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Molecular aspects of the β-decay in Tc clusters

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Abstract

A quantum-chemical tight-binding method has been used in order to investigate the molecular consequences of the spontaneous transmutation of technetium ^{99}Tc into ruthenium ^{100}Ru in spent fuel of nuclear reactors. The Tc_n and Ru_n clusters ($n = 4$, 6, 13) in highly symmetrical geometries and some of their mixed Tc/Ru derivatives have been considered. The reactivity of the remaining Tc sites is predicted to be enhanced as regards chemical attacks either on Tc–Ru bonds or specific Tc sites by various types of reagents (e.g. radicals or ions). The main consequences of this electronic mixing effect between two chemically related, albeit different, elements could be an easier formation of Tc molecular compounds instead of simple clusters during radioactive decay.

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1. Introduction

The $Z = 43$ non-natural radioelement, named technetium (mainly ^{99}Tc) [1] after its discovery in molybdenum targets bombarded with deuterons (1937), is now produced in rather large amounts from the fission products of ^{235}U and ^{239}Pu by means of thermal neutrons or fast electrons [2]. Its signature has been reported later in spectra coming from Belgian Congo pitchblendes as being due to a product of secondary origin [3], and also from ZrO-star atmospheres [4]. Actually, it is extracted either for special purposes (medicine) or as by-product from materials involved in the nuclear fuel cycle. Many isotopes of Tc are known, with various mass numbers, half-life times and radioactive descendants, but the most important one for spent-fuel problems is ^{99}Tc, whose long-lived isomer (2×10^5 years) is a β decaying radionucleide giving ^{99}Ru, the stable ruthenium species [5]:

$$^{99}\mathrm{Tc} \rightarrow {}^{99}\mathrm{Ru} + \beta + 0.292\ \mathrm{MeV}. \quad (1)$$

Another way is the simple neutron capture:

$$^{99}\mathrm{Tc} + \mathrm{n} \rightarrow {}^{100}\mathrm{Ru} + \beta. \quad (2)$$

Technetium presents numerous oxidation degrees ranging from −II to +VII. In the spent fuel, technetium is found as Tc(0) in mixed metallic aggregates containing mainly platinoids. With the scope of explaining the effect of Tc on the structure of alloys of uranium and fission products, the study of alloys containing elements entering into the composition of the fission products (Zr, Nb, Mo, Tc, Ru, Rh and Pd) is of central interest. If the decay and burn-up of the ruthenium formed are neglected, its accumulation resulting from the irradiation of Tc by neutrons or the possible β-decay of Tc has to be considered in the first place. It turns out to be important to apprehend how behave the electronic structures of

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Tc-containing clusters when a Tc atom is replaced by a Ru. Here, we are primarily interested in the chemical consequences of the transmutation of Tc into Ru inside nuclear materials. Polynuclear metal compounds are presently investigated by various theoretical and experimental techniques, whose results have been the subject of well-documented surveys, especially in the case of palladium [6]. On the other hand, understanding their properties in terms of electronic structure through a combined use of data of various origins is not immediate, and the situation is still worse for Tc, and in a less extent for Ru, which have been largely ignored up to now (see, however [7]).

The study of clusters is an interdisciplinary field involving atomic, molecular, solid state physics but also quantum chemistry and even nuclear physics methods ranging from sophisticated quantum mechanics to simple phenomenological models or semi-empirical approximations. In the present paper we have tried to elucidate the consequences of a β-decay on the electronic picture of technetium metallic compounds, by computing energy and charge distributions of some Tc, Tc–Ru and Ru clusters within the framework of the molecular orbital method. Accurate ab initio determination of electronic structures for systems formed by transition metals of the second period has been found to be possible in some cases [8,9], but such calculations are limited up to now to pure clusters of small size, due to their theoretical intricacies and their prohibitive computational costs. So, we have applied the same simulation technique as in our previous work on the Pd catalytic activity [10]: This consists in simulating the main features of ab initio treatments by means of semi-empirical calculations of tight-binding/extended Hückel type which may be applied to at least medium-size clusters and leads in the same time to clear-cut chemical interpretations. From the beginning of our work, we have limited ourselves to clusters formed by fourth-row atoms, in spite of striking chemical similarities between Tc and its homologues of third and fifth rows, Mn and Re. Actually, the variation observed in the fourth row for properties directly connected to the atomic structure is quite regular [11], at variance with the other two rows because of the poor overlap of the 3d orbitals on nearest neighbors [12], and on the other hand of the relativistic 6s, 6p-shell contraction and 5d-shell expansion [13a,13b]. A comprehensive study of these effects would be outside the scope of the present paper.

2. Theoretical framework

Our tight-binding methodology can be summarized as follows:

(i) The extended Hückel method (EXTHUC) in the primitive form developed by Wolfsberg and Helmholz for the study of transition metal anions [14], the application of which has been revisited recently for coordination complexes of metals [15], has been chosen as the starting point of our theoretical approach for clusters. This means that the molecular orbitals are computed in a non-iterative way from a Hamiltonian matrix whose diagonal elements for s, p, d basis functions are extracted from spectroscopic Slater–Condon parameters for atoms [16], and the off-diagonal elements evaluated by means of the standard formula:

$$H_{\mathrm{pq}} = K\big(H_{\mathrm{pp}} + H_{\mathrm{qq}}\big)S_{\mathrm{pq}}. \tag{3}$$

The values H_{pp} collected by Alvarez for most elements [17] have been selected and the overlap integrals, S_{pq}, have been calculated from Slater integrals with the exponents recommended by Pietro and Hehre for the second-row transition metals [18]. As pointed out on the fifties [19], the extended Hückel method (EXTHUC) is completely equivalent to a tight-binding approach including overlap; for clusters, it generates the usual band model of solids when the size of the compounds considered increases to infinity [20].

A rather large set of K parameters (two or more) may be found in the literature concerning inorganic compounds (see for instance [21]), instead of the value $K = 1.75$ selected by Hoffman for organic chemistry [22]. In the present case, our choice $K = 3$ has a computational advantage: there is clear-cut distribution of the occupied molecular orbitals into two families, those having a dominant s-character, which can be associated to the skeleton of the cluster, and those having a dominant d-character, which mimic the d-band of solids in the case of finite-size system. The orbital energies e_{d}, forming an almost closed shell are distributed around the H_{dd} matrix elements in a rather small interval, whereas the energies of the former look like the eigenvalues of the topological graph formed by a network including n equivalent vertices [23]. If, for simplicity, the matrix element H_{pq} associated to every atom pair of the graph is supposed to have a common value γ one finds a lowest eigenvalue e_i equal to $(n-1)\gamma$ and $(n-1)$ highest eigenvalues equal to $-\gamma$. Therefore, it is possible to isolate the pseudo d-band of the cluster by taking a not too small K value; increasing K, however, does not imply a corresponding variation of the binding energy of the cluster because the core repulsion terms included in the treatment has to be readjusted accordingly. To do that, our program has the possibility of computing electronic energy derivatives with respect to atomic displacements, in other words of having indispensable Hellmann–Feynman forces.

(ii) The total one-electron energy spectrum is computed as a sum of occupied orbital energies:

$$E_1 = \sum_i v_i e_i \tag{4}$$

using appropriate occupation numbers v_i, as described in Ref. [10]. For the d-dominant orbitals, v_d is fixed to the average population of the d-orbitals of the isolated atom in its chemical significant d^qs^1 valence states, i.e. $v_d = q/5$ for a pure cluster P_n and $(nq + nq')/5(n + n')$ for a mixed cluster $P_nQ_{n'}$. The total number of remaining electrons, exactly equal to the number of atomic centers, is distributed among the s-dominant orbitals with the double occupancy or an equidistribution for those located below or above the d-block. [1]

(iii) In the usual EXTHUC frame, the calculation of atomization energies (binding energies) is computed by subtracting the atomic energies from the sum E_1 of molecular orbital energies. Separating the part A included in E_1 as the sum of the $(4d^q5s)$ matrix elements H_{pp} from their molecular counterpart B, one obtains the atomization energy equal to B. We have added an appropriate repulsion part C to B in order to have a correct behavior of the potential energy curves through a Born–Mayer term of the form

$$E_c = \sum_{k'} \sum_{k \neq k'} \alpha_{PQ} e^{-\beta_{PQ}(r_{k,k'} - d_{PQ})}, \tag{5}$$

where the constant α_{PQ} is a specific energy prefactor for the pair of atoms P, Q located at centers k and k' and the exponential describes the repulsive trend of the ion–core interaction in terms of dimensionless reduced distances $\beta_{PQ}(r_{k,k'} - d_{PQ})$ [25,26]. The constant d_{PQ} is most often identified to the bulk interatomic distance. Let us point out that the present procedure is valid in so far as the interaction potential inside the molecule has an isotropic form, that is to say for clusters of tetrahedral, octahedral and icosahedral geometries studied in this paper, but it could be extended to anisotropic cases using α_{PQ} and β_{PQ} vectorial coefficients for the x, y, z directions.

As regards α and β bond parameters, our parameterization technique consisting in two conditions to be satisfied by the results of preliminary calculations for tetrahedral pure clusters M_4 (namely atomization energies in agreement with ab initio values and exact balance between the electron and nuclear forces in order to ensure the size consistency of the whole procedure) differs somewhat from the one previously used for Pd and Rh because theoretical data are lacking for Tc and Ru. Defining a factor λ as the ratio between our preliminary estimation and the ab initio value of the atomization energy for a Rh_n cluster, we have considered λ as a transferable quantity for Tc and Ru. Using such a factor, we have inferred ab initio values of the Tc_n and Ru_n clusters from which α_{Tc-Tc} and α_{Ru-Ru} are adjusted in conformity with our previous treatment for Rh. Parameters β_{PQ} have been kept constant independently of the size of the cluster, while α_{PQ} have been re-optimized to have Hellmann–Feynman forces acting on the atoms of the Tc and Ru clusters vanishing. We have estimated the parameters. α_{PQ}, β_{PQ} and d_{PQ} corresponding to pairs of technetium–ruthenium atoms in mixed clusters by taking the geometrical means of their α_{PP}s and the arithmetical means of their β_{PP}s and d_{PP}s. Using geometric means for the α_{PQ} prefactors was suggested by the Born–Mayer original paper [27].

(iv) Electronic distributions computed from Mulliken population analysis make striking differences apparent between the M_4 and M_6 pure clusters, which have zero net charges for symmetry reasons, and the 'magic' M_{13} compounds: Initially, an important unrealistic charge transfer appears from the center atom to the surface ones, notwithstanding the fact that the values assigned to the corresponding s, p, d matrix elements in Eq. (1) are the same. This is reminiscent of the state of affairs formerly observed for π-electron systems described by non-alternant graphs [28], as it is presently the case for 13-atom clusters. The failure of the Hückel scheme can be circumvented by introducing correction terms with appropriate signs on the H_{PP} elements, the magnitude of which is determined by the net charges lying on each atom [29]. Model Hamiltonians based on ab initio molecular orbital theories [30,31] may be also quoted in order to justify this procedure.

Our interest being the modeling of large clusters with more or less equivalent atoms, we have determined the charge corrections of the M_{13} compounds by assuming zero net charges on the surface and center atoms of the icosahedron. The neutrality of the M_{13} pure clusters is recovered by small positive increments of some thousands, in a.u., for the former and, of course, a negative correction twelve times greater for the latter (see below).

3. Numerical implementation

Due to the paucity of relevant data for transition metal clusters of the second period, especially for technetium and ruthenium, we have taken the rhodium compounds as the starting point of our parameterisation using the ab initio calculations of Balasubramanian et al. for Rh_4 [9d] and the bulk properties of metals as guides for linear extrapolation purposes. Big clusters have a huge number of possible conformers, but for computational reasons connected to the isotropic form of the Born–Mayer repulsion term, we have limited the present study to clusters of regular forms: Thus, the tetrahedral and octahedral pure compounds have been computed in their T_d and O_h usual geometries, and the 13-center cluster in the I_h 'magic' geometry (a form generally pre-

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[1] Since the occupation numbers v_i are not necessarily integers, our model does not correspond to a one-determinant v-representable density matrix, but to a v-representable ensemble, as it is the case for the multiplet structure of transition elements in the sense of the DFT theory [24].

ferred for icosahedral compounds, as being more stable than, say, a cubooctahedron [32]). For the Tc_4 and Ru_4 tetramers, interatomic distances have been scaled from bulk distances taking the theoretical result for Rh_4 as a reference. For the 6- and 13-atom clusters formed of Tc and Ru atoms, a similar extrapolation has been done using the bond lengths of Rh_6 and Rh_{13} obtained by a three-point interpolation procedure in terms of graph-theory bond orders for Rh_2, Rh_4 and bulk. Mixed clusters $P_nQ_{n'}$ are considered as resulting from the superposition of two homonuclear clusters of $(n+n')$ atoms (with their own geometry) putting in coincidence their center of mass and finally keeping the Q atoms at the same place as in a $Q_{n+n'}$ cluster having the same center. Due to the different lengths of the Tc–Tc and Ru–Ru bonds, mixed clusters derived from the parent geometries present a lower symmetry and their Tc–Ru lengths are just the arithmetic averages of the Tc–Tc and Ru–Ru bonds for clusters of the same size; this relationship is pretty well verified experimentally by the value of the Pd–Rh bond length [33]. Symmetry and geometrical data are given in Fig. 1.

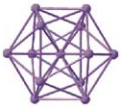
	$d_{Tc-Tc}=4.8545$ $d_{Ru-Ru}=4.7500$
	$d_{Tc-Tc}=4.9468$ $d_{Ru-Ru}=4.9210$
	$d_{Tc-Tc}=5.0415$ $d_{Ru-Ru}=4.9330$
Bulk	$d_{Tc-Tc}=5.11$ $d_{Ru-Ru}=5.01$

Fig. 1. Geometries of the clusters (bond length in a.u.).

As already stated, our simulation procedure lies on the adjustment of the α_{PQ} and β_{PQ} parameters in such a way that the E_1 quantity, Eq. (4), (written as a $(A+B)$ sum, A being the energies of separated atoms included in E_1 through the matrix elements H_{dd} and H_{ss}, B the molecular residuum), and completed by the core repulsion term C given above, Eq. (5), yields a correct value for the total atomization energies $B+C$ for the reference. The necessary data are those extrapolated from Rh_4 by the recipe described above. The parameters we have selected for the present EXTHUC calculations are listed in Table 1.

The atomization energy (AE) of a cluster, P_n, formed from n atoms of metal P linked among themselves by m bonds is the energy difference of the process, $P_n \rightarrow nP$, where P is taken in its lowest configuration of chemical interest, namely $4d^ms^1$, $m = 6, 7, 8$ for Tc, Ru, Rh respectively. AE increases systematically with n, so that it is more appropriate for comparisons to evaluate either the atomization energy per atom (AE/n) or better per bond (AE/m) [34].

The differences of atomization energies between Tc_n Ru_n, Rh_n molecules arise from the matrix elements H_{dd} and H_{ss}. Since covalent effects (mainly due to the s and p orbitals) are present in molecular clusters, variations of these parameters could be compared with the trend observed for the electronegativities of atoms rather than valence-shell atomization energies; the values for the best bulk mimicking clusters are consistent with the values reported in the most recent table of (Tc = 1.36, Ru = 1.42, Rh = 1.45) [1].

4. Results for mixed Tc–Ru clusters

4.1. Energy, charge and spin distributions

The predictions of the quantum-mechanical methods concerning chemistry are conveniently presented by

Table 1
EXTHUC (H_{PP} in a.u., exponent ζ) and core (α_P, β_P) parameters

P		K	H_{PP}	ζ	β_P	α_{P_n}		
						P_4	P_6	P_{13}
Tc	4d–4d		−12.82	3.00	0.0697	0.054	0.038	0.022
	5s–5s	3	−10.07	1.85				
	5p–5p		−5.40	1.85				
Ru	4d–4d		−12.70	3.20	0.526	0.055	0.031	0.017
	5s–5s	3	−9.0	1.75				
	5p–5p		−5.0	1.75				
Rh	4d–4d		−12.50	3.45	0.618	0.041	0.045	0.017
	5s–5s	3	−8.09	1.75				
	5p–5p		−4.57	1.75				

distributing the outcome of the calculations performed for a given molecule between its atoms and/or bonds. This is true not only for the electronic structure, usually depicted in terms of charges and spin densities, but also for energy parameters, as in the present case the AE, that is for a cluster the binding energy with respect to the set of its atomic constituents.

Let us summarise our procedure for the analysis of atomisation energies of mixed clusters in terms of bond increments. For a pure cluster P_n, the quantity AE defined as the energy balance of the process $P_n \rightarrow nP$ increases systematically with n, so that it is customary to consider the atomisation energy per atom (AE/n) if one is interested by the evolution of the cluster energy towards a bulk property. A more chemical description consists in enumerating the number m of effective bonds in the cluster $(n \leqslant m \leqslant n(n-1)/2)$ and considering the atomisation energy per bond (AE/m). However both procedures are clearly doubtful for mixed clusters formed of different atoms P and Q, thus including different types of bonds P–P, Q–Q, P–Q. Our approach of the problem is the following: Consider, for simplicity, a pair of monosubstituted clusters $P_{n-1}Q$ and $Q_{n-1}P$ whose parents, P_n and Q_n, have the same number m of bonds. We can calculate atomisation energies $\mathrm{AE}_P/n = D_P$ and $\mathrm{AE}_Q/n = D_Q$ or, alternatively, atomisation energies per bond $\mathrm{AE}_P/m = E_{PP}$ and $\mathrm{AE}_Q/m = E_{QQ}$. From these basic quantities as reference data, we can try to express the atomisation energies AE_{PQ} of the mixed clusters in terms of atom increments δ_a and bond increments δ_b, that is for $P_{n-1}Q$:

$$\mathrm{AE}_{PQ} - (n-1)D_P - D_Q = \delta_\mathrm{a}, \tag{6}$$

$$\mathrm{AE}_{PQ} - (m - m_Q)E_{PP} - m_Q E_{PQ} = \delta_\mathrm{b}, \tag{7}$$

m_Q being the number of $P - Q$ bonds. The second procedure requires the evaluation of the bond parameter

Table 2
Results for tetramers (energies in a.u.)

	Tc_4	Tc_3Ru	Tc_2Ru_2	$TcRu_3$	Ru_4
E_tot	−13.451	−13.855	−14.255	−14.649	−15.038
$E_\mathrm{tot} - \Sigma E_\mathrm{atom}$	−0.667	−0.667	−0.663	−0.653	−0.638
$\Sigma\delta_\mathrm{a}$	−0.167	−0.660	−0.652	−0.645	−0.159
$\Sigma\delta_\mathrm{b}$	−0.111	−0.660	−0.652	−0.645	−0.106
$(E_\mathrm{tot} - \Sigma E_\mathrm{atom}) - \Sigma\delta_\mathrm{a}$		−0.008	−0.010	−0.008	
$(E_\mathrm{tot} - \Sigma E_\mathrm{atom}) - \Sigma\delta_\mathrm{b}$		−0.008	−0.010	−0.008	
$\varepsilon_\mathrm{Tc-Ru}$		−0.003	−0.003	−0.003	

Table 3
Results for hexamers (energies in a.u.)

	Tc_6	Tc_5Ru	$TcRu_5$	Ru_6	Tc_4Ru_2 (zz)	Tc_4Ru_2 (zx)	Tc_3Ru_3 (zzx)	Tc_3Ru_3 (xyz)	Tc_2Ru_4 (zx)	Tc_2Ru_4 (zz)
E_tot	−20.250	−20.676	−22.329	−22.732	−21.096	−21.096	−21.512	−21.512	−21.923	−21.922
$E_\mathrm{tot} - \Sigma E_\mathrm{atom}$	−1.074	−1.096	−1.133	−1.132	−1.112	−1.112	−1.124	−1.124	−1.131	−1.130
$\Sigma\delta_\mathrm{a}$	−0.179	−1.084	−1.122	−0.189	−1.093	−1.093	−1.103	−1.103	−1.112	−1.112
$\Sigma\delta_\mathrm{b}$	−0.090	−1.084	−1.122	−0.094	−1.093	−1.093	−1.103	−1.103	−1.112	−1.112
$\varepsilon_\mathrm{Tc-Ru}$		−0.003	−0.003		−0.002	−0.003	−0.003	−0.004	−0.003	−0.002

Table 4
Results for 13-atom monosubstituted clusters (energies in a.u.)

	Tc_{13}	$Tc_{12}Ru$ center	$Tc_{12}Ru$ surface	$TcRu_{12}$ center	$TcRu_{12}$ surface	Ru_{13}
E_tot	−45.067	−45.501	−45.482	−49.895	−49.907	−50.295
$E_\mathrm{tot} - \Sigma E_\mathrm{atom}$	−3.519	−3.549	−3.530	−3.499	−3.511	−3.495
$\Sigma\delta_\mathrm{a}$[a]	−0.271	−3.518	−3.518	−3.497	−3.497	−0.267
$E_\mathrm{tot} - \Sigma E_\mathrm{atom} - \Sigma\delta_\mathrm{a}$	−0.084	−0.031	−0.012	−0.002	−0.014	−0.083
$\Sigma\delta_\mathrm{b}$[a]		−3.516	−3.518	−3.499	−3.497	
$E_\mathrm{tot} - \Sigma E_\mathrm{atom} - \Sigma\delta_\mathrm{b}$		−0.033	−0.012	−0.000	−0.014	
$\varepsilon_\mathrm{Tc-Ru}$		−0.003	−0.002	−0.000	−0.002	

[a] In the case of the 13-atom clusters, the coincidence of the $\Sigma\delta_\mathrm{a}$ and the $\Sigma\delta_\mathrm{b}$ is purely numerical.

Table 5
Results for 13-atom disubstituted clusters (energies in a.u.)

	Tc$_{11}$Ru$_2$^{a} ortho	Tc$_{11}$Ru$_2$^{a} para	Tc$_{11}$Ru$_2$^{a} meta	Tc$_2$Ru$_{11}$^{a} meta	Tc$_2$Ru$_{11}$^{a} para	Tc$_2$Ru$_{11}$^{a} ortho
E_{tot}	−45.820	−45.821	−45.820	−49.412	−49.413	−49.413
$E_{tot} - \Sigma E_{atom}$	−3.465	−3.465	−3.464	−3.420	−3.421	−3.421
$\Sigma\delta_a$	−3.445	−3.445	−3.445	−3.394	−3.394	−3.394
$E_{tot} - \Sigma E_{atom} - \Sigma\delta_a$	−0.020	−0.021	−0.019	−0.027	−0.027	−0.027
$\Sigma\delta_b$	−3.445	−3.445	−3.445	−3.393	−3.393	−3.393
$E_{tot} - \Sigma E_{atom} - \Sigma\delta_b$	−0.019	−0.020	−0.019	−0.027	−0.028	−0.028
ε_{Tc-Ru}	−0.002	−0.002	−0.002	−0.002	−0.002	−0.003

[a] In the disubstituted $P_{11}Q_2$ clusters, ortho means that the Q atoms are close neighbours, meta the two Q atoms are separated by a single P atom and para the Q atoms are diametrically located.

E_{PQ}, for which we have chosen the Pauling arithmetic rule for bond energies:

$$E_{PQ} = \tfrac{1}{2}(E_{PP} + E_{QQ}) \tag{8}$$

a relationship working well for dissociation energies of heteronuclear diatomics with transition metals [35]. If so, Eq. (7) can be rewritten [2]

$$(\mathrm{AE}_{PQ} - \delta_b) = \left(m - \frac{m_Q}{2}\right)E_{PP} + \frac{m_Q}{2}E_{QQ}. \tag{9}$$

Extension of this formula to polysubstituted systems is straightforward. Even if in some cases, e.g. the tetrahedral and the octahedral clusters, both increments coincide for algebraic reasons, bond parameters δ_b have to be preferred because the quotient $\varepsilon_{PQ} = \delta_b/m_Q$ has a formal structural meaning, namely that of a positive or negative energy increment (deficit or excess of energy respectively), localized on the mixed bonds of the $P_{n-1}Q$ molecule. Atomisation energies corresponding to the process $P_n \rightarrow nP$ are connected to the magnitude of the energy stored in a cluster; if the latter becomes available for chemical reactions, we are led to interpret ε_{Tc-Ru} as a reactivity index with respect to reactions involving bonds specifically.

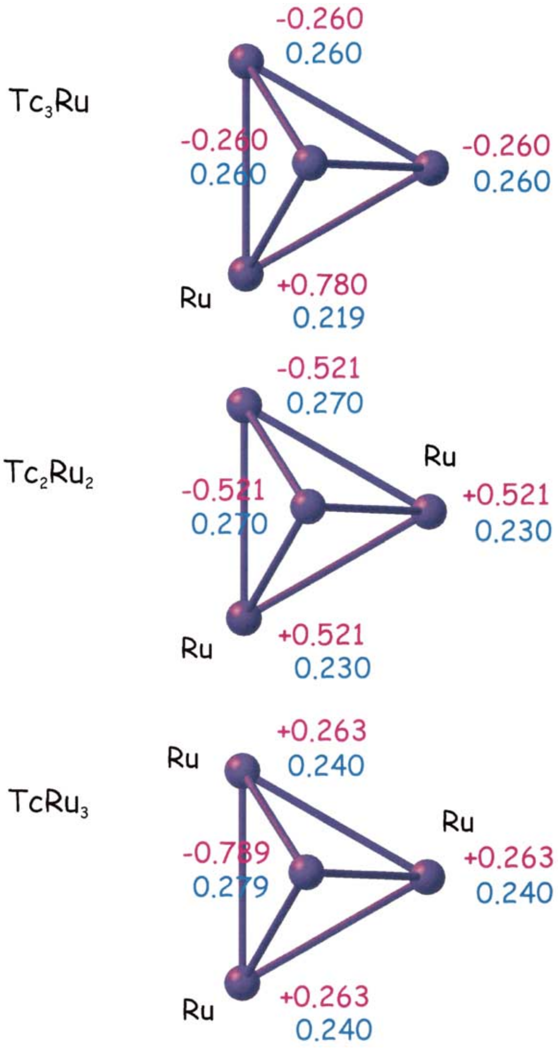


Fig. 2. Net atomic charges (in pink) and condensed Fukui indices (in blue) for the mixed tetramers.

Rough, but significant predictions concerning the attack of specific positions in a molecule by various reagents (ions or radicals) may be often made by inspecting the distribution of charge and spin densities among the various atoms, as given by conventional Mulliken population analysis for total and unpaired-electron densities including overlap. In addition to charges, the spin distribution is relevant for probing the reactivity of the different sites of clusters formed by transition metals having incomplete outer shells of electrons. The corresponding quantities given in form of unpaired-electron distributions normalised to unity and, for simplicity, averaged for similarly located atomic centers, are useful as indices for reactions involving radicalic species, but also for reactions with cations and anions in the frame of the frontier-electron theory; indeed they coincide with the so-called condensed Fukui functions [36], whose values are identical for electrophilic, nucleophilic and radicalic reactions in the case of

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[2] Eq. (8) of Ref. [10] should be rewritten (δ_a instead of δ_b).

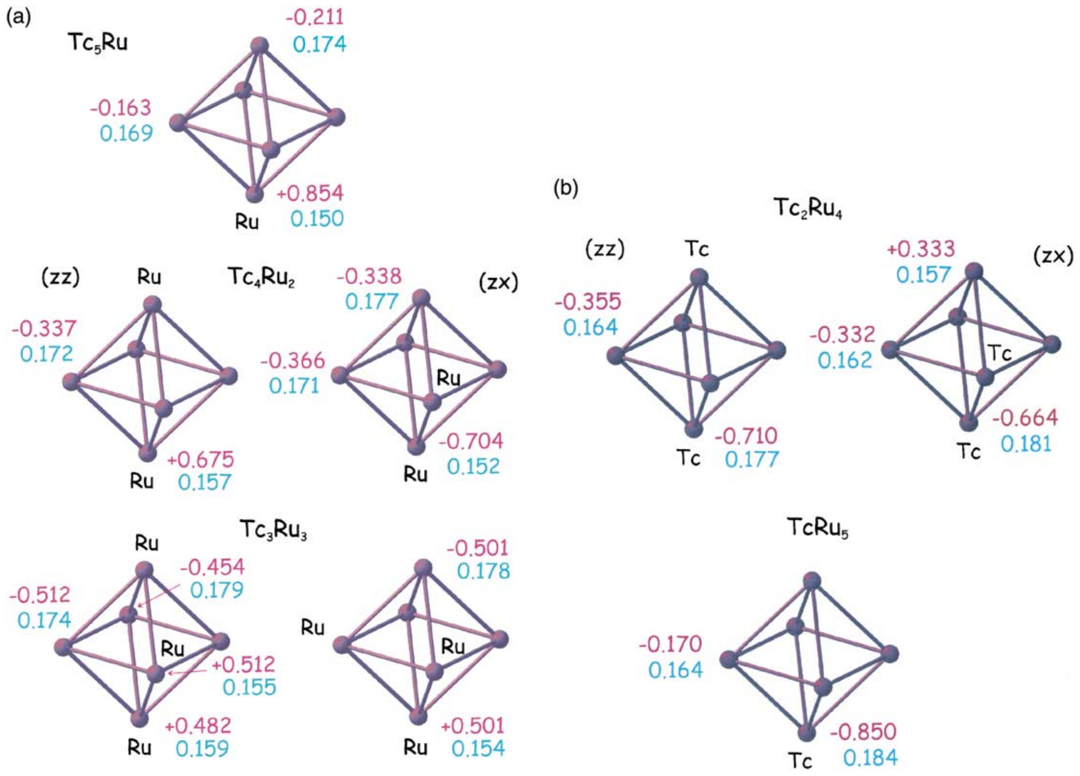

Fig. 3. Net atomic charges (in pink) and condensed Fukui indices (in blue) for the mixed hexamers.

HOMO and LUMO molecular orbitals belonging to the same set of energy levels.

4.2. Comments and conclusion

The values of the energies obtained for pure and mixed Tc–Ru clusters with 4, 6 and 13 atoms are presented in Tables 2–5. The AEs reported line 2 of Tables 2–4 for pure Tc_n and Ru_n clusters exhibit a different behaviour, according as 4- and 13-atom or 6-atom compounds are considered: AE is greater (in absolute value) for $n = 4$ and 13 in Tc than in Ru, whereas the inverse situation is observed for $n = 6$. This state of affairs can be related to the differences in geometrical structures and preclude any significant comparison with the cfc bulk cohesive energies for which specific calculations could be made for clusters of increasing size with appropriate geometries (see for instance [37]). As for Pd and Rh clusters [10] negative ε values indicate that the mixed bonds act as a reservoir of energy. In some respect, the stored atomisation energy in Tc–Ru bonds plays the same role as the excess of resonance energy in some C–C bonds of aromatic hydrocarbons as revealed by the distribution of their π bond orders (see [38]); so, we are entitled to predict a particular affinity of the Tc–Ru bonds to chemical reagents involved in addition reactions.

In Figs. 2 and 3 are reported the values of the atomic charges and the condensed Fukui indices of the mixed tetramers and hexamers. [3] They indicate that the mixed Tc–Ru clusters have important atomic net charges; they are the result of the combined effects of the delocalisation of the electron cloud between equivalent centers (as in pure clusters), and the change of nuclear charges due to Tc–Ru transmutations. As a consequence, some mixed clusters (especially those having the same number of Tc and Ru atoms) look like very much to intramolecular ion pairs [39] with large dipole moments and intense rotation spectra. This suggests that some reactions on mixed clusters could be preferentially orientated on well-defined centers.

The use of condensed Fukui indices, given in the figures for tetrahedral and octahedral clusters, enables us to analyse more precisely the characteristics of the site attack. Let us say that the Fukui indices for chemically equivalent positions on the surface of Tc–Ru icosahedra are in line with the trend observed in simpler tetramers and hexamers. In a $Tc_{12}Ru$ cluster, the mean value of the

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[3] Figures for mixed 13-atom clusters are not given because they are too cumbersome, due to the various sets of equivalent positions in disubstituted compounds.

Fukui indices for a Tc-surface atom is 0.0621 or 0.0647 for a Ru-top or a Ru-center substitution as compared to 0.0615 for Tc_{13} itself; reciprocally, that of a Ru-surface atom in $Ru_{12}Tc$ clusters is 0.0680 or 0.0652 for a Tc-top or a Tc-center substitution as compared to 0.0690 for Ru_{13} itself. The corresponding figures are 0.0628, 0.0627 and 0.0631 for Tc-surface atoms in ortho, meta or para $Tc_{11}Ru_2$ compounds, whereas they are 0.0672, 0.0672 and 0.0666 for Ru-surface atoms in ortho, meta and para $Ru_{11}Tc_2$ compounds. We can state that the Fukui indices of the technetium atoms in $Tc_nRu_{n'}$, increase with n' (as far as $n' < n$), from the value corresponding to the pure cluster to a maximum value depending on the size of the cluster. As previously noted, increasing indices from pure to mixed clusters mean a greater site reactivity whatever the nature of the attacking agent is.

To conclude we feel that the unavoidable decay of technetium nuclei may cause an increasing reactivity of technetium sites in clusters towards chemical reagents, say M, involved both in bond additions or atom attacks. Among the possible mechanisms leading to the dissemination of undesirable Tc–M compounds we would recall the so-called balloon effect invoked in the heterogeneous catalysis by iron [40]: it would consist of the removal of a (gaseous) molecule with technetium from the metal surface subsequent to chemisorption of the M species. In line with this event, the interesting possibility of transmutating technetium into ruthenium by neutron capture may be recorded [41].

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