

The Electronic Structure of the Group 6 Oxyanions $[\text{MO}_4]^{2-}$, where M = Cr, Mo, W, and Element 106

By V. Pershina and B. Fricke

Theoretical Physics Department, University of Kassel, D-34132 Kassel, Germany

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Abstract

The electronic structure of the group 6 oxyanions $[\text{MO}_4]^{2-}$, where M = Cr, Mo, W, and element 106 have been calculated using the Dirac-Slater Discrete Variational method. Results of the calculations show a relative decrease in the metal-oxygen bond strengths for the $[\text{E106O}_4]^{2-}$ ion in the solid state compared to that for the $[\text{WO}_4]^{2-}$ anion. Calculated energies of the electronic charge-transfer transitions are indicative of a strong possible luminescence of $[\text{E106O}_4]^{2-}$ in the blue-violet area. In solutions $[\text{E106O}_4]^{2-}$ will be the most stable ion out of the entire series. Estimated reduction potential $E^\circ(\text{E106O}_4^{2-}/\text{E106O}_4^-)$ equal to -1.60V shows only a slightly increased stability of the +6 oxidation state for element 106 in comparison with W.

1. Introduction

Complex formation of the transactinide elements has been studied by the exchange solvent extraction which has been applied to oxy- and oxyhalide complexes of element 104 [1] and to halide- and oxyhalide complexes of element 105 [2]. An interesting behavior of element 105 has been observed in these experiments: it was extracted together with Nb and Pa and not together with Ta. Since a new series of the liquid chromatography experiments [3] is to be conducted with the aim to study the behavior of element 106 in aqueous solutions relative to the lighter analogs Mo and W, a theoretical investigation of the complex formation of element 106 in acid/basic aqueous solutions as well as of the stability of different oxidation states is of importance.

In our earlier work [4] we have studied theoretically the complex formation of group 5 elements, including Pa, and have shown that the trend in the formation of pure halide complexes in group 5 does not continue in going from Ta to Ha. Thus, element 105 was shown to form oxyhalide complexes like those of Nb and Pa and not like those of Ta. Tantalum proved to have a specific position in the group and the highest tendency to form pure chloride complexes. The bonding metal-oxygen and metal-chlorine was shown to change in a different way within groups 5 and 6. In addition, the metal-chlorine bonding for particular coordinations [5] decreases in going from element 104 to element 106. Taking this into consideration one cannot

make simple extrapolations in the properties in going from the 5d to the 6d elements. Relativistic effects change the spatial distribution of the valence wave functions and their energies so that one cannot predict bonding made by these orbitals extrapolations from the 3d to the 5d and further to the 6d elements. Thus, relativistic molecular orbital calculations are needed in each case when a particular type of compound is considered.

Since the complex formation of element 106 has not been studied until now, we decided to start with calculations of the simplest oxyanions $[\text{MO}_4]^{2-}$ which are basic units of many crystalline compounds of Cr, Mo, and W. They also exist as independent units in aqueous basic solutions in the one-atom-at-a-time chromatography experiments.

Many of the compounds containing chromate, molybdate and tungstate ions have been well studied experimentally: structural data as well as data on electronic and vibrational spectra in solid state and solutions are available [6, 7]. Effects of covalency have also been studied for these compounds [8]. One of the important subjects of the research has been an investigation of the luminescence of the solid molybdates and tungstates [9, 10].

There are numerous calculations of the electronic structure of the $[\text{CrO}_4]^{2-}$ ion (see, e.g., [11]) and some nonrelativistic calculations of the $[\text{MoO}_4]^{2-}$ and $[\text{WO}_4]^{2-}$ ions [12, 13]. Some theoretical works on the electronic structure of the d-elements oxyanions [14] have been devoted to the interpretation of luminescence.

In this work we will present results of the calculations of the electronic structure of the $[\text{MO}_4]^{2-}$ ions, where M = Cr, Mo, W, and element 106 (E106) and will analyse the properties of the $[\text{E106O}_4]^{2-}$ ion relative to the lighter analogs. In Sec. 2 some comments on the relativistic Dirac-Slater Discrete Variational Method (DS DVM) are given. Sec. 3 contains results of the calculations and their discussion.

2. Method and details of the calculations

2.1. Dirac-Slater Discrete-Variational method

Calculations of the $[\text{MO}_4]^{2-}$ ion have been performed using the DS DVM description of which and its

application to the different halide and oxyhalide compounds of the transactinides can be found elsewhere [15, 16, 4, 5]. As in our previous works the basis set included valence ns , $np_{1/2}$, $np_{3/2}$, $(n-1)d_{3/2}$, and $(n-1)d_{5/2}$ orbitals. Both full electron and frozen-core approximations have been used. Calculations of the molecular integrals have been done numerically using 9000 integration points. Double point group representations have been used for the molecular symmetry orbitals.

Mulliken population analysis [17] has been used to study the distribution of the electron density and bonding. As a measure of the covalent bonding the overlap population (OP) parameter will be used in this paper. The partial OP between orbital j and k on centers r and s are expressed as follows

$$n(j_r, k_s) = \sum_i n(i; j_r, k_s) = \sum_i 2N(i)c_{ij}c_{ik}S_{j_r k_s}. \quad (1)$$

Here c_{ij} are MO coefficients, S_{ij} is an overlap integral between orbitals j and k , $N(i)$ is the number of electrons on molecular orbital i .

The total overlap population is

$$n = \sum_{j,k} n(j_r, k_s). \quad (2)$$

2.2. Input parameters

The calculations have been performed for two sets of metal-oxygen distances: for short bond lengths realized in the solid state compounds containing these anions, and for longer bond lengths which can be realized in the aqueous solutions. For the solid state $[\text{MO}_4]^{2-}$ anions the M–O separations have been taken from the available measurements of the mean bond lengths in the AMO_4 scheelite compounds [6]: $R_{\text{Mo-O}} = 1.759 \text{ \AA}$ for CaMoO_4 and $R_{\text{W-O}} = 1.786 \text{ \AA}$ for CaWO_4 . For the chromate anion $R_{\text{Cr-O}}$ were taken equal to 1.64 \AA as those in CaCrO_4 [18]. For $[\text{E106O}_4]^{2-}$ the $R_{\text{E106-O}}$ was assumed to be 0.06 \AA larger than that in the tungsten anion. This is the shortest bond length which was accepted on the basis of the differences in the covalent radii for the WH_6 and E106H_6 compounds obtained in Ref. [19]. This takes into account relativistic bond contraction. A larger bond distance E106–O has been also considered in the calculations. A perfect T_d symmetry has been accepted for all the complexes.

For the anions in solutions the bond distances were taken as those in Ref. [13], while the calculations have also been done for the distances which are sums of ionic radii [20] being only 0.01 \AA larger. The used in the calculations bond lengths will be shown in the following tables of results.

3. Results of the calculations and discussion

3.1. Molecular energy levels

Trends in the molecular orbital energies for the group 6 oxyanions $[\text{MO}_4]^{2-}$, where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, and

Table 1. Energies (negative) of molecular levels, energy gap (ΔE) and crystal-field (A) parameters for $[\text{MO}_4]^{2-}$, ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, and E106) (in eV)

| | $[\text{CrO}_4]^{2-}$ | $[\text{MoO}_4]^{2-}$ | $[\text{WO}_4]^{2-}$ | $[\text{E106O}_4]^{2-}$ | |
|--------------------|-----------------------|-----------------------|----------------------|-------------------------|-------------------|
| | 1.64 \AA | 1.759 \AA | 1.786 \AA | 1.84 \AA | 1.87 \AA |
| HOMO ^a | 8D8 | 11D8 | 16D8 | 21D8 | 21D8 |
| E | 6.14 | 6.23 | 6.25 | 6.56 | 6.48 |
| LUMO ^b | 9D8 | 12D8 | 17D8 | 22D8 | 22D8 |
| E | 2.77 | 1.98 | 1.53 | 1.72 | 1.89 |
| ΔE | 3.37 | 4.25 | 4.72 | 4.84 | 4.59 |
| $A(\text{calc.})$ | 1.50 | 1.72 | 1.07 | 0.96 | 1.03 |
| $A(\text{exp.})^c$ | 1.22 | 1.69 ^d | 1.13 ^d | – | – |

^a HOMO – highest occupied MO. ^b LUMO – lowest unoccupied MO.

^c Ref. [7]. ^d Calculated [12].

Table 2. Effective charges (Q_M) and valence orbital populations (q_j) for $[\text{MO}_4]^{2-}$, ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, and E106)

| Ion | $R_{\text{M-O}}$ \AA | Q_M | q_s | $q_{p_{1/2}}$ | $q_{p_{3/2}}$ | $q_{d_{3/2}}$ | $q_{d_{5/2}}$ |
|-------------------------|----------------------------------|-------|-------|---------------|---------------|---------------|---------------|
| $[\text{CrO}_4]^{2-}$ | 1.64 | 0.73 | 0.18 | 0.18 | 0.35 | 1.85 | 2.73 |
| $[\text{MoO}_4]^{2-}$ | 1.759 | 0.71 | 0.22 | 0.20 | 0.37 | 1.84 | 2.68 |
| $[\text{WO}_4]^{2-}$ | 1.786 | 0.71 | 0.37 | 0.30 | 0.44 | 1.77 | 2.42 |
| $[\text{E106O}_4]^{2-}$ | 1.84 | 0.58 | 0.56 | 0.39 | 0.33 | 1.86 | 2.29 |
| $[\text{E106O}_4]^{2-}$ | 1.87 | 0.52 | 0.60 | 0.39 | 0.34 | 1.87 | 2.30 |

E106, remind those for the group 5 oxychloride complexes in solutions [4] and are different from those for the group 6 hexachlorides [5]. The energies of the highest occupied MO (HOMO) of the 100% $2p(\text{O})$ character and of the lowest unoccupied MO (LUMO) of the predominantly d -character (e.g., in $[\text{E106O}_4]^{2-}$ this orbital is of 54% $6d(\text{metal})$ and 46% $2p(\text{O})$ character) along with the energy gap (ΔE) separating these orbitals are given in Table 1. Though there is an increase in the value of ΔE in going from the Cr to E106 ion, the LUMO in $[\text{E106O}_4]^{2-}$ is more stabilized than the one in $[\text{WO}_4]^{2-}$. In addition, the increase in ΔE (which is rather small in going from the W to the E106 ion) is realized only at the shortest distances $R_{\text{E106-O}}$. If the real distances $R_{\text{E106-O}}$ are larger, then there is no increase in the energy gap and $[\text{E106O}_4]^{2-}$ will have lower stability towards the process of reduction and a larger electron affinity than that of $[\text{WO}_4]^{2-}$.

3.2. Charge-density distribution and bonding

In Table 2 the effective charges on metal atoms (Q_M) and valence orbital populations are given as a result of the calculations. The values of effective charges diminishing in going from the Cr to the E106 complex are indicative of the decreasing ionicity in this direction. This decrease comes mainly at the expense of a strong relativistic stabilization of the $ns_{1/2}$ and $np_{1/2}$ or-

Table 3. Partial overlap population^a (OP), total overlap population data and M–O stretching frequencies ν_1 for $[\text{MO}_4]^{2-}$, (M = Cr, Mo, W, and E106)

| AO | $[\text{CrO}_4]^{2-}$ | $[\text{MoO}_4]^{2-}$ | $[\text{WO}_4]^{2-}$ | $[\text{E106O}_4]^{2-}$ | |
|---------------------------------|-----------------------|-----------------------|----------------------|-------------------------|--------|
| | 1.64 Å | 1.759 Å | 1.786 Å | 1.84 Å | 1.87 Å |
| $ns_{1/2}$ | 0.29 | 0.30 | 0.40 | 0.41 | 0.41 |
| $np_{1/2}$ | 0.25 | 0.27 | 0.36 | 0.41 | 0.41 |
| $np_{3/2}$ | 0.49 | 0.49 | 0.57 | 0.45 | 0.44 |
| $np(\text{tot})$ | 0.74 | 0.76 | 0.93 | 0.86 | 0.85 |
| $(n-1)d_{3/2}$ | 0.73 | 0.81 | 0.84 | 0.83 | 0.81 |
| $(n-1)d_{5/2}$ | 1.11 | 1.24 | 1.31 | 1.37 | 1.35 |
| $(n-1)d(\text{tot})$ | 1.84 | 2.08 | 2.15 | 2.20 | 2.16 |
| M–4O(tot) | 2.10 | 2.28 | 2.81 | 2.84 | 2.86 |
| $\nu_1, \text{cm}^{-1\text{b}}$ | – | 879 | 910 | – | – |

^a OP between the indicated in the left column AO of the metal atom and the valence orbitals of the four oxygen atoms.

^b For CaMO_4 compounds [8].

bitals with increasing atomic number in the group and, as a consequence, increasing populations of these orbitals. Involvement of the valence orbitals in bonding in terms of the OP data is shown in Table 3. From these data one can see that there is a drastic increase in bonding in going from $[\text{CrO}_4]^{2-}$ to $[\text{WO}_4]^{2-}$ (which is confirmed by increasing M–O stretching frequencies given in Table 3), while in going from $[\text{WO}_4]^{2-}$ to $[\text{E106O}_4]^{2-}$ this increase is very small and comes mainly at the expense of the $7p_{1/2}$ and $6d_{5/2}$ orbital contributions to bonding. Thus, at the shortest E106–O bond lengths the covalent bonding in $[\text{E106O}_4]^{2-}$ is nearly of the order of that in $[\text{WO}_4]^{2-}$. Since the ionic contribution to the metal-oxygen bonding in $[\text{E106O}_4]^{2-}$ is the smallest in the series, the bonding in this complex would be probably weaker than that in $[\text{WO}_4]^{2-}$. With increasing bond lengths the complex of element 106 would be even less stable (it has nearly the same covalent contribution and much lower ionic one). Thus, out of the entire series of the anions under consideration the bonding metal-oxygen in the tungstate ion is obviously the strongest. In comparison with the molybdate complex, the tungstate one has the same effective charge on the metal atom but a much higher covalent contribution. This increase in bonding is confirmed by increasing symmetric stretching frequencies ν_1 which are shown in Table 3.

3.3. Electronic charge-transfer transitions and luminescence

It is known that complexes consisting of a central highly-charged transition metal ion without d electrons surrounded by a number of oxygen ions, such as $[\text{NbO}_4]^{3-}$, $[\text{TaO}_4]^{3-}$, $[\text{MoO}_4]^{2-}$, $[\text{WO}_4]^{2-}$, luminescence [9, 10]. From a point of luminescence intensity and phosphor applicability $[\text{WO}_4]^{2-}$ has been studied the most extensively [10(c,d)]. From the point of view of absorption spectroscopy and energy level calculations

the $[\text{CrO}_4]^{2-}$ ion is a well known representative on which a very large number of papers have been published (see, e.g., [11]). Calculations of the energies of the charge-transfer transitions have been performed in [11, 13]. The electronic structure of the $[\text{MoO}_4]^{2-}$ anion has also been calculated by these authors [13].

In work [21] it was shown that the absorption and emission (luminescence) spectra of these complexes has to be ascribed to charge-transfer transitions from the occupied oxygen orbitals to the vacant orbitals of d -character. It was also shown that the higher the energy of the first absorption transition, the more probable is efficient luminescence.

The ion $[\text{CrO}_4]^{2-}$ at the normal circumstances does not show luminescence since the first absorption band is situated in the visible, i.e., at relatively low energies. The experimental data on the dichromate ion $[\text{Cr}_2\text{O}_7]^{2-}$ show the absorption in the wide range of energies starting from 563.5 nm to 430 nm (the most intensive band) [10(a)]. It was reported [9] that luminescence has recently been observed for CaCrO_4 .

In comparison with the isoelectronic chromate ion the absorption and emission spectra of the molybdate complex are shifted to higher energies. This makes luminescence a more general phenomenon for the molybdate than for the chromate complex. CaMoO_4 shows a green emission under optical band excitation which is the intrinsic molybdate emission. The energy of the maximum of the excitation band is about 4.5 eV [10(b)].

In the case of the tungstate group the increase in the energies of the charge-transfer transitions is so large that a number of tungstates with efficient luminescence at room temperatures are known. In CaWO_4 optical band edge excitation at 240 nm yields a strong blue emission at 420 nm [10(c,d)].

In the $[\text{MO}_4]^{2-}$ ion having the T_D symmetry the absorption and excitation transitions are prescribed to the $t_1 \rightarrow e$ electronic transitions, giving rise to four lines in the excitation spectra corresponding to the transitions from the ground to the four excited states 3T_1 , 3T_2 , 1T_1 , 1T_2 . Using our density-functional method (DS DVM) and applying the transition-state procedure we have been able to calculate the average energy of the $t_1 \rightarrow e$ transition (averaging over the 3T_1 , 3T_2 , 1T_1 , 1T_2 states). These energies together with the experimental excitation energies for the solid CaMO_4 are given in Table 4 where one can see quite a good agreement between the calculated and experimental values. In the $[\text{E106O}_4]^{2-}$ complex with the shortest distances in the solid state the calculated energies of the charge-transfer transitions prove to be shifted even more to the area of high values than those of the tungstate complex. It means that if such a compound containing the $[\text{E106O}_4]^{2-}$ anion had been obtained, it would have shown a strong luminescence, stronger than that of the tungstate complex, with the emission being in the blue-violet area.

The same would be obviously valid for the $[\text{HaO}_4]^{3-}$, $[\text{HaO}_6]^{7-}$, $[\text{HaO}_6]^{11-}$ complexes of element

Table 4. Lowest energies of the charge-transfer transitions ($E_{\pi-d}$) for $[\text{MO}_4]^{2-}$, ($M = \text{Cr, Mo, W, and E106}$) and redox potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$

| | $[\text{CrO}_4]^{2-}$ | $[\text{MoO}_4]^{2-}$ | $[\text{WO}_4]^{2-}$ | $[\text{E106O}_4]^{2-}$ | |
|---|-----------------------|-----------------------|----------------------|-------------------------|----------------------|
| $R_{\text{M-O}}^a$ | 1.64 Å | 1.759 Å | 1.786 Å | 1.84 Å | 1.87 Å |
| $E_{\pi-d}$, eV(calc.) ^b | 3.34; 3.36 | 4.48; 4.50 | 4.98; 5.00 | 5.05; 5.07 | 4.79; 4.80 |
| $E_{\pi-d}$, eV(exp.) ^c | 3.32 | ≈4.50 | 5.17 | — | — |
| $R_{\text{M-O}}^d$ | 1.66 Å | 1.77 Å | 1.79 Å | 1.85 Å | 1.88 Å |
| $E_{\pi-d}$, eV(calc.) | 3.31; 3.32 | 4.43; 4.44 | 4.98; 4.99 | 5.04; 5.06 | 4.77; 4.78 |
| $E_{\pi-d}$, eV(exp.) ^e | 3.32 | 5.34 | 6.23 | — | — |
| $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$, V ^f | 0.1 | (-1.0) | (-1.55) ^g | (-1.60) ^g | (-1.34) ^g |

^a Bond lengths in the solid state. ^b Two values are given for the transition ($t_1 \rightarrow e$) due to the relativistic splitting of the t_1 level. ^c Ref. [9]. ^d Estimated bond lengths in solutions. ^e Ref. [7]; the values for $[\text{MoO}_4]^{2-}$ and especially for $[\text{WO}_4]^{2-}$ seem to be too large relative to both the values of the transition energies in the solid state and to the value for $[\text{CrO}_4]^{2-}$. ^f Ref. [22]. The value for Mo in brackets is an estimated one. ^g Estimated value (this work).

105 where the energies of the charge-transfer transitions will be probably higher than those of the corresponding complexes of tantalum.

3.4. Group 6 oxyanions in solutions and stability of the +6 oxidation state

Though the metal-oxygen bonding in the oxyanion of element 106 will be probably weaker than the W–O bonding in the tungstate ion, the stability of the $[\text{E106O}_4]^{2-}$ complex in aqueous solutions will be enhanced by a large hydration energy. Having the largest size, this anion will have the largest hydration energy among all the complexes $[\text{MO}_4]^{2-}$ under consideration:

$$\Delta G_{\text{hyd}} = \frac{A(Z)}{\varepsilon[(r_{\text{M}^{2-}} + r_x(Z))]},$$

where ε is the dielectric constant of water or an aqueous phase, $r_{\text{M}^{2-}}$ is the radius of the ion under consideration, and $r_x(Z)$ is a radius parameter to be added to the crystal ionic radius and which depends on Z .

Since the bond lengths in aqueous solutions will be slightly larger than those in the solid state, the charge-transfer transitions for the $[\text{MO}_4]^{2-}$ ion will be shifted to the area of lower energies. The calculated values of these transitions are given in Table 4. The trend is similar to that for the solid-state complexes: the highest energy is only for the shortest E106–O bond lengths in $[\text{E106O}_4]^{2-}$.

Since the knowledge of the stability of the +6 oxidation state is of importance, we have estimated the standard redox potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ for the ions under discussion using the $E_{\pi-d}$ energies which determine the stability of systems towards the process of reduction. A linear correlation (Fig. 1) between the known values of these potentials for the complexes of Cr and Mo [22] and the calculated energies of the charge-transfer transitions, corresponding to this process of reduction, gives the values of $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ for the complexes of W and element 106. These values are shown in Table 4. Thus, for the shortest bond

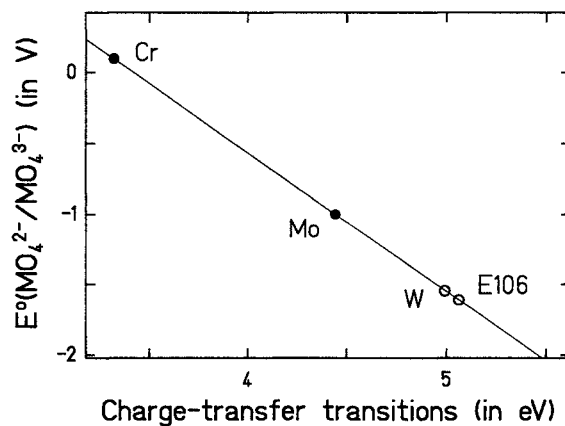


Fig. 1. Correlation between standard redox potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ and energies of the lowest charge-transfer transitions in the $[\text{MO}_4]^{2-}$ complexes of Cr, Mo, W, and E106. $[\text{E106O}_4]^{2-}$ has been calculated with the shortest possible bond lengths.

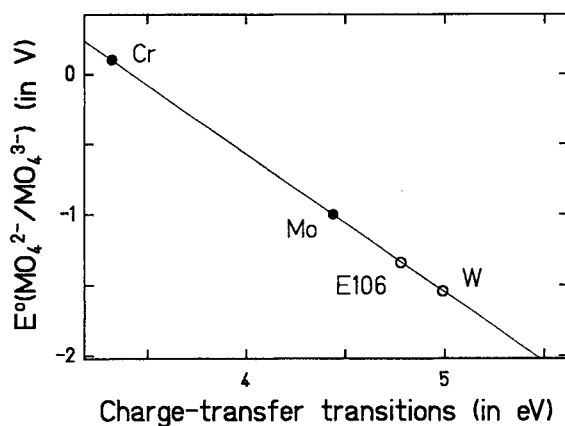


Fig. 2. Correlation between standard redox potentials $E^0(\text{MO}_4^{2-}/\text{MO}_4^{3-})$ and energies of the lowest charge-transfer transitions in the $[\text{MO}_4]^{2-}$ complexes of Cr, Mo, W, and E106. $[\text{E106O}_4]^{2-}$ has been calculated with 0.03 Å larger bond lengths than the shortest ones.

lengths $R_{\text{E106-O}}$ the stability of the +6 oxidation state will be slightly more pronounced for element 106 than for W. For the larger bond lengths the potential is already lower than that for the tungstate ion (Fig. 2)

which means that the +6 oxidation state of element 106 will be less stable than the +6 oxidation state of W. That shows, that if in groups 4 and 5 the maximum oxidation state markedly increases in going from the 5d to the 6d elements, in group 6 this increase is not so pronounced. This confirms our conclusion [5] about a relative decrease in the stability of the maximum oxidation state in going from group 4 to group 6.

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