6d than 5f orbitals, with 6d decreasing and 5f orbital mixing increasing from Th-Pu. Energy-degeneracy driven covalency was more dominant in the Pu species than the Np and U analogues⁷, in agreement with studies of the actinyls⁸⁹. Interestingly, this assertion has been challenged by recent RASSCF simulations, suggesting that the enhanced An 5f – Cl 3p hybridisation determined by simulations for certain actinides (for example, Np and Pu) may be dependent on the methodology employed⁹¹. A direct comparison of lanthanide and actinide bonding in the +3 oxidation state was provided using XAS in, to the best of the authors' knowledge, the only report of the Am-Cl bond⁹². As with the lighter actinides, Am 6d bonding contributions in [AmCl₆]³⁻ dominated those of the 5f

shell but, remarkably, Eu 5d contributions in the lanthanide analogue $[\text{EuCl}_6]^{3-}$ were of similar magnitude to those in the Am complex. Eu 4f covalency was, however, substantially lower than the 5f covalency of the Am complex, confirming a hypothesis put forward by Seaborg over five decades earlier⁹³.

Considering other lanthanide analogues, fascinating evidence of a 4f contribution to bonding in the Ce(IV) compound $[\text{CeCl}_6]^{2-}$, nearly twice that reported for the 5f contribution in the U(IV) analogue, has been reported⁹⁴. TDDFT was again used to demonstrate a common bonding motif across the trivalent lanthanides from Ce to Gd, wherein non-negligible Ln 5d orbital mixing of up to 13% was identified from MO decomposition.

While the chemistry of cerium in the +4 oxidation state is well-established, only recently has access to this state for praseodymium and terbium been made readily possible⁹⁵⁻⁹⁷, and XAS has again been employed in the study of such systems. O K edge spectroscopy was leveraged to complement a combined magnetic and multiconfigurational simulation study. Pr 4f/O p hybridisation was given as the mechanism responsible for the unusual electronic and magnetic properties of extended +4 praseodymium compounds⁹⁸. DFT was also employed to interpret Ln L_3 edge data in lanthanide oxides LnO_2 (Ln = Ce, Pr and Tb)⁹⁹, demonstrating substantial and similar Ln 4f – O 2p orbital mixing in CeO_2 and PrO_2 , with a reduction in mixing for TbO_2 .

Returning to the actinides, uranium binary oxides have been investigated using uranium M_4 edge HERFD-XAS¹⁰⁰. The Anderson impurity model was used to differentiate between various chemical environments of the U centre, providing direct observation of the +5 oxidation state in such systems. A similar approach has also been used to demonstrate the interplay between experiment and simulation to contrast the electronic structures of actinide oxides with uranyl nitrate and torbernite where, for example, the variation in the crystal-field splitting of both the U 5f and 6d manifolds owing to the chemical environment could be quantified¹⁰¹. Furthermore, U $M_{4,5}$ edge HERFD XAS data on hexavalent uranium compounds with systematically lowered symmetry ($O_h \rightarrow D_{4h} \rightarrow D_{3d}$)¹⁰² were reported in which symmetry-dependent quantitative variations in spectroscopic features were observed. A combination of DFT and multiplet theory demonstrated that the dominant features were primarily a result of excitations into formally non-bonding 5f orbitals, with well-reproduced variation between systems.

Finally, an established approach to bond characterisation in f element compounds employs direct interrogation of structural metrics, from which substantial thermodynamic insight can be obtained¹⁰³. While historically restricted to X-ray Diffraction (XRD) data, for which high quality single crystals are required, the advent of X-Ray Absorption Fine Structure Spectroscopy (EXAFS) has extended this approach to the study of species in solution. A notable example is the combined EXAFS and DFT study of hydroxypyridinone (HOPO) complexes of Am–Cf in the +3 and +4 oxidation states. Here, the experimentally determined stability of the tetravalent over the trivalent species were reproduced theoretically with a commensurate increase in energy degeneracy-driven covalency reported¹⁰⁴.

In summary, the synergy of theory and experiment has proven essential in providing detailed understanding of the physical processes responsible for the observed phenomena reported by X-

ray spectroscopy researchers. In particular, peak assignment is almost entirely dependent on theoretical input, and features of more complex spectra have driven theorists to creatively apply state-of-the-art analysis to provide rationalisation. Furthermore, X-ray spectroscopy provides data best understood *via* the application of some of our most sophisticated simulation methodologies, rejuvenating interest in these approaches. Together, X-ray spectroscopy and simulation have elucidated the broad characteristics of f element covalency. Alongside the well-established enhanced covalency of actinide compounds compared to lanthanide analogues, trends of decreasing covalency with lower oxidation state, as well as reduced covalency and a transition to an energy degeneracy-driven origin across the early-mid actinide series, have been established.

[H1] Emerging Approaches

NMR and X-ray spectroscopies have been dominant in probing bond covalency in f element complexes, but other approaches also support fruitful interactions between experiment and theory. The literature regarding the application of these spectroscopic techniques is currently rather sparse but includes a number of notable studies.

The first application of EPR to the study of covalency was reported for the trivalent organometallic $[\text{An}(\text{Cp}^{\text{tt}})_3]$ ($\text{An} = \text{Th}, \text{U}$; $\text{Cp}^{\text{tt}} = \eta^5\text{-C}_5\text{H}_3\text{tBu}_{2-1,3}$) compounds¹⁰⁵. The experimental g tensor was determined for both compounds, supporting a $^4I_{9/2}$ ground multiplet for the uranium compound, an assignment supported by CASSCF-simulated g tensors. Employing Hyperfine Sublevel Correlation (HYSCORE) spectroscopy, greater spin delocalisation, and therefore covalency, was demonstrated in the U compound than in the Th analogue. The Th compound also provided surprising similarities in bonding to that of an analogous Yb compound. However, QTAIM analysis was unable to differentiate between the weak covalency observed in these complexes, with conflicting ρ_{BCP} and DI trends. Very recently, the same approach has been applied to study a range of lanthanide analogues ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}$). Much smaller hyperfine interactions than those found in the actinide compounds were observed, with *ab initio* simulations supporting the assertion of negligible covalency in these 4f organometallics¹⁰⁶. Finally, EPR was also employed in a comparative study of the related $[\text{M}(\text{Cp}'')_3]$ ($\text{An} = \text{U}, \text{Nd}$; $\text{Cp}'' = (\text{trimethylsilyl})\text{cyclopentadienyl}$) complexes and their isocyanide adducts¹⁰⁷. Again, CASSCF demonstrated a dominant $^4I_{9/2}$ ground multiplet for both compounds, providing g tensors in qualitative agreement with experimental values. NO analysis supported the presence of π bonding interactions between the U centre and the Cp'' ligands, a characteristic largely absent in the Nd analogue and rationalised by the greater radial extent of the 5f over the 4f orbitals.

The +3 oxidation state of U was also targeted in a combined EPR and MCD¹⁰⁸ study of its tris(3,5-dimethyl-1-pyrazolyl)borate (Tp^*) complexes¹⁰⁹. CASSCF simulations were again employed to rationalise experimental data, identifying substantial orbital angular momentum contributions to the observed magnetic behaviour. MCD was used to investigate 5f-5f transitions, observable owing to the large SOC present in open shell actinide compounds, with the groupings of these sharp, narrow transitions providing evidence of only slight covalent bond character. This assertion was supported by NLMO analysis, which revealed U character of 12% or less in all bonds, with the 5f shell providing only a small contribution to this figure. MCD has also been used to investigate the

rare U(V) oxidation state in the $[\text{UCl}_6]^-$ anion¹¹⁰, a study which reports a notable advance in the field, through the *ab initio* simulations of the MCD spectrum of an actinide complex. RASSCF-simulated NOs revealed non-negligible Cl 3p contributions to formally metal-based orbitals, with an expected impact on magnetic properties¹¹¹. Simulations provided good agreement with experimentally determined *g* factors, and simulated MCD spectra enabled the assignment of experimental features to either LMCT or U 5f \rightarrow 6d transitions, with quantitative agreement obtained only *via* the inclusion of dynamical correlation (Figure 3). A similar approach was taken in the study of the electronic structure of $[\text{Ln}^{\text{II}}\text{Cp}'_3]^-$ (Ln = Y, Pr, Gd; Cp' = $\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$) compounds¹¹². Broadening of the assigned 4f \rightarrow 4f transitions in the Pr complex was interpreted as being indicative of 4f-5d mixing. This may be expected to have a subsequent effect on bond character, as seen in the UV-vis region containing 5d-5d and 5d- π^* transitions, where the ligand character of the orbitals was found to impact the transition energy¹¹³.

Whilst EPR and MCD spectroscopies have some limitations in their applicability, with the former requiring open-shell electronic structures and the latter also best suited to paramagnetic systems, they nevertheless provide valuable complementary insight to the more established spectroscopies that form the main focus of this review, deepening our understanding of the complex electronic structures of the target species, as well as presenting new challenges and driving advances in our simulation methodologies.

[H1] Conclusion and Outlook

In this contribution, we have shown how recent studies have led to enhanced insight into the covalency of the f element-other element bond through the close linking of computational chemistry with experiment, primarily NMR and X-ray spectroscopies. In some cases, these studies have shown that covalency in f element complexes is even larger than in analogous transition metal systems – gone are the days when f element bonding could be dismissed as being purely ionic!

The complex nature of the transitions underlying the X-ray spectroscopic phenomena discussed in this review exposes weaknesses in our current computational methodologies. TDDFT, the most commonly applied simulation approach, is hampered by it being unable to account for core-hole relaxation effects. This manifests primarily in the need for large energy shifts to provide quantitative agreement with experiment, while the validity of the linear response formalism ubiquitous to current approaches could also be questioned when dealing with the intrinsically high-frequency X-rays. While active space approaches allow a substantial degree of core-hole relaxation, they typically only account for spin-orbit coupling in a *post hoc* fashion. Although this is of limited importance in ligand K edge spectroscopy, the splitting of the actinide 3d_{3/2} and 3d_{5/2} sublevels is ~ 200 eV, with a consequent impact on electronic structure. Active space approaches also suffer from the “exponential bottleneck” in terms of resource requirements, limiting them to relatively small and chemically well-defined systems. The future, however, is bright: algorithms explicitly incorporating SOC are becoming more widespread, while techniques circumventing the exponential bottleneck are in active development, although yet to be applied to this specific area of research.

The NMR section focused on diamagnetic systems, a considerable limitation in f element chemistry. The most obvious extension of this field, therefore, would be to open shell molecules, though this is far from straightforward in practice. As Fernández-Alcarón and Autschbach noted: “NMR of

paramagnetic molecules remains a frontier⁴⁷, although some progress has been made¹¹⁴⁻¹¹⁸. DFT is the workhorse technique of diamagnetic NMR studies, but it is unlikely that this will be the case for open shell systems. One then runs into the issues noted above concerning active space *ab initio* methods: to get sufficient spin-polarisation and dynamic correlation in the wavefunction requires very large active spaces. Although in their infancy, machine learning approaches offer hope in improving the description of strongly correlated systems¹¹⁹ and, in time, quantum computation may come to the rescue, alleviating such issues and allowing an ever-closer relationship between theory and experiment to be realised.

Glossary

Ab Initio Ligand Field Theory (AILFT)³⁰⁻³² – A theoretical approach for describing the detailed effects of the chemical environment on the electronic structure of the central ion of a coordination complex, taking into account both zero-field and crystal field splitting as well as spin-orbit coupling.

Bond Critical Point (BCP)³⁹ – In the context of the QTAIM, a point where the gradient of the electronic density vanishes and two of the eigenvalues of the Hessian are negative and the other positive. Also known as a (3,-1) critical point. Used to assess the degree of electronic charge accumulation in the internuclear region between two atoms and therefore as a measure of covalency.

Delocalisation Index (DI)³⁹ – In the context of the QTAIM, a measure of the number of electrons shared between two atoms in a molecule, derived from the 2nd order reduced density matrix. Formally, the covariance of the electron populations of the two atoms. Used as measure of covalency and of bond order.

High Energy Resolution Fluorescence Detection (HERFD)⁸⁸ – A technique for the extraction of XAS data from Resonant Inelastic X-ray Scattering maps, exploiting the longer core-hole interaction lifetime of an intermediate state to improve resolution.

Hyperfine Sublevel Correlation (HYSCORE)¹²⁰ – A two-dimensional EPR correlation technique, used to resolve overlapping signals from different ions in a molecule.

Interacting Quantum Atoms (IQA)⁴² – An extension of the QTAIM which partitions the total energy of molecular systems into intra- and interatomic terms to provide information on binding and stability, amongst many other chemical properties.

Mayer Bond Order (MBO)³⁸ – An analysis technique which can be considered as an extension of the Wiberg Bond Index (see below), incorporating non-orthogonality in the atomic basis.

Natural Bond Orbital (NBO)³⁵ – An orbital obtained from a decomposition of the density matrix focussing on the maximisation of localised 1- and 2-centre regions in order to recover the closest approximation of a Lewis-type description of electronic structure as possible.

Natural Localised Molecular Orbital (NLMO)³⁵ – An orbital encompassing the characteristics of NBOs extended to incorporate acceptor-donor delocalisation. NLMOs can be considered “semi-localised”, lying between NBOs and MOs in terms of localisation.

Natural Transition Orbital (NTO)³⁶ – An orbital obtained from diagonalisation of the transition density matrix. Used to express electronic excitation in terms of a minimal number of orbital transitions.

Quantum Theory of Atoms in Molecules (QTAIM)³⁹ – An analysis method based on the electron density as a fundamental quantity. Characterises a molecule in terms of a set of critical points (satisfying the Poincaré-Hopf relationship) and contiguous, space-filling atomic basins, from which chemical properties can be unambiguously derived.

Wiberg Bond Index (WBI)³⁷ – An analysis technique for obtaining an approximation to the formal bond order between bound atoms, based on summation of the square of off-diagonal elements of the density matrix expressed over an orthogonal atomic basis.

Author contributions

NK wrote the Introduction, and researched and wrote the NMR section. AK wrote the Electronic Structure Methods and Analysis section, and researched and wrote the XAS and Emerging Techniques sections. Both authors wrote the Conclusions and Outlook. Both authors reviewed and edited the manuscript before and after submission.

Competing interests

The authors declare no competing interests.

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Tables / Figures / Boxes

<i>s, p and d elements</i>	<i>f elements</i>
valence orbitals are the most radially extended	valence f orbitals are not the most radially extended
valence orbitals overlap significantly with orbitals of other elements both spatially and energetically \Rightarrow covalency is driven by both forms of overlap	valence f orbitals have significant overlap with orbitals of other elements only energetically \Rightarrow f-based covalency is driven primarily by orbital energy matching
covalency leads to build-up of electron density in the internuclear region and enhanced bond strength	f-based covalency does not lead to significant build-up of electron density in the internuclear region and lesser increases in bond strength

Table 1. Summary of the differences between covalency in the s, p and d blocks, and f-based covalency in the lanthanide and actinide series.

Figure 1. Correlation of calculated ^{77}Se NMR chemical shifts with the Quantum Theory of Atoms in Molecules (QTAIM) delocalization index (DI). **a** Correlation for the An-Se bond in a series of early actinide complexes $[\text{An}(\text{Se})(\text{L})(\text{NR}_2)_3]^q$. **b** Correlation for the TM-Se bond in a series of analogous transition metal complexes. Adapted from reference 52. The QTAIM DI is a well-established bond order/covalency metric in computational chemistry, and the very strong linear correlations observed clearly illustrate that NMR chemical shifts are sensitive reporters of metal–selenium covalency. That separate correlations are observed for the Th vs U (and Pa) systems is due to the principal atomic orbitals employed by the metals in their bonding; the Th systems use their 6d orbitals, with almost no 5f contributions, whereas the Pa and U compounds have appreciable 5f-based covalency.

Figure 2. X-ray absorption and emission process in uranyl. **a** Molecular structure of the uranyl ion $[\text{UO}_2]^{2+}$. **b** Schematic of the excitation process responsible for the pre-edge features in oxygen K edge (red arrow) and uranium M edge (green arrow) X-ray absorption spectra of uranyl. Ψ and Ψ^* are bonding and antibonding molecular orbitals, respectively, while ϕ_{U} and ϕ_{O} are uranium and oxygen valence atomic orbitals, respectively, and λ is a mixing parameter governing the degree of covalency. **c** Absorption and emission processes responsible for uranyl 3d4f Resonant Inelastic X-ray Scattering (RIXS). E_{ex} and E_{em} are excitation and emission energies, respectively. **d** Subsequent RIXS map: the vertical scan at maximum excitation intensity produces the Resonant X-ray Emission Spectrum (REXS) (grey) while the horizontal scan at maximum emission intensity produces the U M edge High Energy Resolution Fluorescence Detection (HERFD) X-ray Absorption spectrum (green), which can be directly compared to the lower resolution data produced by standard X-ray absorption spectroscopy (XAS) (purple). RIXS map adapted with permission from reference 70.

Figure 3. Magnetic Circular Dichroism (MCD) spectroscopy of pentavalent uranium hexachloride. **a** Electric field vectors of left- (LCP) and right- (RCP) circularly polarised light. **b** In the presence of an external magnetic field, paramagnetic species with degenerate ground states experience Zeeman splitting (ΔE) and exhibit differential absorption with respect to incident light polarisation with substantial intensities when $\Delta E \approx kT$. Differential absorption is zero in the absence of an external field. $|i\rangle$ and $|f\rangle$ are initial and final electronic states, respectively, while $\Delta\epsilon$ is the differential absorption between LCP and RCP. B is the magnetic field, g is the Landé g -factor, μ_{B} is the Bohr magneton, k is the Boltzmann constant and T is the temperature. **c** Molecular structure of the uranium hexachloride anion, $[\text{UCl}_6]^-$, which is paramagnetic with a degenerate ground state due to the presence of a single 5f-electron localised on the pentavalent uranium centre. **d** Symmetry labelled MCD spectrum of $[\text{UCl}_6]^-$, emphasising the importance of the inclusion of dynamical correlation in order to obtain quantitative agreement between theory and experiment. Experimental spectrum with $B = 7$ T, recorded at 5 K (Expt. 7T: black line), theoretical spectrum including dynamical correlation *via* 2nd order perturbation theory (PT2-SO: blue line) and theoretical spectrum in the absence of dynamical correlation (SCF-SO: red line). $\Delta\epsilon$ is the differential absorption

between LCP and RCP, whereas ΔE is the absorption energy. C-terms give the magnitude of the dominant MCD contribution to the spectra. Spectra reproduced with permission from reference 110.

Summary

We describe recent advances in the understanding of covalency in the f element–other element bond through the synergistic application of computational quantum chemistry with nuclear magnetic resonance and X-ray spectroscopies.