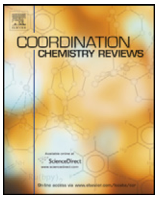
Coordination Chemistry Reviews 253 (2009) 606–624

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

The highest oxidation states of the transition metal elements

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doi:10.1016/j.ccr.2008.07.014

A R T I C L E I N F O

Article history:
Received 30 April 2008
Accepted 20 July 2008
Available online 30 July 2008

Dedicated to the memory of Neil Bartlett (1932–2008).

Keywords:
Fluorine chemistry
High oxidation states
Oxo complexes
Oxyfluorides
Quantum-chemical calculations
Transition metal elements

A B S T R A C T

The highest accessible formal oxidation states of the d-block elements are scrutinized, both with respect to the available experimental evidence and quantum-chemical predictions. The focus is on fluoride, oxide, and oxyfluoride systems. The field has evolved significantly over the past 15 years due to the availability of quantitative computational predictions of thermochemical stabilities, and of spectroscopical parameters of a number of key molecules. The demands on the computational methodology used, as well as the experimental boundary conditions needed are reviewed, and reasons for the observed trends in oxidation states throughout the 3d, 4d, 5d, and 6d series are discussed.

1. Introduction

> “*One of the major goals of inorganic chemistry is to prepare compounds of elements in unusual oxidation states. - In 1969, 238 oxidation states were known of the elements with atomic number Z between 21 and 100, that is in average 3 per element*”
> C. K. Jørgensen, *Naturwissenschaften*, 1976, 63, 292.

Consistent with this quotation by Jørgensen over 30 years ago, the concept of oxidation states is one of the most important classifications within the general and fundamental ordering principle of the Periodic Table [1,2] (see Fig. 1), indispensable throughout most of chemistry. Unusual oxidation states, both high and low, tend to capture the imagination of chemists. In this review, we focus on the highest oxidation states of the elements of the d-block, either those predicted theoretically or those confirmed experimentally. The discovery of novel inorganic species in high oxidation states helps to enhance and expand chemical understanding of the behavior of the elements and their compounds. Whether by planning or by serendipity, hitherto unrecognised trends in the Periodic Table may thus be revealed. A striking example is the discovery of noble-gas compounds by Bartlett in the 1960s [3,4]. Higher oxidation states are by no means only of academic interest: complexes in high oxidation states may serve as fluorinating agents [5,6], oxidants [7,8] and catalysts [9–13].

One development that has fundamentally transformed the search for high oxidation states since another illuminating article by Jørgensen in the 1980s [14] is the increasing use of state-of-the-art quantum-chemical methods. Jørgensen was still rather pessimistic about the quantum-chemical methods [14]. Since then their predictive accuracy has achieved a level that allows quantitative computations of thermochemical and kinetic quantities to an extent that the existence or nonexistence of certain molecular species may be predicted with remarkable success. Moreover, the quantitative computation of spectroscopic parameters may aid decisively in the subsequent experimental identification of novel species. There are many success stories of this approach in different areas of research (see, e.g., ref. [15] for a recent report on the prediction of new species by quantum chemistry). To give just two examples: (a) The possible existence of the $[N_5]^+$ ion, along with its structure, was computationally predicted in 1991 [16]. In 1999, the salt $[N_5][AsF_6]$ was synthesized and structurally characterized [17]. (b) Closer to the topic of this article, speculations about mercury in oxidation state IV had been around since the late 1970s [14,18]. In 1993, HgF_4 was predicted to exist as gas-phase molecule by quantum-chemical calculations [19,20]. In 2007, it has been characterized by IR spectroscopy in neon and argon matrices [21]. This observation does not only represent a new oxidation state for mercury, but it establishes this element as a true d-block transition metal element.

In this chapter, we review the highest experimentally known oxidation states of the d-block elements, as well as the highest possible oxidation states suggested by state-of-the-art quantum-chemical calculations. Since the publication of ref. [14], various aspects of high oxidation states of the transition metal series have been reviewed [22–36] (see also older reviews [30,31,33,37,38]). Here we will try to be comprehensive with respect to the d-block

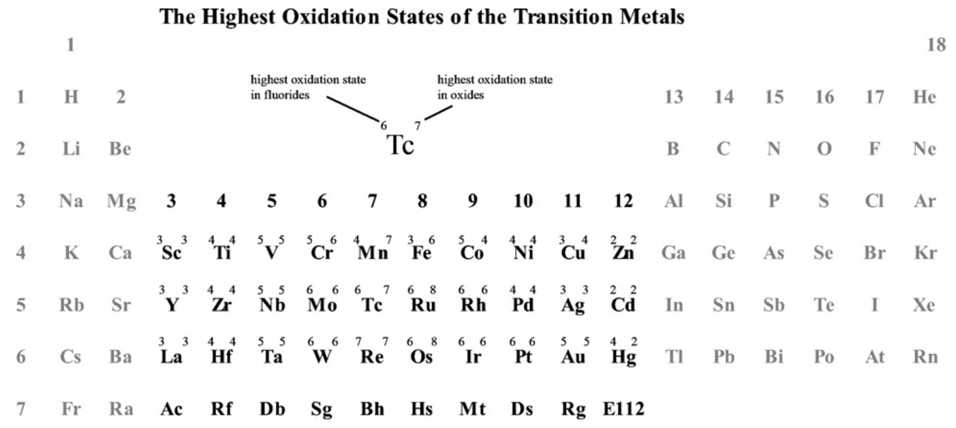

Fig. 1. Periodic Table, showing the highest experimentally known oxidation states in homoleptic fluorides and oxides, respectively.

elements covered, but will focus almost exclusively on fluoride, oxide, and oxyfluoride complexes in the truly highest oxidation states of the transition metals. Moreover, we will dwell more on those cases where the situation is open for further developments rather than on elements for which the highest oxidation states possible have been reached beyond doubt. A main emphasis will be on the interplay between quantum-chemical predictions and experimental characterization. Before going through the 3d–6d series explicitly, we will also briefly discuss the concepts of oxidation state, the requirements placed on suitable ligands needed to achieve high oxidation states, the quantum-chemical methods available to predict the existence and stabilities of high-oxidation-state compounds, and the experimental possibilities to verify the highest oxidation states.

2. The oxidation state concept

A quest for the highest attainable oxidation states requires a proper definition of the term “oxidation state”. We may distinguish a formal oxidation state, as defined by a number of well-known, simple rules [39,40], and a physical or spectroscopic oxidation state as introduced by Jørgensen [39] and used frequently, e.g., in bioinorganic chemistry. The latter may be non-integer [41] and is often assigned based on specific spectroscopic parameters, e.g., isomer shifts and quadrupole coupling constants in Mössbauer spectroscopy in case of Fe, Ru, Au [42] and some other elements (see also below).

Our emphasis will be on the formal oxidation state, which for a central atom in a transition metal complex is usually defined as the charge remaining when the ligands have all been removed in their most stable form. The bonding electron pairs between the metal center and the ligands are then assigned exclusively to the most electronegative bonding partners, often the ligands [39,40]. This description is of course most realistic when bonding is largely ionic.

When appreciable covalent bonding or redox-active “non-innocent” ligands [39] are involved, identification of a formal oxidation state may be more complicated, and the assignment thus obtained may differ significantly from the actual electronic charge distribution between metal and ligands. A pertinent example in the realm of high oxidation states is the recent report of the complex [Pd(dmpe)(1,2-$C_6H_4(SiH_2)_2$)], where the Pd center was thought to be coordinated to six silyl ligands and was thus assigned the highly unusual and unique oxidation state Pd(VI) [43]. Other authors subsequently presented convincing arguments for assignment to the much lower Pd^{II} oxidation state [44–46], combined with partial intramolecular Si···Si bonding between the ligands. Another example from bioinorganic chemistry pertains to the famous “Compound I” in the heme enzyme $P450_{cam}$. This important reactive intermediate has often been described as an oxo-Fe^V–porphyrin complex. However, closer examination by modern QM/MM calculations indicates that the system is more appropriately described as a Fe^{IV} oxo complex with a porhyrin radical cation (a Fe^V-type state is computed too high energetically to play a significant mechanistic role; see, e.g., ref. [47] and references therein). These examples illustrate some of the difficulties that may be encountered for nontrivial bonding situations. We will therefore in the following concentrate on very electronegative ligands like F and O, and will avoid examples in which the ligands are redox active or in which metal–metal bonding occurs [14]. Ambiguities arising over assignments of formal oxidation states should thus be minimized. Finally, it should be noted that computed partial atomic charges, e.g. as obtained from a population analysis, may not be equated with the formal oxidation state (see ref. [48] and references therein), except for the most ionic situations.

3. Coordinating ligands and stabilization of high oxidation states

The choice of ligand sets is of course crucial to obtain stable compounds in high oxidation states. As has been discussed in ref. [14], fluoro- and oxo-ligands are usually preferred for the stabilization of the highest oxidation states, both in main-group and transition metal chemistry. In the transition metal series, oxo-ligands figure prominently in the earlier groups of a given row, whereas fluoride complexes most often represent the highest oxidation states for the later transition elements (and for the 4f elements) [14]. Obviously, the high electronegativities of fluorine and oxygen make them particularly suitable to stabilize high formal oxidation states. Fluorine exhibits the highest electronegativity in the Periodic Table. On the other hand, the F—F bond in F_2 is one of the weakest known covalent bonds, with a bond energy of only 154.5 kJ mol^{-1} [49,50]. This is mainly due to large interelectronic repulsions among nonbonding electrons around the small fluorine atom (“lone-pair bond-weakening” [49,51–54]). The weak F—F bond favors the stabilization of transition metal fluorides in high oxidation states with respect to F_2 elimination and, at the same time, results in elemental fluorine being such an extremely reactive molecule.

A disadvantage in the use of fluoride ligands for the stabilization of the highest oxidation states of the earlier and middle d-elements is the monovalency of fluoride, compared to the divalent oxo-ligand. For example, $Os^{VIII}O_4$ is well known and of comparably moderate oxidation strength, whereas $Os^{VIII}F_8$ is disfavored by the large coordination number and the resulting steric repulsions between the ligands. Osmium octafluoride has not yet been unequivocally established by experiment (see below). On the other hand, the lower electronegativity of oxygen, and the much stronger O═O bond (494 kJ mol^{-1} in O_2; while the O—O bond in peroxo complexes is probably weaker, the M—O_2 bonding may compensate for this) tends to open exothermic decomposition pathways for high-valent oxo and oxyfluoride complexes. Thus, monooxofluoride-complexes like $OsOF_5$ or $IrOF_5$ may actually be more attractive synthetic targets than dioxo-species [55]. The OF molecule is much less stable (bond energy 205 kJ mol^{-1}) than O_2, and thus elimination is less favorable. Homolytic bond dissociation or bimolecular reactions may, of course, still favor decomposition (e.g., $2MOF_x \rightarrow 2MF_x + O_2$), thus manifesting the driving force of O═O bond formation. Under conditions, where bimolecular pathways are prohibited such as in low-temperature matrix-isolation spectroscopy, monooxofluoride complexes may yet prove to be particularly important. As has been pointed out by Jørgensen [14], oxo ligands offer an additional advantage in that their complexes may be obtained in aqueous solution by deprotonation of bound hydroxy ligands.

High oxidation states (albeit often not the highest ones) may be stabilized also by an appreciable range of more sophisticated ligand frameworks. In particular, weakly-coordinating anions (WCAs) should be noted. Examples are $[AsF_6]^-$, $[As_2F_{11}]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$, $[OSeF_5]^-$, and $[OTeF_5]^-$, to mention only a few. Delocalization of negative charge over a large anion volume creates weakly basic, low-nucleophilicity anions that are difficult to oxidize. Given their often bulky nature, they also tend to diminish the tendency of the complexes that have formed to oligomerize. This is thought to create a coordination environment around the metal center in the condensed phase that is as close as possible to the gas-phase situation [56–59]. The larger dinuclear anions $[Sb_2F_{11}]^-$ and $[As_2F_{11}]^-$ are supposed to be even more weakly coordinating, because their negative charge is more delocalized (the trinuclear $[Sb_3F_{16}]^-$ and tetra-nuclear $[Sb_4F_{21}]^-$ ions are also known [58,59]). Larger, also very effective WCAs of the type $[E(OTeF_5)_6]^-$ (E = As, Sb, Bi, Nb) are known [56,57,60]. They are often discussed as “bulky fluoride analogues”, and their abilities to stabilize high oxidation states [60]

Table 1
Comparison between anionic, neutral, and cationic representatives of the highest experimentally known oxidation states of the transition metal fluorides

Element	Ox.	Anionic	Ox.	Neutral[a]	Cationic
Sc	III	$[ScF_6]^{3-}$ [359,360]	III	ScF_3	
Ti	IV	$[Ti_2F_{11}]^{3-}$ [361]	IV	TiF_4	
V	IV	$[VF_6]^{2-}$ [362]	IV	VF_4	
Cr	V	$[CrF_6]^-$ [150]	V	CrF_5	$[CrF_4]^+$ [124]
Mn	IV	$[MnF_6]^{2-}$ [154,363]	IV	MnF_4	
Fe	III	$[FeF_6]^{3-}$ [364]	III	FeF_3	
Co	IV	$[CoF_6]^{2-}$ [168–170]	III	CoF_3	$[CoF_4]^+$ [365]
Ni	IV	$[NiF_6]^{2-}$ [169,178,244]	IV	NiF_4	
Cu	IV	$[CuF_6]^{2-}$ [34,193–195]	III	CuF_3	
Zn	II	$[ZnF_3]^-$ [366]	II	ZnF_2	
Y	III	$[YF_6]^{3-}$ [360,367]	III	YF_3	
Zr	IV	$[ZrF_7]^{3-}$ [368], $[ZrF_8]^{4-}$ [368,369]	IV	ZrF_4	
Nb	V	$[NbF_n]^{q-}$ ($n = 6–8$, $q = 1–3$) [370–372]	V	NbF_5	
Mo	VI	$[MoF_8]^{2-}$, [373] $[MoF_7]^-$ [374]	VI	MoF_6	
Tc	V	$[TcF_6]^-$ [375–377]	VI	TcF_6	
Ru	V	$[RuF_6]^-$ [378]	VI	RuF_6	
Rh	V	$[RhF_6]^-$ [242,378,379]	VI	RhF_6	
Pd	IV	$[PdF_6]^{2-}$ [233]	IV	PdF_4	
Ag	III	$[AgF_4]^-$ [248]	III	AgF_3	
Cd			II	CdF_2	
La	III	$[LaF_6]^{3-}$ [360,367]	III	LaF_3	
Hf	IV	$[HfF_7]^{3-}$ [380], $[HfF_5]^-$[381]	IV	HfF_4	
Ta	V	$[TaF_6]^-$ [382] $[TaF_8]^{3-}$[383]	V	TaF_5	
W	VI	$[WF_8]^{2-}$ [373], $[WF_7]^-$[374]	VI	WF_6	
Re	VII	$[ReF_8]^-$ [384]	VII	ReF_7	
Os	VI	$[OsF_7]^-$ [385]	VI	OsF_6	
Ir	V	$[IrF_6]^-$ [385,386]	VI	IrF_6	
Pt	V	$[PtF_6]^-$ [3]	VI	PtF_6	$[PtO_3]^+$ [b]
Au	V	$[AuF_6]^-$ [227]	V	AuF_5	
Hg	II	$[HgF_3]^-$ [387]	IV	HgF_4	

[a] For the references to the neutral fluorides, see Table 2 and text.

[b] The observation of this cation is doubtful [30,312].

and unusual cations are well documented [57,60]. The group electronegativity of this kind of ligands is thought to be comparable to that of fluorine [60,61]. In this context we may also mention the recent characterization of the complex anion $[Ni(SnB_{11}H_{11})_6]^{8-}$ [62–65], which has been taken as an Ni^{IV} system. However, the high overall negative charge and the formal dinegative ligand charge raise the question of the redox-innocence of the ligands.

Redox-noninnocence is also a potential issue for other types of ligands, which have been utilized particularly for 3d transition metal systems in bioinorganic chemistry or related model complexes, e.g., carbamate ligands [14]. We will not pursue this topic in detail and again refer to $P450_{cam}$ as discussed above as an example. An important point that does not seem to have been sufficiently appreciated is that for the heaviest d-elements (5d series and below), the effects of special relativity reinforce the preference for very electronegative ligands like fluorine in enhancing the stabilities of the highest oxidation states. An explanation is given towards the end of this paper (see also refs. [19–21,66–71]).

An unwritten rule among inorganic fluorine chemists maintains that the highest attainable oxidation states of the elements are most likely to be stabilized as anions. Table 1 compares the highest known oxidation states in neutral and anionic fluoride complexes. Interestingly, in the most critical groups (i.e., Mn and beyond for the 3d series and Ru/Os and beyond for the 4d/5d series; see below), the highest oxidation states occur for the neutral rather than for the anionic complexes. This may actually reflect the aforementioned steric repulsions among fluoride ligands for the higher coordination numbers that are attained in anionic complexes. This does not of course mean that the neutral complexes are generally more stable than the anionic ones. In fact, the number of known high-oxidation state anionic species is by far larger, indicating that it is less difficult to access the higher oxidation states. In fact, many neutral complexes in the highest oxidation states have been synthesized by use of an anionic precursor in the same oxidation state because they are more easily accessible [72,73]. Clearly, bond polarity and steric repulsion (between different metal–ligand bonding orbitals, nonbonding valence orbitals, and between the metal $(n-1)$s,p subvalent shell – see following section) have to be considered. Given that the contributions of electrostatic interactions in ion-pair compounds in the solid state are difficult to estimate without explicit computation, this places some limitations on our ability to predict the most promising route to a given extreme oxidation state based on qualitative arguments alone. We also note that the contribution made by anionic stabilization depends on the d-configuration. For example, we expect square planar d^8 systems to benefit less from coordination of another anionic ligand than, e.g., an early transition metal complex.

4. Quantum-chemical predictions

The dramatically increased role of quantum-chemical predictions of new oxidation states and species, and the role of computations in the characterization process since the mid to late 1980s obviously derives from the improved quantitative accuracy of the available methods and growth of available computational power, which currently allows the routine application of powerful post-Hartree-Fock ab initio methods (e.g. coupled-cluster methods) to molecules with up to about 10–20 atoms (or sometimes more), enough to approach mononuclear complexes with relatively simple ligands like F or O. In addition, appreciable developments related to density functional theory (DFT), in particular improved exchange-correlation functionals and numerically stable, advanced computer codes since the mid 1980s [74], have made larger complexes accessible.

Nevertheless, a number of important points have to be kept in mind when dealing with the prediction of novel species in general, and in particular when dealing with the highest oxidation states of the transition metal elements. While some researchers appear to be satisfied when a molecular structure has been identified as a (local) minimum on the potential energy surface, this is generally insufficient. It is at least necessary to evaluate the thermochemistry of the most relevant decomposition pathways of the molecule or ion in question. When doing so, the actual experimental conditions must also be considered. Obviously, the gas phase has the advantage of (a) minimal environmental interactions and (b) decreased probability of bimolecular reaction paths. However, the elevated temperatures necessary for the creation of certain gaseous species create other problems. Thermal effects and, in particular, entropic contributions come into play. For example, if one considers the elimination of F_2 in the gase phase from a high-valent metal fluoride, $MF_n \rightarrow MF_{n-2} + F_2$, it is clear that entropy will favor the right-hand side of the equation, and thus the lower oxidation state, increasingly so with increasing temperature. In the computations, this must at least be modeled by calculating entropic and thermal contributions from harmonic vibrational frequency analyses. The most favorable situation for making predictions is therefore a low-temperature inert-gas matrix experiment where these effects are significantly diminished and, hopefully, environmental effects are minor.

If only endergonic pathways for unimolecular decomposition are found, chances of positive identification in a matrix-isolation spectroscopy experiment are promising. In case of exergonic reaction paths, the matter is more complicated, because activation barriers for these pathways need to be examined. If the barriers are sufficiently high, there is still hope that a new (metastable) species or new oxidation state may be identified. Taking the recent identification of HgF_4 in Ne and Ar matrices as a particularly appropriate example, the calculations had indicated that unimolecular F_2 elimination is somewhat endergonic at the lowest temperatures but becomes exergonic above 30–50 K [21]. This suggested that under typical matrix-isolation conditions, HgF_4 should be accessible, and it was eventually characterized by its asymmetric Hg–F stretching frequency in the IR, which is somewhat higher than that of HgF_2, as predicted computationally. It turned out that HgF_4 is also photolyzed under the UV irradiation conditions used to generate the fluorine atoms that oxidize Hg to its tetravalent state in the first place. Optimization of the illumination conditions, and the favorable properties of the Ne matrix used finally led to success where previous experimental attempts had been unsuccessful [21].

Matters become much more complicated when one attempts to predict the existence of a species under more normal condensed-phase conditions because aggregation and/or solvation energies of all species present under the assumed conditions must be taken into account. Continuing with the example of HgF_4, it was clear that aggregation of HgF_2 (with its ionic fluoride structure) is much more favorable than that of HgF_4, which is expected to exhibit a layered structure comparable to that of XeF_4. Thus, destabilization of the higher oxidation state relative to the lower oxidation state results [20]. This is the likely reason why HgF_4 has not been unequivocally identified under condensed-phase conditions and is why the authors recently chose to computationally evaluate the stabilities of Hg^{IV} species with larger, weakly-coordinating anions, where aggregation of the Hg^{II} complexes is less favorable [69]. Unfortunately, the computations revealed at least one exothermic and thus certainly exergonic pathway for decomposition under "gas-phase-like" conditions in all cases studied. The barriers for these reactions have thus far not been evaluated with sufficient reliability, and it has not been possible to unambiguously establish the existence of the most promising target complexes [69].

The need to evaluate thermochemical stabilities and, often, kinetic labilities of transition metal complexes by computations places substantial demands on the underlying quantum-chemical approaches. The quantitative description of transition metal thermochemistry is complicated by the significant importance of electron correlation, in particular the so-called nondynamical correlation. This is particularly pronounced for redox thermochemistry, where differential correlation effects of this type are large. Pauli repulsion between the subvalence $(n-1)$s,p shells of the transition metals and the ligand valence orbitals typically leads to a stretched-bond situation with resulting large nondynamical correlation, as has been analyzed in detail by Buijse and Baerends [75] for the MnO_4^- ion (see also ref. [76]). Indeed, these correlation effects tend to be larger the higher the oxidation state of a given metal. This arises from (a) a radial contraction of the metal d-orbitals for the higher oxidation state and thus diminished overlap with ligand orbitals, (b) the need of bonding overlap with even more orbitals in the higher oxidation state, and (c) enhanced metal d-character of the metal–ligand bond. All of these factors contribute to enhanced Pauli repulsion in the higher oxidation state and thus to large differential correlation effects. This is again illustrated by HgF_4 when considering F_2 elimination to give HgF_2: the latter molecule is essentially a main-group complex with very little mercury 5d-orbital involvement in bonding [20]. Correlation effects are thus moderate, and nondynamical correlation is even less important. In contrast, bonding in HgF_4 is dominated by the 5d-orbitals. As these are of much smaller radial extent than the 6s orbitals, the aforementioned Pauli-repulsion problem (mainly between bonding orbitals and the mercury 5p shell) comes into play, and one has a stretched-bond situation in HgF_4. As a consequence, nondynamical correlation effects are much larger on the left-hand than on the right-hand side of the elimination reaction [20].

Thus, quantum-chemical methods are required that deal, in a balanced way, with the correlation effects on both sides of the equation. Unless a qualitative zeroth-order description of the wave function of the molecule in question by a single Slater determinant (i.e. by a Hartree–Fock wave function) fails, single-reference post-Hartree–Fock methods should be adequate to deal with the problem. Because many electrons have to be correlated, a size-consistent method is also needed. Single-reference coupled-cluster approaches have thus emerged as a powerful tool in the evaluation of the relevant redox thermochemistry in this field. Fig. 2 shows the dependence of the calculated reaction energy of F_2 elimination from HgF_4 on the method. It is assumed that the

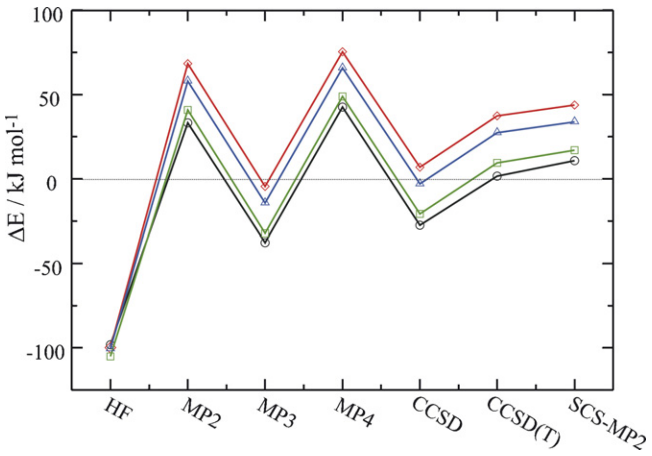

Fig. 2. Computed energies for the elimination reaction $HgF_4 \rightarrow HgF_2 + F_2$ at different levels of theory and with different fluorine basis sets: (○) aug-cc-pVDZ, (□) aug-cc-pVTZ, (△) aug-cc-pVQZ, (◇) aug-cc-pV5Z.

CCSD(T)/aug-cc-pV5Z results are the most accurate, and they therefore serve as benchmark data. Notably, coupled-cluster methods with only single and double substitutions (CCSD) typically include an insufficient amount of nondynamical correlation and thus tend to underestimate the stability of the higher-oxidation-state complex (i.e., the equilibrium is too far to the right-hand side; cf. Fig. 2) [55,68,77–80]. Inclusion of triple excitations (typically at the CCSD(T) level) has turned out to be mandatory in describing the redox thermochemistry of many high-valent fluoro and oxo complexes [55,68,77–80]. Note that the so-called T1 diagnostic of the CCSD wavefunction [81–83] may often be used to estimate whether a single-reference coupled-cluster approach is sufficiently accurate, or whether some multi-reference approach has to be applied. In closed-shell cases, T1-diagnostics values above 0.02 may indicate problems with a single-reference approach, whereas values up to 0.04 may still be acceptable in open-shell cases.

Dynamical correlation has to be included to a large extent, and this also tends to be more important on the left-hand side of the equation. Therefore, calculations with one-particle basis sets that are too small underestimate the stability of the higher oxidation state. As the size of basis set in a CCSD(T) calculation may be rapidly limited by the available computational ressources, one often has to estimate the remaining correlation error (preferrably by a basis-set extrapolation method). Fortunately, the direction of the error is known, i.e., the stability of the high oxidation state is too low. It should also be noted that MP2 calculations are not recommended, because they dramatically overestimate correlation effects and the stability of the higher oxidation state (Fig. 2). A semi-empirical, spin-scaled variant of MP2 (SCS-MP2 [84]) is thought to cure some of the deficiencies of the MP2 method in many areas of application [85–91]. Fig. 2 suggests that this may also hold, to some extent, for the redox-thermochemistry of high-valent fluorides, but more validation studies will be needed. Hartree–Fock calculations without inclusion of Coulomb correlation underestimate stabilities even more than they are overestimated by MP2 (Fig. 2).

When one needs to deal with larger systems, e.g., with a complex bearing large WCA-type ligands [69], CCSD(T) calculations with reasonably large basis sets become too computationally demanding. In such cases, the structure optimization should at least be carried out by a computationally more expedient method that still incorporates the predominant correlation effects. DFT has turned out to provide these capabilities and has in general become of dramatically increased importance in the field of coordination chemistry [68,74,92–94]. For even larger systems, the computations of thermochemical data and reaction barriers can no longer be done at the CCSD(T) level, and thus DFT is also used for such computations. However, there is a multitude of exchange-correlation functionals, and DFT has the disadvantage that a systematic improvement towards an exact treatment of exchange and correlation effects is not possible in the same way as for post-Hartree–Fock methods. In the latter, in principle, the one-particle basis set and multi-determinant expansion may be systematically improved towards the exact wave function. It is therefore important to calibrate DFT functionals, either against experiment or against more reliable computational methods. Because experimental thermochemical data are scarce in the field of high oxidation states of transition metal elements, it is necessary to validate against ab initio calculations. In the cases of redox thermochemistry and activation barriers, the best available CCSD(T) data for small to medium-sized molecules may be used to identify a reliable DFT model to be subsequently applied to larger systems. Such validation studies for high-valent fluoride complexes and related species demonstrate a dramatic dependence on the admixture of exact (Hartree–Fock type) exchange in hybrid functionals [68,77,79,92]. “pure” semilocal functionals of the GGA type (generalized gradient approximation) dramatically overestimate the stabilities of highly oxidized fluoride complexes towards, e.g., F_2 elimination, and are comparable to results obtained at MP2 level (LDA provides even greater overestimation) [68,77,79,92]. On the other hand, large exact-exchange admixtures, e.g., 50% in functionals like BHLYP, favor elimination too readily (the authors have often found that the BHLYP reaction energies are fortuitously close to the CCSD energies, which also underestimate the stabilities for the higher oxidation states). Interestingly, the B3LYP functional, and hybrid functionals with similar exact-exchange admixtures in the 20–30% range, turned out to provide reasonable agreement with the best CCSD(T) results [21,55,68,71,77–80,95]. This class of functionals is thus well suited for application to larger complexes where coupled-cluster methods become too expensive. This is interesting, because B3LYP has been shown to exhibit substantial deficiencies in other areas of transition metal thermochemistry [96–99]. We suspect that the 20% exact-exchange admixture in this functional provides a reasonable balance of the differential nondynamical correlation effects for the different (high) oxidation state fluoro or oxo complexes involved (performance was similar for, e.g., $HgCl_4$ or HgH_4 [68]). It is also necessary to bear in mind the much larger basis-set dependence of coupled-cluster versus DFT calculations. i.e., enlargement of a given basis set in a CCSD(T) calculation may still shift the thermochemistry significantly to the left-hand side of the elimination reaction when the DFT calculation is already essentially converged with respect to the one-particle basis set. Good agreement between B3LYP and CCSD(T) has also been noted for some relevant reaction barriers [77].

Last but not least, for complexes with heavier atoms we need to account for relativistic effects [100,101]. This is absolutely mandatory in the 5d series but becomes already significant for 4d (and the latest 3d) elements. Fortunately, for structures, vibrational frequencies, thermochemistry or kinetics, the predominant scalar (spin-free) relativistic effects may be included in a straightforward manner, and with excellent accuracy, by use of suitably parametrized relativistic pseudopotentials (“effective-core potentials”, ECPs) [102–105]. Comparison with non-relativistically parametrized ECPs even allows the importance of relativity for a given reaction to be estimated. In the 5d (and 6d) series, the higher oxidation states are invariably stabilized by relativity (see Section 7 for a detailed discussion of the reasons) [20,77,100,106–108].

While scalar relativity is thus potentially important, spin-orbit effects have so far been found to be of minor importance for the relevant redox thermochemistry, even in the 5d series, and even when open-shell species are involved [20,55,66]. The spin-orbit effects tend to be moderate in an absolute sense and even partially cancel on the both sides of the reaction equation [55,66]. It may be anticipated that this may be different for superheavy transition metal elements in the 6d series, and that spin-orbit effects may have to be routinely included to predict the relative stabilities of different oxidation states.

Finally the authors note that many claims of the possible stabilities of unusual complexes in extremely high oxidation states have been made based on clearly inadequate computational levels, e.g. X_α-SW calculations, or on taking the mere existence of a minimum on the potential energy surface as evidence for the existence of the compound in question, in the absence of any detailed thermochemical evaluations (see, e.g., papers quoted in refs. [22–24,35]).

5. Techniques to experimentally verify high oxidation states

While our focus is on formal oxidation states (see above), a variety of spectroscopic techniques aim at the determination of physical or spectroscopic oxidation states. In the favorable case of redox-inactive ligands and of relatively ionic bonding, the two definitions coincide, and we should thus briefly mention some of the techniques available to get information on oxidation states from experiment.

5.1. Mössbauer spectroscopy

Mössbauer or γ-resonance spectroscopy [109–113] is one of the techniques trusted most in the assignment of oxidation states. The isomer shift δ results from the electrostatic interaction between nuclear and electronic charge distribution [114]. δ is defined as the energy difference between the sample and a reference nucleus (see also Filatov's review [115] in this issue). The electronic environment (oxidation state) influences δ distinctly, and thus the isomer shift (together with quadrupole and hyperfine splittings) provides a relatively direct access to the physical oxidation state. Unfortunately, only some elements and isotopes are Mössbauer active. Among the transition metal elements, Mössbauer spectra may be measured for the 3d elements Fe, Ni, Zn, the 4d elements Tc and Ru, and essentially the entire 5d row.

5.2. X-ray photoelectron spectroscopy (XPS)

XPS is a quantitative surface spectroscopy technique [116]. XPS spectra are recorded by irradiating the sample under investigation by X-rays and simultaneously measuring the kinetic energy and the amount of electrons scattered during the process. The electron binding energies depend characteristically on the oxidation state, with larger binding energies for higher oxidation states. XPS is thus also a favored technique to determine oxidation states (see also ref. [30] and references therein).

5.3. X-ray absorption near edge structure (XANES)

In contrast to XPS or other photoemission techniques, XANES [117–119] measures not the initial photoelectron itself but a fluorescent photon, an Auger electron, or an inelastically scattered photoelectron created in a subsequent process after X-ray irradiation. Variants of XANES differ by the intensity of the X-ray irradiation (softer X-rays provide NEXAFS [117], harder ones EXAFS [117]). The advantage of NEXAFS is, that it is not only element specific but gives also information about the binding energy of electrons and thus on chemical environment and oxidation state. A pertinent example is a relatively recent NEXAFS investigation of plutonium compounds, where the measured edge energies were progressively shifted to higher energies with increasing oxidation state [120]. Several Pu oxidation states from III to VI have been detected via this technique in an environmental sample of a nuclear test area [120].

5.4. Mass spectrometry

As a first analytical method with a more indirect character in the determination of oxidation states, we may mention mass spectrometry (MS) [121–125]. It provides the mass-to-charge ratio of the cation or anion in the gas phase. Several ionization and detection techniques exist [121]. Oxidation states may be inferred only in the absence of different structural alternatives for the composition of the ion in question, with only redox-inactive ligands. The assignment may be aided by quantum chemical calculations (see above). Examples for MS-detected high oxidation states are the M^V complexes $[CoF_4]^+$ [126] and $[AuO_2]^+$ [127].

5.5. Matrix-isolation spectroscopy

Matrix-isolation spectroscopy comprises several experimental techniques in which guest molecules or atoms are trapped in rigid host materials under cryogenic conditions [128–131]. As the species are embedded in a host material at low temperature, diffusion processes are prevented or slowed down, entropic disadvantages of the high-oxidation-state species may be minimized (see above), and bimolecular reactions cannot take place, except with the host material. This is often an ideal environment for the stabilization of high oxidation states. The trapped species can ideally be characterized by IR, Raman or several other spectroscopy techniques. Apart from Mössbauer spectroscopy, the assignment of oxidation states is done indirectly, e.g. by comparison of measured IR bands with quantum chemical calculations (due to the weak interaction with the host material, comparison with gas-phase calculations is often sufficient) or with the frequencies known for related species. Some recent examples of high oxidation states characterized by matrix-isolation spectroscopy are $Hg^{IV}F_4$ [21] and $Ir^{VI}(OO)O_2$ [132] (many more examples for specific examples are provided in Section 6).

5.6. NMR and EPR spectroscopy

Magnetic resonance spectroscopy methods are sometimes also applied to the detection of compounds in high oxidation states. Obviously, this requires that the species in question is stable on the time scale of the magnetic resonance experiment, which in the NMR case excludes very short-lived species. The NMR chemical shift of the central atom may be relatively specific for a given oxidation state [133], but it depends on many other variables as well. Therefore no direct conclusions about oxidation states are possible, unless quantum-chemical calculations may provide additional information. The same holds for electronic g-tensors and hyperfine couplings measured in EPR spectroscopy. For example, the identification of short-lived $[Hg(cyclam)]^{3+}$ in 1976 [134] was probably correct, but the assignment to a Hg(III) oxidation state is doubtful (see next section).

Further techniques could be mentioned here but are outside the scope of this article. Specific techniques are applicable to short-lived isotopes of superheavy 6d elements [135–138].

6. Results for individual transition metal elements

The focus here will be on cases with a non-trivial situation for the highest oxidation states. The more straightforward cases will be mentioned more briefly or are included only in Table 2. This holds, in particular, for the earlier transition metals, where the maximum attainable oxidation states for fluorides and oxides alike are identical to the group number. Coverage of superheavy transition metal elements (the transactinides or 6d series) will be brief, as experimental data are scarce and the number of computational studies is also limited.

6.1. The 3d series

Scandium, titanium, and vanadium all display the maximum oxidation states achievable for their respective groups, for oxides as well as for fluorides (Table 2).

6.1.1. Chromium

This is the first element in the series in which the highest theroretically attainable oxidation state (VI) has not yet been achieved for oxides, fluorides and oxyfluorides alike. While the binary Cr(VI) oxide, various anionic oxo complexes, and oxyfluorides in the VI oxidation state are well known (Table 2), earlier

Table 2

Summary of the highest oxidation states of the transition metal elements as represented by oxides, oxyfluorides, and fluorides[a]

Element	Oxides	Oxyfluorides[a]	Fluorides	Predicted
3d				
Sc	Sc_2O_3 [58]	ScOF [388,389]	ScF_3 [58]	
Ti	TiO_2 [58]	$TiOF_2$ [390] TiOF [391]	TiF_4 [58]	
V	V_2O_5 [58] $[VO_4]^{3-}$ [392,393]	VOF_3 [394] VO_2F [395]	VF_5 [58]	
Cr	CrO_3 [58] $[CrO_4]^{2-}$ [311] $[Cr_2O_7]^{2-}$ [311]	$CrOF_4$ [58,396–400] CrO_2F_2 [58,146,401–403]	CrF_5 [139] $[CrF_6]^-$ [150] $[CrF_4]^+$ [124]	
Mn	$[MnO_4]^-$ [58] Mn_2O_7 [58]	MnO_3F [402,404]	MnF_4 [151]	
Fe	$Fe(OO)O_2$ [160] $[FeO_4]^{2-}$ [166]	$Fe_2O_2F_2$ [391,405] FeOF [406,407]	FeF_3 [165] FeF_4 [125]	
Co	$Co(OO)O_2$ [175]	–	$[CoF_4]^+$ [365]	
Ni	NiO_2 [58,179,180,182]	–	NiF_4 [178] $[NiF_6]^{2-}$ [25]	
Cu	$[CuO_2]^-$ [185] $[Cu_3O_6]^{5-}$ [187]	–	CuF_3 [196] $[CuF_6]^{2-}$ [193]	
Zn	ZnO [408]	–	ZnF_2 [311]	
4d				
Y	Y_2O_3 [58]	YOF [409]	YF_3 [58]	
Zr	ZrO_2 [58]	$ZrOF_2$ [410,411]	ZrF_4 [58]	
Nb	Nb_2O_5 [58] $[NbO_4]^{3-}$ [311]	$NbOF_3$ [412,413] NbO_2F [414] Nb_3O_7F [415]	NbF_5 [58]	
Mo	MoO_3 [58] $[MoO_4]^{2-}$ [311]	$MoOF_4$ [58,416] MoO_2F_2 [58,417–419]	MoF_6 [58,215]	
Tc	Tc_2O_7 [205–207] $[TcO_4]^-$ [205,208,420]	TcO_3F [209,421–423] TcO_2F_3 [423–427] $TcOF_5$ [428,429] $(TcO_2F_2)_2O$ [209]	TcF_6 [214,215]	TcF_7, $[TcF_6]^+$ [95]
Ru	$[RuO_4]$ [58]	$RuOF_4$ [224,430–433] $RuOF_3$ [434]	RuF_6 [215]	
Rh	RhO_3 [222] $Rh(OO)O_2$ [229]	– –	RhF_6 [58]	
Pd	PdO_2 [58]	–	PdF_4 [231]	PdF_6 [239]
Ag	Ag_2O_3 [247]	–	AgF_3 [73]	
Cd	CdO [408]	Cd_4OF_6 [435]	CdF_2 [58]	
5d				
La	La_2O_3 [58]	LaOF [409]	LaF_3 [58]	
Hf	HfO_2 [58]	$HfOF_2$ [411,436]	HfF_4 [58]	
Ta	Ta_2O_5 [58] $[TaO_4]^{3-}$ [58]	TaO_2F [414] $TaOF_3$ [423,437]	TaF_5 [58]	
W	WO_3 [438] $[WO_4]^{2-}$ [311]	WOF_4 [58,416,423,439], WO_2F_2 [423,440]	WF_6 [58,215]	
Re	Re_2O_7 [261] $[ReO_4]^-$ [311]	ReO_3F [423,441–443], ReO_2F_3 [423,441–444], $ReOF_5$ [443,445]	ReF_7 [267,446]	
Os	OsO_4 [263,276–281]	OsO_2F_4 [289,447] OsO_3F_2 [448,449]	OsF_6 [215,282–285]	OsF_n ($n = 7, 8$) [78,293] $OsOF_6$ [78,293]
Ir	IrO_3[132] $Ir(OO)O_2$ [132]	–	IrF_6[215]	IrF_7[55] $IrOF_5$ [55] $[IrF_6]^+$ [55]
Pt	PtO_3[315]	$PtOF_2$ [257,319]	PtF_6 [305]	
Au	$[AuO_2]^+$ [127]	–	AuF_5 [326,328]	$AuF_5{\cdot}F_2$ [79]
Hg	HgO	–	HgF_4 [19,450]	

[a] Only neutral oxyfluorides are listed. A few examples of anionic oxyfluorides are: $[FeO_2F]^{2-}$, [451] $[NiOF]^-$, [451] $La_{1-x}Sr_xCuO_3$ ($0 \leq x \leq 0.25$), [186] $NaBa_2Cu_3O_6$, [187] $[MoO_3F]^-$, [452,453] $[Mo_2O_5F_7]^{4-}$, [454] $[TcO_2F_4]^-$, [424,425] $[WO_3F_4]^{4-}$, [455] $[W_3O_9F]^-$, [452] $[WO_2F_3]_2{}^{2-}$, [456] $[WO_2F_4]^{2-}$, [452,457] $[ReOF_6]^-$, [374] $[ReO_2F_4]^-$, [427,442] $[Re_2O_4F_7]^-$, [427,442] $[Re_3O_6F_{10}]^-$, [427,442] *fac*$[OsO_3F_3]^-$. [458,459]. See ref. [32] for a more detailed review of oxyfluorides.

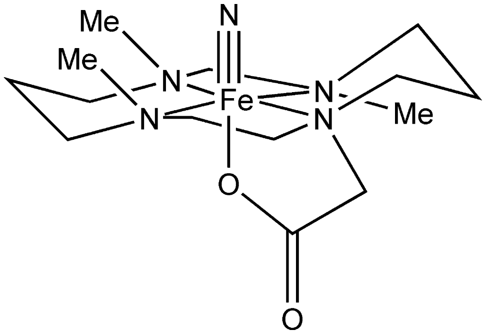

Fig. 3. The first organometallic Fe(VI)-nitrido complex, $[(Me_3cyac)FeN](PF_6)_2$ [155].

reports of CrF_6 in matrix isolation [139–143] were shown by Willner [144,145] to be due to misassigned vibrations for the pentafluoride, CrF_5, which had been known before [146]. While quantum-chemical calculations at ab initio and DFT levels [147–149] give an octahedral structure for CrF_6 (with a relatively small barrier towards a trigonal Baylar twist), detailed studies of thermochemistry and kinetics of the decomposition pathways with reliable state-of-the-art methods appear to be lacking. A detailed study on a series of hexafluorochromate (V) salts has recently been published [150].

6.1.2. *Manganese*

The highest achievable oxidation state for manganese is VII, represented by the binary oxide, various salts of the permanganate ion, and a number of oxyfluorides (Table 2). The highest known manganese fluoride is MnF_4 [151]. Several fluoromanganate complexes in oxidation state IV exist, for example $(XeF_5)_2MnF_6$ [25,152]. There has been speculation and experimental attempts to prepare higher manganese fluorides like MnF_5 or $[MnF_6]^-$ [25,153], but preparation has thus far been unsuccessful. For more details concerning manganese complexes see the review of Levason and McAuliffe [154].

6.1.3. *Iron*

The highest oxidation state of iron characterized experimentally is Fe(VI), in form of various salts (or solutions) of the $[FeO_4]^{2-}$ ion [31], and very recently in form of a six-coordinated nitride complex [155]. The latter was characterized by Mössbauer and X-ray absorption spectroscopy. DFT calculations have supported an octahedral structure (Fig. 3) with a terminal Fe≡N triple-bond length of 157 pm, which is in excellent agreement with the predicted triple-bond length of 156 pm [156]. Previous claims of the electrochemical preparation of Fe^{VIII} in form of FeO_4 in solution [157,158] are certainly incorrect. Low-temperature matrix-isolation IR spectroscopy experiments in conjunction with quantum-chemical calculations clearly show that if FeO_4 were obtained, the structure would correspond to a side-on bonded peroxide complex, which is again probably best described as an Fe(VI) system [159–161]. The single IR active stretching band of a tetrahedral FeO_4 molecule could not be seen in these experiments. Calculations at B3LYP and CCSD(T) levels confirmed the higher stability of the peroxide complex [159,161–164].

Again, binary fluorides cannot compete with oxo complexes in terms of stabilization of the highest oxidation states. The highest iron fluoride characterized experimentally beyond doubt thus far is FeF_3 [165], three oxidation states lower than observed in $[FeO_4]^{2-}$. In 2003, the observation of FeF_4 by Knudsen effusion mass spectrometry and FTIR spectroscopy was reported [125]. However, so far the assigment remains tentative and lacks independent confirmation. Preparation of a hexafluoroferrate(IV), Cs_2FeF_6, under high temperature and pressure conditions starting from Cs_2FeO_4 has also been reported [166,167]. But again characterization was incomplete and the assignment tentative.

6.1.4. *Cobalt*

The highest oxidation state of cobalt that has been unambiguously established is V. The tetrafluoride cation $[CoF_4]^+$ has been identified in the gas phase by mass spectrometry in a reaction between CoF_3 and TbF_4 at higher temperatures [126]. This also implies the existence of $Co^{IV}F_4$ in the gas phase. Interestingly, the highest oxidation state attained in a homoleptic fluorocobaltate anion is only IV in $[CoF_6]^{2-}$ as its Cs^+, Rb^+, and K^+ salts [168–170]. The highest condensed-phase binary cobalt fluoride is CoF_3 [165,171].

A number of organometallic Co(V) complexes have been reported. In the case of $(Co(1\text{-norbornyl})_4]BF_4$, a high ligand field of the four norbornyl ligands has been assumed to stabilize the tetrahedral low-spin d^4 configuration [172–174]. In other cases, a combination of hydrido and silyl ligands appears to stabilize a similar bonding environment, albeit the type of ligands may give rise to alternative descriptions of the cobalt oxidation state than Co^V. Thus, these examples may be less clearcut than the others [172–174].

Matrix-isolation IR experiments (combined with DFT calculations) using laser-ablated cobalt atoms together with co-deposited oxygen in an argon environment led to the tentative assignment of several vibrational bands to a dioxo-peroxo complex $Co(O_2)O_2$, which would correspond to cobalt in the VI oxidation state [175]. This result may need further verification, given that detailed quantum-chemical investigations (CCSD(T) and B1LYP DFT levels) of CoO_n ($n = 1–4$) complexes indicated the diperoxide $Co^{IV}(O_2)_2$ to be the most favored configuration for CoO_4 [176]. Recent matrix-isolation experiments using a different technique to introduce the cobalt atoms have not shown any evidence for a dioxo-peroxo complex [177]. It was furthermore suggested, that the previous assignments of bands to peroxo and superoxo complexes might be due to oligomeric species [177].

6.1.5. *Nickel*

The highest nickel oxidation state for a fluoride is IV which is represented by the $[NiF_6]^{2-}$ anion and by the binary fluoride NiF_4 [25,72,178]. Nickel tetrafluoride is known to be one of the most powerful oxidizing agents and Ni(IV) solvated in anhydrous HF may be even more reactive [25,27]. A pertinent overview of nickel(IV) chemistry has been given [25].

A variety of nickel–oxygen species have been identified [179–182] by matrix-isolation IR spectroscopy of the reaction products between Ni atoms and O_2 (some of the species are also formed with thermally activated Ni atoms [183]). Analysis of the vibrational bands suggests several Ni(IV) species, including the linear dioxide O–Ni–O [179,182], the di-peroxo complex $Ni(O_2)_2$, and possibly the peroxo-oxo complex $Ni(O_2)O$. Some bands were also assigned (supported by DFT calculations) to the complex $Ni(O_2)O_2$. Taking the side-on dioxygen as a peroxo ligand, this would represent a genuine Ni(VI) species. However, description as a neutral O_2 molecule bound side-on to a Lewis-acidic NiO_2 molecule may be more likely, making this another Ni(IV) species. We may thus summarize that Ni(IV) so far remains the highest well-characterized nickel oxidation state. NiO_2 has also been studied by photoelectron spectroscopy in the gas phase [184].

6.1.6. *Copper*

There appears to be agreement [23,29,34,185], that the highest oxidation state of copper is Cu(IV), represented by a number of mixed-valence Cu^{III}/Cu^{IV} solid-state oxide materials like $La_{1-x}Sr_xCuO_3$ ($0 \leq x \leq 0.25$) [186] or $NaBa_2Cu_3O_6$ [187] (relevant in the context of high-temperature superconductivity [188–192]), and by the hexafluorocuprates(IV), $Cs_2[CuF_6]$ and $Rb_2[CuF_6]$ [37,193–195]. Binary CuF_3 has recently been prepared as a red substance by solvolysis of $[CuF_6]^{3-}$ in aHF at 195 K [25,196,197]. CuF_3 decomposes at temperatures above 213 K [25]. Interestingly, no binary Cu^{IV} fluoride is known [198], i.e. anionic complexation appears to be important (fluorocuprates(III), $[CuF_6]^{3-}$, are also known [34,58]). The same effect seems to hold for the oxides, where binary Cu_2O_3 is thus far unknown, whereas Cu^{III} may be stabilized in $KCuO_2$ [185] as well as in the more complex mixed oxides that comprise high-T_c superconductors, see above.

6.1.7. *Zinc*

So far, zinc has complied with its classification as a post-transition metal element by exhibiting only oxidation states up to II. There has been recent interest in compounds with formal Zn^I oxidation state and Zn–Zn bonding [199–204]. In contrast to the heavier congener mercury, where relativity stabilizes the higher oxidation state IV in form of HgF_4 [20,21,71] (see Sections 1 and 7), ZnF_4 has been computed to be very unstable with respect to F_2 elimination and is unlikely to exist [20,21,71]. Matrix-isolation IR studies using laser-ablated zinc atoms only gave evidence for ZnF_2 and its oligomers [21]. Recent computational studies on group 12 M^{III} fluoride species at CCSD(T) and B3LYP levels indicated that the neutral trifluorides are rather unstable (interestingly, ZnF_3 was not less stable than HgF_3) [71]. Anionic complexes were computed to be somewhat more favorable, but no firm predictions for experimentally accessible species have been made [71]. Oligomeric species may be interesting targets for further computational work before any recommendations for experimentally accessible Zn^{III} species can be made.

6.2. *The 4d series*

The first four elements of the series, yttrium, zirconium, niobium, and molybdenum, represent the expected situation, where the highest oxidation state in each group corresponds to the group number. This holds for oxides, oxyfluorides, as well as fluorides (Table 2).

6.2.1. *Technetium*

For technetium we see a similar situation as discussed above for manganese, as the highest oxidation state VII is represented by the binary oxide Tc_2O_7 [205–207], by the pertechnate ion $[TcO_4]^-$ [95,208], and by the oxyfluorides TcO_3F, TcO_2F_3, $TcOF_5$, $[TcO_2F_9]^+$, $[TcOF_4]^+$, and $[TcO_2F_4]^-$, whereas no homoleptic technetium(VII) fluoride is presently known (Table 2). The oxo-bridged dimeric Tc_2O_7 may be viewed as intermediate between polymeric MoO_3 and monomeric RuO_4. The $[TcO_3]^+$ cation has been characterized by NMR in form of $[TcO_3][AsF_6]$ [209]. Moreover, a number of alkyloxotechnetium(VII) complexes have been prepared and characterized [210–212]. In analogy to $[ReH_9]^{2-}$ (see below), an enneahydridotechnate(VII), $[TcH_9]^{2-}$ has also been characterized by NMR and IR techniques [209,213]. More information relevant to high oxidation states of technetium is available in a book on technetium chemistry [208].

In the case of the homoleptic fluoride complexes, the highest oxidation state characterized so far is VI in TcF_6 [214]. Technetium hexafluoride and several other hexafluorides have recently been reinvestigated very carefully by X-ray crystallography and DFT methods [215]. State-of-the-art quantum-chemical calculations (CCSD(T) and B3LYP energetics) [95] indicate that TcF_7 should be observable at least under matrix-isolation conditions, when bimolecular decomposition reactions are minimized. Technetium heptafluoride (Fig. 4) would be the first heptafluoride in the 4d series by analogy with the 5d homologue ReF_7, which is well known (see below). The $[TcF_6]^+$ cation was also computed to be a promising Tc^{VII} fluoro species [95], and would be analogous to the well-known $[ReF_6]^+$ (see below). The presence of only six rather than seven ligands in this cation might reduce ligand repulsion compared to TcF_7.

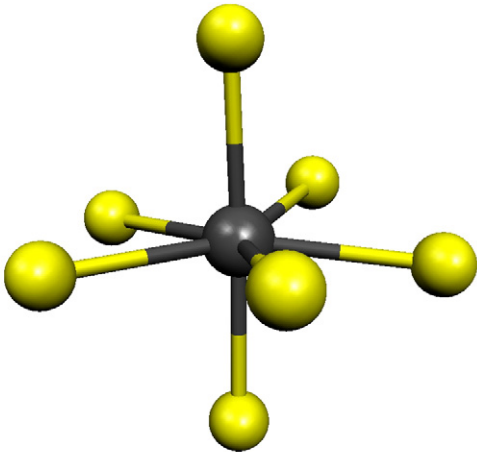

Fig. 4. DFT-optimized structure for technetium heptafluoride [95].

6.2.2. *Ruthenium*

The maximum oxidation state of ruthenium, VIII, appears to be exclusively represented by RuO_4. Ruthenium tetroxide was first synthesized in 1924 [216]. It is interesting that this compound may not be prepared from its elements like its heavier homologue, OsO_4 [30]. This indicates that the M^{VIII} state of the 5d element is more stable. Recently, the first structural data for RuO_4 were obtained by single-crystal X-ray diffraction, showing that the compound exists in two crystal modifications [217]. Before, only isotypism of RuO_4 with OsO_4 had been reported based on powder diffraction experiments [218]. Several quantum-chemical investigations of RuO_4 and its properties have been published [219–221]. The molecular ions $[MO_4]^+$ (M = Ru, Os) have been observed in the mass spectra of the tetroxide [222]. However, ionization from predominantly ligand-centered MOs is assumed, and thus no new oxidation state may be invoked. The $[Ru^{VII}O_4]^-$ and $[Ru^{VI}O_4]^{2-}$ anions are also known and have been studied as oxidizing agents in organic chemistry [12,13].

Ruthenium octafluoride has been reported as a side product in addition to the main product, RuF_5, from the fluorination of Ru and RuO_2 [223]. This result has never been confirmed and seems unlikely to be correct. Under similar reaction conditions, i.e. F_2 treatment of hydrolysis products of $RuOF_4$ or RuF_4, no RuF_8 was found, but RuO_4 was produced [30,224]. It has been speculated that the yellow "RuF_8" reported was actually a mixture of RuO_4 and SiF_4 or HF [30,224]. The highest ruthenium fluoride presently known is RuF_6, and the highest oxyfluoride is $RuOF_4$ (Table 2). Preliminary quantum-chemical calculations (CCSD(T) and B3LYP levels) on the higher ruthenium fluorides of RuF_n ($n = 7, 8$) indicated that both species have appreciably exothermic decomposition channels for concerted F_2 elimination and for homolytic bond breaking, with only moderate activation barriers [225]. This is additional evidence against the existence of RuF_8, which is even more unlikely in view of the fact that its heavier homologue, OsF_8, which would be expected to be more stable, is also presently unknown (see below).

6.2.3. *Rhodium*

The highest known oxidation state for rhodium is VI in RhF_6 [226]. The high oxidizing power of RhF_6 is apparent from the fact that it can oxidize O_2, which in the 5d hexafluoride series occurs first for PtF_6 [227,228].

Matrix-isolation IR spectroscopy of products of the reaction between laser-ablated Rh atoms and O_2 provided evidence for a species described as $RhO_2(O_2)$ [229]. DFT calculations suggested that this is a doublet complex with a side-on bound peroxo ligand and terminal oxygen ligands, analogous to a corresponding Ir complex found in similar experiments (see below). This assignment would also be consistent with a Rh^{VI} complex, albeit the shorter O—O bond length compared to the iridium analogue might be taken as indication of a partial contribution from resonance structures representing lower oxidation states [229].

Notably, with Rh the relative stabilities of fluorides and oxides in the higher oxidation states appear to have reached a turning point in the 4d series, where the fluorides start to become more stable than oxygen-ligated species. The decreased stability of the oxo complexes may be related to Pauli repulsion between filled metal d- and the oxygen p-orbitals [230], which becomes more important for non-d^0 complexes of the later d-elements, or to the enhanced Pauli repulsion with the 4p subvalence orbitals as a result of the very short M–O distances that are involved.

6.2.4. *Palladium*

The highest experimentally well-established palladium oxidation state is IV. This is represented by PdO_2, PdF_4 [231], and $[PdX_6]^{2-}$ complexes (X = F, Cl, OH) [232,233]. Palladium dioxide is known both as a gas-phase molecule, as studied by photoelectron spectroscopy [184] and in the solid state both as water-free oxide with a rutile structure and as a hydrate $PdO_2{\cdot}nH_2O$ ($n = 1, 2$) [30,234–237].

An early report of the gas-phase preparation of PdF_6 relied almost exclusively on a single IR band [238], and it appears unlikely that PdF_6 has been obtained under the conditions indicated. A recently DFT study suggested that PdF_6 could be stable [239]. This result needs further investigation, as preliminary ab initio calculations up to and including the CCSD(T) level indicate a very complicated and demanding quantum-chemical description of PdF_6 and its decomposition products [240].

There had been early reports of Pd^V as the $[PdF_6]^-$ anion in $[O_2]^+$[241], Na^+[242], or Cs^+ [243] salts [25]. However, closer examination of both photochemical and thermal reactions in anhydrous HF provided no evidence for accessible Pd^V species [244]. It was suggested that the solutions were dominated by Pd^{IV} species such as $(O_2)_2PdF_6$ and $(O_2)PdF_5$ [244]. Similarly, earlier claims of $Cs[PdF_6]$ [243] have been attributed to mixtures of $Cs_2[PdF_6]$ and PdF_4 [25]. It must be concluded that there is no hard evidence so far for Pd^{VI} (note the ambiguous oxidation state of a recent Pd-silyl species [43–46]) or Pd^V.

6.2.5. *Silver*

The highest well-established oxidation state of silver is III in form of either oxides or peroxides [245,246] (e.g., Ag_2O_3 is well characterized [247]), salts of the square planar $[AgF_4]^-$ ion [248], and the binary fluoride, AgF_3 [73]. The latter may be prepared by reaction of $[AgF_4]^-$ complexes with fluoride acceptors [73,178]. Prior reports on the synthesis of AgF_3 [249–251] have been shown to be probably incorrect [25]. Silver trifluoride is an extremely strong oxidizer [25,27], and solvated Ag^{III} in anhydrous HF is, in fact, one of the most powerful oxidizers known [25,27]. An extensive review on silver fluorides has been provided by Grochala and Hoffmann [252], with the background of possible superconducting properties.

There have been several, more or less incomplete characterizations of Ag^{IV} complexes $K_2[AgF_6]$ and $Cs_2[AgF_6]$ [37,248,253–255]. The status of $[AgF_6]^{2-}$ or of other Ag^{IV} complexes is thus surprisingly less well established than for the lighter homologue $[CuF_6]^{2-}$ (see above). Experimental attempts to oxidize $[AgF_4]^-$ with KrF_2 or to obtain $[AgF_6]^-$ with photo-excited F_2 were so far unsuccessful [73,256,257]. This contrasts with the relatively easy oxidation of Au^{III} to Au^V (see Eq. (1)) [25]. Quantum-chemical calculations have indicated that F_2 elimination from $[AgF_6]^-$ may be endothermic (CCSD(T) results) [258]. However, this refers to the isolated gas-phase anion and does not yet take into account environmental, thermal or entropic effects. Thus, these calculations provide no support for the aforementioned older claims of preparation under condensed-phase conditions.

$$\begin{aligned} &\mathrm{XeF_5AuF_4 + KrF_2 \xrightarrow{aHF,\ 253\,K} XeF_5AuF_6 + Kr} \\ &\mathrm{XeF_5AgF_4 + KrF_2 \xrightarrow{aHF,\ 253-295\,K} no\ \ reaction} \end{aligned} \qquad (1)$$

6.2.6. *Cadmium*

As for the lighter group 12 homologue zinc, relativistic effects on the thermochemistry of cadmium are also not sufficient to provide the extra stabilization of the IV state found computationally for mercury and eka-mercury (see below). Fluorine elimination from CdF_4 is predicted to be strongly exothermic [20,71]. So far, cadmium remains a post-transition metal element, and it oxidation states do not extend beyond the II state (Table 2).

Recent calculations on group 12 M^{III} fluoride complexes [71] indicated neutral monomeric CdF_3 to be an unlikely target. Anionic stabilization was notable, but thus far it has not been possible to identify particularly suitable Cd^{III} targets. Possibly, oligomeric complexes may provide stabilization, but this remains to be evaluated.

6.3. *The 5d series*

The maximum available transition state in the 5d series agrees with the group number up to OsO_4, but homoleptic fluorides only fulfill this expectation up to and including Re(VII), at which point the present discussion commences.

6.3.1. *Rhenium*

A very early report of Re_2O_8 [259] was soon afterwards shown to be erroneous [260]. The highest oxidation state of rhenium, VII, is well represented by many types of compounds, which are only briefly touched upon here. Regarding oxygen compounds, among others, the binary oxide Re_2O_7 [259,261], many salts of the rather stable perrhenate anion $[ReO_4]^-$ [262–264], and an appreciable variety of oxyfluorides are known (Table 2). Moreover, a very extensive organometallic chemistry of Re(VII) with oxo and imido ligands exists, which has substantial synthetic and practical importance. The most famous representative of this class is methylrheniumtrioxide, MTO [210,265].

Rhenium heptafluoride is well established and is the only known heptafluoride of the transition metals [266]. Neutron powder diffraction shows it to have a distorted pentagonal bipyramidal structure [267]. Salts with the $[ReF_6]^+$ cation and, e.g., $[Sb_2F_{11}]^-$ or $[Au_2F_{11}]^-$ counteranions are also known [25,268,269]. Assuming hydride ligands to represent anionic H^-, Re(VII) species with hydride ligands are also well known, including the trifold-capped trigonal prismatic $[ReH_9]^{2-}$, derivatives $[ReH_7L_2]$ (L = various phosphines), or $CpReH_6$ [270].

6.3.2. *Osmium*

The highest known oxidation state for all transition metals is VIII. Apart from RuO_4 discussed above, this oxidation state is represented by the important OsO_4 (including its complexes with bases [271–274] and references therein), and by the oxyfluorides OsO_3F_2 and OsO_2F_4. Osmium tetroxide is surprisingly stable (bp 131.2 °C) [275], and therefore well characterized [263,276–281]. The descrip-

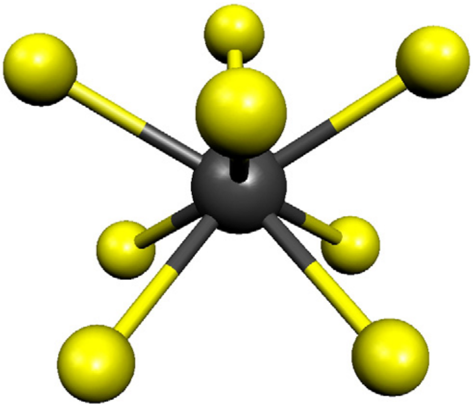

Fig. 5. DFT-optimized structure for osmium octafluoride [78].

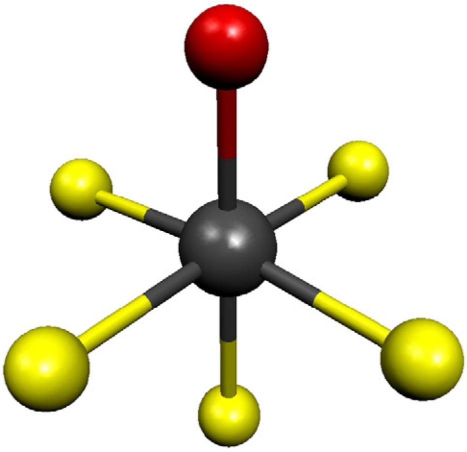

Fig. 6. DFT-optimized structure for $IrOF_5$ [55].

tion of its extensive chemistry as oxidizer, for example in organic chemistry, is beyond the scope of this review. Anionic osmium(VIII) oxo complexes with additional nitrido or hydroxo ligands are also known (see ref. [30] and references therein).

Interestingly, the highest well-characterized osmium fluoride of osmium is OsF_6 [215,282–285]. The octafluoride, OsF_8, is presently unknown, despite a long speculative history (see Fig. 5). An early report [283] of the preparation of OsF_8 was much later proven wrong [282], and the early observations are attributed to OsF_6. Similarly, a report on OsF_7 in 1966 [286] was recently [287] shown not to be reproducible using the original synthetic conditions which entailed the reaction of osmium metal powder with F_2 at 620 °C and 400 bar followed by rapid cooling. A report of $OsOF_6$ [288] was also shown to be incorrect [289,290], although $OsOF_5$ is well known [287,291,292].

Recent quantum-chemical evaluations [78] (see also ref. [293]) of structures and stabilities of higher osmium fluorides and oxyfluorides indicate, that the difficulties encountered in the preparation of higher osmium fluorides and $OsOF_6$ appear to be related to bimolecular decomposition pathways in the condensed phase. The gas-phase stabilities of OsF_8, OsF_7, and $OsOF_6$ were found to be rather respectable at CCSD(T) level, with a somewhat exothermic F_2 elimination for OsF_8 with an appreciable activation barrier, but endothermic F_2 elimination and only endothermic alternative decomposition channels for OsF_7 and $OsOF_6$ [78]. This points to matrix-isolation spectroscopic identification of these compounds as a viable technique for their preparation and characterization. Possible preparation routes have been evaluated computationally [78].

6.3.3. *Iridium*

So far, the highest experimentally well-established stable oxidation state of iridium is VI. It is represented by IrF_6 and by a number of perovskites containing the $[IrO_6]^{6-}$ anion. Iridium hexafluoride is less reactive and oxidizing than PtF_6 and thus comparably well characterized (see, e.g., refs. [215,294–297] and references therein). The VI oxidation state in the relevant perovskites has been determined by XANES [298,299].

Matrix-isolation IR spectroscopy in solid Ar under cryogenic conditions on reaction products resulting from laser-ablated iridium atoms and oxygen provided vibration spectroscopic evidence for the side-on coordinated peroxide complex $IrO_2(O_2)$ [132]. Assignment to an Ir^{VI} peroxide complex was supported by DFT calculations is a way that was more definitive than for the Rh analogue (see above). Furthermore, some bands were tentatively assigned to IrO_3, which would represent another Ir^{VI} species [132]. No evidence has been found for $Ir^{VIII}O_4$. Indeed, the isotope scrambling observed in annealing studies excludes tetrahedral IrO_4 as a stable species under these low-temperature conditions [132]. The very early suggestion of IrO_4 in the gas phase [300] had long been disproved by equilibrium measurements of the gas phase over Ir or IrO_2 solids, which were assumed to have the composition "IrO_3" in the absence of structural proof [301,302]. The β-decay of isotopic OsO_4 and subsequent observation by Ir Mössbauer spectroscopy suggested the $[IrO_4]^+$ cation, but the authors did not associate this with a true Ir^{IX} species in view of the known ionization energies of oxide ligands and the electron affinity of the central ion [14,18,303]. We may thus conclude that no oxide species above Ir^{VI} has been experimentally proven so far. Reports on iridium(VI) hydroxo complexes together with peroxo and superoxo complexes [35,304] are also so far unconfirmed.

Recent state-of-the-art quantum-chemical evaluations (CCSD(T) and B3LYP levels) of the highest possible oxidation states of iridium fluorides up to IrF_9 [55] indicated the highest oxidation state with realistic chances of experimental observation to be Ir^{VII}. Ir^{VIII} and Ir^{IX} fluorides all exhibited strongly exothermic decomposition pathways with typically low barriers. Both IrF_7 and $IrOF_5$ (see Fig. 6) were suggested to be interesting targets, e.g. in matrix-isolation studies, as the unimolecular decomposition pathways were either endothermic or had appreciable barriers [55]. A very intereresting candidate for oxidation state VII is $[IrF_6]^+$, which has only endothermic unimolecular decomposition pathways and should be observable as molecular ion in the mass spectrum of IrF_6 vapor [55].

6.3.4. *Platinum*

The highest experimentally established oxidation state of platinum is VI, as represented by the PtF_6 [305]. Platinum hexafluoride is one of the strongest oxidizers of the 5d transition metals. It has played a key historical role in the oxidation of O_2 to $[O_2][PtF_6]$, leading finally to the discovery of the first true noble-gas compound, originally formulated as $XePtF_6$ [3]. The pentafluoride PtF_5 is also known as a tetramer in the solid state [306] (see also ref. [307]), and various salts of $[PtF_6]^-$ have been characterized [3,4,308,309].

While PtO_3 is sometimes mentioned in textbooks [310,311], both its gas-phase and conventional condensed-phase existence are not well documented. The data include a never confirmed observation of $[PtO_3]^+$ [312] in the mass spectrum, the suggestion of a gas-phase observation of PtO_3 (possibly a peroxide [313]), and speculations on the electrochemical oxidation of Pt^{IV} compounds in basic media [314]. Such early data have been reviewed in reference [30]. The highest well-characterized oxide that is stable under

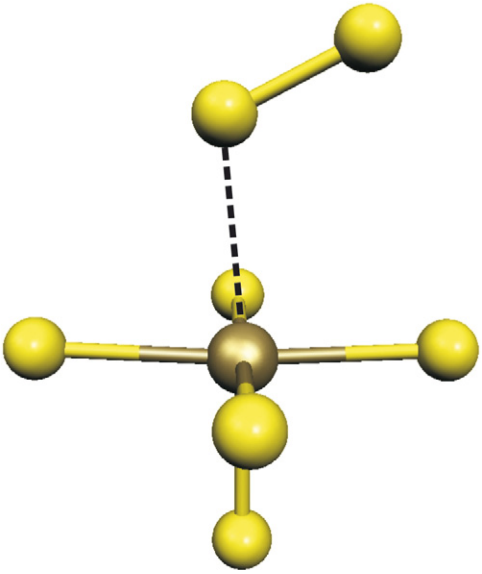

Fig. 7. DFT-optimized structure for the $Au^{V}F_5{\cdot}F_2$ complex, thought to be responsible for the IR band previously assigned to $Au^{VII}F_7$ [79].

"normal" conditions is PtO_2 [184,237]. Further data are available from low-temperature matrix-isolation IR spectroscopy of products from reactions between laser-ablated platinum atoms and oxygen [182,315]. Vibrational spectroscopic evidence was found for a number of Pt^{IV} oxo and peroxo species. Additionally, a tentative assignment to trigonal PtO_3, supported by DFT calculations (B3LYP calculations suggested triplet $Pt^{VI}O_3$ to be only slightly above triplet $Pt^{IV}O(O_2)$). Further calculations, which also suggested $Pt^{VI}O(O_2)_2$, are less reliable, because they only used a GGA-type functional [316].

Quantum-chemical calculations on the higher platinum fluorides, PtF_7 and PtF_8, indicate that they are unstable and unlikely to be accessible [80,317]. There are early reports of the synthesis of $PtOF_4$ [318] and $PtOF_3$ [319]. However, 2 years later the same authors showed that the compound assumed to be $PtOF_4$ was, in fact, $[O_2]^+[PtF_6]^-$ [320]. The reported preparation of $PtOF_3$ pertained most likely rather to $PtOF_2$ [257]. Preliminary quantum-chemical investigations of platinum oxides and oxyfluorides suggest $PtOF_3$ and $PtOF_2$ to be thermochemically stable, at least under matrix-isolation conditions [321].

6.3.5. *Gold*

The highest well-established oxidation state of gold is V, represented by various $[AuF_6]^-$ salts [322–324] with the counterions $[O_2]^+$ [325], $[KrF]^+$ [326], $[Xe_2F_3]^+$ [326], $[NO]^+$ [326], etc., and by the (more strongly oxidizing) neutral AuF_5 [227,325,326]. Gas-phase electron diffraction shows that in the gas phase, AuF_5 is present as a mixture of the dimer and the trimer, both featuring octahedrally coordinated gold atoms [327,328]. In the solid state, dimers are present [328]. Earlier claims of the preparation of AuF_7 [329,330] were recently shown by quantum-chemical calculations not to agree with frequencies computed for a true heptafluoride, which is indeed a local minimum on the potential energy surface [77]. The IR vibrational band at $734 \pm 4\,cm^{-1}$ previously assigned to "AuF_7" was subsequently shown by calculations to most likely arise from the complex $AuF_5{\cdot}F_2$ [79], another Au(V) species (see Fig. 7). A short review on gold fluoride chemistry up to 2004 is available [331].

Evidence for Au^{V} and Au^{IV} coordinated to oxygen ligands is more complicated. The $[AuO_2]^+$ cation has been observed in the course of sputtering a gold target in an Ar/O_2 discharge and was characterized by glow discharge mass spectrometry [127]. In matrix laser-ablation experiments in solid argon [332] and neon [333], intense vibrational bands near $817.9\,cm^{-1}$ [332] and $824.1\,cm^{-1}$ [333], respectively, have been assigned to linear $Au^{IV}O_2$, as supported by DFT calculations.

A recent detailed experimental and theoretical investigation of gold–oxygen complex anions can be found in ref. [334]. Quantum-chemical calculations on gold compounds are reviewed in detail in a series by Pyykkö [335–337].

6.3.6. *Mercury*

Like the other group 12 elements, zinc and cadmium, mercury have usually been considered a post-transition metal [59,338], as the outermost shell of d-orbitals is filled and does not participate significantly in chemical bonding. Mercury(II) was thus naturally considered the maximum oxidation state. For any higher oxidation state of this group, the d-orbitals would have to be involved in bonding, thus changing fundamentally the classification of this element in the Periodic Table from a post-transition element to a transition metal. The correctness of an early report on a short-lived, electrochemically generated, EPR- and UV–vis-spectroscopically characterized cationic Hg(III)(cyclam) complex [134] has been unclear. Recent calculations suggest that the cyclam ligand has been oxidized, and the oxidation state is really Hg^{II} [339]. However, the 1976 report led to speculations on the stability of higher oxidation states of mercury [14,18], in particular on $Hg^{IV}F_4$. In 1993, quantum-chemical calculations (QCISD(T) level) showed that HgF_4 is thermochemically stable with respect to F_2 elimination under gas-phase-like conditions, a computational result that has been confirmed over the years at the highest available ab initio levels [19,20,66–69] (see also the discussion in Section 4). This prediction has very recently been realized by matrix-isolation IR spectroscopy [21]. Under cryogenic conditions, mercury was reacted with excess fluorine in either an argon or a neon matrix, using ultraviolet irradiation from a mercury arc lamp to photodissociate [21]. It was shown that the use of neon, instead of argon, as a matrix material, leads to larger amounts of HgF_4. The experiments also have demonstrated that HgF_4 is a photosensitive species, which decomposes at a slower rate under the same irradiation conditions as it is formed.

So far, no bulk quantities of Hg^{IV} species have been prepared. Computations show, that very electronegative ligands are needed, i.e. $HgCl_4$ is very unlikely to exist [66,68]. Computations on Hg^{IV} complexes with strongly electronegative weakly-coordinating anion ligands (e.g. $AsF_6{}^-$, $SbF_6{}^-$, $OTeF_5{}^-$, $OSeF_5{}^-$) [69], that might allow the generation of gas-phase-like conditions in the bulk phase, indicated that in each case at least one exothermic decomposition pathway is available. Barriers for these processes are thus far unknown. Most likely, very low temperatures will, in any case, be needed for the synthesis of any Hg^{IV} complexes [21,69].

A recent quantum-chemical study on group 12 M^{III} fluoride complexes [71] indicated HgF_3 to be an unlikely target, whereas anionic complexes were somewhat more stable. Oligomeric species may also be interesting to study computationally [71].

6.4. *Superheavy elements*

Obviously, very few reliable experimental data are available for the 6d series, i.e. for the transactinides [135–137,340–342], as these are only available in minute quantities and for a short time. Therefore, most information so far comes from relativistic quantum-chemical calculations. What can be said from experiment, is that for the elements of groups 3–8 (Lr, Rf, Db, Sg, Bh, Hs), the maximum oxidation state probably reaches the group number as for the other d-series (see above). Computational results suggest, that the relativistic expansion of the 6d shell increases bond ionicity even more than for the 5d homologues and thus also stabilizes the highest oxidation state further [343–347]. A recent review summarizes the theoretical description of structures and properties of superheavy element compounds [348].

Further interesting computational data are available for elements 111, 112, and 113 from the work of Seth et al. [106,108,349]. For group 11, i.e. Cu, Ag, Au, and element 111 (eka-gold or roentgenium, Rg), the fluorometallate anions with oxidation states I, III, and V have been studied at coupled-cluster (up to CCSD(T)), MP2, and DFT (B3LYP) levels, using relativistic ECPs [258]. Stabilities of the higher oxidation states (III, V) are further enhanced for roentgenium compared to gold. For example, F_2 elimination from $[RgF_6]^-$ has been computed to be about 100 kJ mol^{-1} more endothermic than for $[AuF_6]^-$ (273 kJ mol^{-1} compared to 165 kJ mol^{-1} at CCSD(T) level) [258].

Similar calculations for [112] F_4 indicate that the tetrafluoride of eka-mercury is also stabilized relative to HgF_4 by enhanced relativistic effects [108]. There is thus even more justification to classify element 112 as a transition metal element than for mercury [106]. This has led Seth et al. to also examine element 113 (eka-thallium) [107]. Indeed, the 6d-orbital participation in bonding for some M^{III} halides was found to be appreciable, and some structural pecularities were noted. Fluorine elimination from $(113)F_5$ and $(113)H_5$ was, however, clearly exothermic, and it was concluded that preparation of the pentafluoride and pentahydride may be difficult. It was speculated that $[(113)F_6]^-$ may be an interesting target for future work [107].

7. General trends and summary

Some key general trends and observations may be extracted from the wealth of available information discussed in the previous sections. Figs. 8–10 summarize trends among the highest known oxidation states for the fluorides and oxides. The plots include several quantum-chemical predictions that, in the authors' opinion, seem promising but have not yet been confirmed experimentally. The well-known differences among the 3d, 4d, and 5d series are apparent from comparisons of the graphs. While the maximum oxidation state reaches the group number up to group 8 in the 4d and 5d series (thus far without homoleptic Ru(VIII) or Os(VIII) fluorides), the absence of FeO_4 is the first sign of the lower preference of the highest oxidation states in the 3d series. This observation extends to the later elements, and the highest oxidation state is also generally less stable for the earlier 3d elements, even if it exists. This reflects the small radial extent of the 3d orbitals due to the lack of a radial node, giving rise to severe problems with Pauli repulsion [76]. The 3p shell has almost the same radial extent and thus prevents good overlap between the 3d shell and ligand orbitals. This generally makes the stretched bonds weaker for the 3d elements. Most notably, such Pauli repulsion is expected to be largest for the highest oxidation state, where the 3d orbitals are particularly contracted. The Pauli repulsion between the more ligand-based orbitals will of course also be largest for the 3d complexes due to the smaller distances involved. Moreover, one would expect it to be more pronounced for the M—O bonding orbitals in oxo complexes due to the very short M—O distances and high formal bond orders. The most detailed analysis is available for $[MnO_4]^-$ [75].

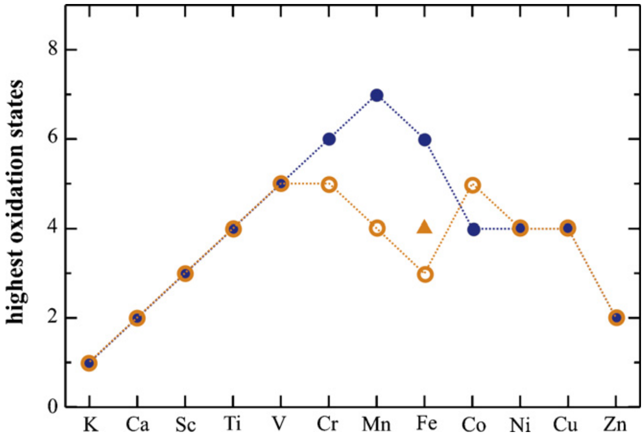

Fig. 8. The highest oxidation states of the 3d transition metal elements. (●) Highest experimentally known oxide species, (○) highest experimentally known fluoride species, (▲) doubtful reports of fluoride species.

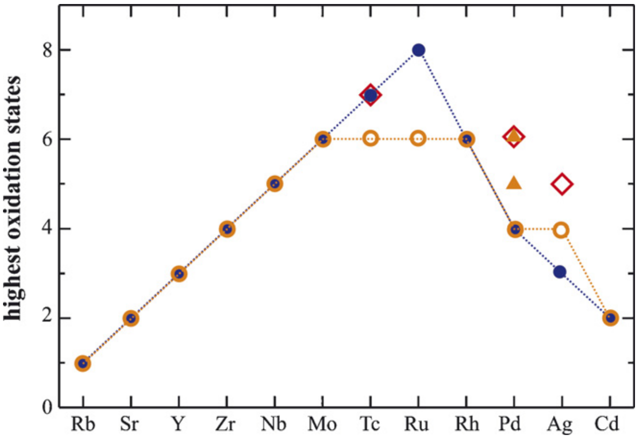

Fig. 9. The highest oxidation states of the 4d transition metal elements. (●) Highest experimentally known oxide species, (○) highest experimentally known fluoride species, (▲) doubtful reports of fluoride species, (◇) quantum-chemically predicted fluoride species.

This Pauli repulsion caused by the subvalent s and p shells exists of course also for the 4d and 5d systems. However, for the 4d complexes, the problem is somewhat diminished, as the radial node of the 4d orbitals results in somewhat more different radii of the 4d and 4p shells. The indirect relativistic expansion of the 5d orbitals leads to further improved overlap between d- and ligand-orbitals. This makes bonding overall strongest in the 5d series, an observa-

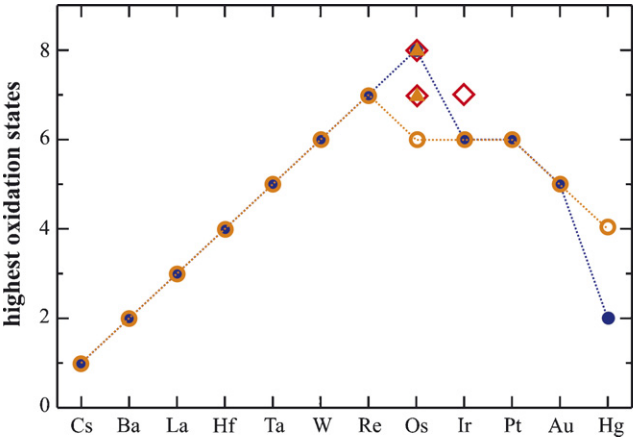

Fig. 10. The highest oxidation states of the 5d transition metals. (●) Highest experimentally known oxide species, (○) highest experimentally known fluoride species, (▲) doubtful reports of fluoride species, (◇) quantum-chemically predicted species.

tion that extends also to the highest oxidation states. The highest oxidation state is well-known to be generally most stable in the 5d series, most likely even more so in the 6d series (see above). For the later elements in a series this also becomes obvious from the observed differences in the maximum available oxidation states.

For the earlier 5d elements, the relativistic enhancement of metal–ligand bond polarity is thought to also aid in the stabilization of the highest oxidation states [100,350]. This is no longer the case for the later 5d elements (e.g., Pt, Au, Hg), where the relativistic contraction of the 6s shell becomes particularly important. Here relativity *increases* the electronegativity. This may be readily inferred from a comparison of Pauling [351,352] and Allred–Rochow [353] electronegativities. The former are up to more than one unit higher than the latter for the late 5d elements. Because the Pauling electronegativities derive from experimental thermochemistry data [351,352] and thus include relativistic effects implicitly, whereas the force model of the Allred–Rochow scale [353] neglects relativity completely, it is clear that these huge differences arise from relativity, and that the Allred–Rochow values are unreliable for the heavier elements. The stabilization of the highest oxidation states for the late 5d elements (and even more so for the late 6d elements) thus does not arise from enhanced ionic bonding contributions. Computations of relativistic effects on Au^{III} versus Au^{I} stabilities [354] still indicate a relativistically increased atomization energy for AuF_3 or $[AuF_4]^-$ due to improved bonding overlap between 5d and ligand orbitals, compared to a relativistically diminished atomization energy for AuF or $[AuF_2]^-$. This is not the case for HgF_4 versus HgF_2 [20]. Here the atomization energies of both tetra- and difluoride are relativistically diminished, due to the contraction of the 6s orbitals. However, the reduction in binding energy for the 6s-orbital-dominated Hg^{II} species due to loss of ionic contributions is more notable, shifting the equilibrium more to the Hg^{IV} state [20]. This relativistic destabilization of the lower oxidation state is much more important when electronegative ligands like fluorine or oxygen are involved. This makes the use of such electronegative ligands even more important to stabilize the highest oxidation states in the 5d series and disfavors ligands that may still be favorable, e.g., in the 3d series.

From the discussion on superheavy 6d-elements above, it is clear that relativity fundamentally alters the chemistry of the 6d elements, even more so than for the 5d series. Other examples are known for the heaviest main-group elements and the actinides (see refs. [355–357] for a few examples). In general, the great importance of relativity makes extrapolations down a group difficult, and even the overall character of a given block of the Periodic Table (s-, p-, d-, and f-blocks) may be affected. The authors believe that the recent observation of HgF_4 [21] may represent an early example, in terms of atomic number, of such a breakdown of the usual classifications, due to the influence of special relativity. Moreover, the trend seems to be enhanced for eka-mercury (see above). Should evidence for an oxidation state V of eka-thallium ever be ascertained (see above), this would be another notable example.

Returning to the comparison between fluoride and oxide species, the available data (Figs. 8–10, Table 2) confirm the previous observation of Jørgensen [14], that the highest oxidation state is best stabilized by oxo ligands for the earlier elements of a series, but better by fluoride ligands for the later elements. Going through the 3d series, one sees the regular increase up to Mn^{VII} in $[MnO_4]^-$ (Fig. 8, blue dots) for oxo-coordination, up to Cr(V) in CrF_5 for fluorides (orange circles). In this series, the preference for the oxides actually continues until Cu, where the highest oxidation states of fluorides and oxides appear to coincide. In the 4d series, the current absence of TcF_7 and of the higher ruthenium fluorides is apparent, whereas the two curves meet at Rh (Fig. 9). Quantum-chemical predictions may provide room for higher fluorides than oxides starting with Pd, but there is no experimental evidence for such a behavior. Finally, in the 5d series (Fig. 10) the current absence of OsF_7 and OsF_8 contrasts with the well-characterized OsO_4 molecule, but the curves intersect at Ir, before HgF_4 marks the highest known oxidation state exclusively represented by a fluoride. Quantum-chemical predictions strongly suggest the existence of Ir^{VII} (Fig. 10), most likely as a fluoride species (but oxide species may not be excluded) [55]. Experimental observation of Ir^{VII} would complete a linear descent of the maximum available oxidation state in the 6th period from Os^{VIII} to Tl^{III} [55], whereas even with all computational predictions in mind, the trends for the later 3d and 4d elements will very likely not become linear. Among the highest 4d fluorides, the plateau comprising the hexafluorides from Mo through Pd is notable. Apart from the absence of an Fe^{IV} fluoride, a similar plateau could be envisioned for the 3d tetrafluorides from Mn through Cu. It should, however, be noted that the experimental status of Cu^{IV} and Ag^{IV} is probably equally uncertain (see above), so that one should not invoke a higher maximum oxidation state for the 3d element in this case. In general, the existence of partly contradictory reports on the highest oxidation states of the later 3d and 4d elements is particularly noteworthy [358], making the discussion of the right-hand portions of Figs. 8 and 9 somewhat more speculative than the left-hand portions of the same figure or of Fig. 10. Another interesting observation is the complete absence of oxyfluorides for the later transition metals (Table 2). There is clearly room for more work to do.

Acknowledgment

The authors are grateful to L. Andrews, N. Bartlett, H. P.A. Mercier, P. Pyykkö, and B. Žemva for stimulating discussions, and to P. Hrobarik, S.A. Losilla, M. Patzschke, and M. Renz for kindly providing so far unpublished results. We would like to express special thanks to G.J. Schrobilgen for careful reading and many helpful suggestions during the preparation of this manuscript. S.R. thanks the Alexander von Humboldt Foundation and the DFG for Research Fellowships.

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