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On the Borderline of Pauling's Bond Order Concept: Metal-Metal Bonding in Icosahedral Chains of Metal-Rich Tantalum Sulfides

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Metal-metal bonding in the icosahedral metal-rich sulfides of Ta is considered from the point of view of extended Hückel calculations *via* Mullikan overlap populations and from the point-of-view of Pauling bond order. It is found that the two approaches are generally consistent, but that the overlap populations provide a more sensitive estimate of reaction energies. The results are consistent with a strong stabilization of the icosahedral clusters by central atom to icosahedral metal atom bonding and a weak destabilization (relative to the disproportionation products) by the icosahedral metal atom bonds.

INTRODUCTION

In recent years research on transition metal binary and ternary sulfide- and phosphide-systems has revealed an impressive array of new chemical compositions and structures. In the initial high-temperature investigations of the sulfides of Nb and Ta new binary compounds such as $Nb_{21}S_8$,[1] $Nb_{14}S_5$,[2] Ta_6S[3,4] and Ta_2S[5] were prepared. On the other hand, the mixed Nb-Ta metal-rich sulfides, $Nb_{1.72}Ta_{3.28}S_2$,[6] $Nb_{0.95}Ta_{1.05}S$,[7] $Nb_{6.74}Ta_{5.26}S_4$[8] and $Nb_{4.92}Ta_{6.08}S_4$[9] were recently prepared by similar high-temperature methods.[10] The key feature for the stability and structural versatility is the existence of metal clusters with extended metal-metal bonds. These materials, along with some solid solutions of Nb and Ta in known phases, were discussed in terms of differential fractional site occupation (DFSO) in 1992.[11] Since that time additional sulfides[12,13] and phosphides[14] have been prepared using the concept of phase stabilization by DFSO.

The concept of DFSO, and indeed much of the discussion of the stability of metal-rich compounds in general, is based upon the idea that in the metal-rich materials relative stability is conferred principally by metal-metal bonding. In a mixed-metal, metal-rich ternary, then, the metal that is the more effective in forming metal-metal bonds tends to concentrate at the more highly metal-bonded sites of a complex structure. The surprising conclusions from this near tautology are: *1.* that novel compounds will form with a variety of site occupations but with nearly fixed composition. *2.* that these compounds will result in new structure types, and *3.* that the structures will be relatively complex, the complexity being favored by the variability of site occupation.

One problem with the development of the concept of DFSO it that a measure of the metallic bonding character of a site, independent of its fractional occupation, is required for its consideration. In the previous work either the number of metal neighbors in the first coordination sphere or, better, the Pauling metal-metal bond order were taken for such a measure. The number of metal neighbors has the disadvantage that, as is well-known, many neighbors at relatively long distances can be equivalent in bond stabilization to a few neighbors at short distances. For example, the alkali metals in the elemental form are certainly univalent, yet they posses the high coordination numbers characteristic of elemental metals.

In order to overcome this shortcoming the empirical Pauling bond-order equation:[15]

$$D(n) = D(1) - 0.6 \log n$$

which assigns an order n to a bond of distance $D(n)$, has frequently been used. However it has been found that in some cases the resulting total bond orders exceed the numbers of electron pairs available,[16] and as a result the calculation of bond-order using this equation, while it has continued, has remained under a cloud of doubt concerning its ultimate usefulness.

More recently simple band-structure methods using the extended Hückel approach have been found useful, for example to calculate the total metal-metal overlap populations of the metal atoms in the various sites of a crystal structure. A first purpose of the work described here was to obtain such overlap populations for some metal-rich compounds in order to strengthen the discussion of the DSFO concept with estimates of metal-bonding character based upon the calculated overlaps. A second purpose was to check a proposed reinterpretation of the Pauling bond-order equation, namely that the Pauling bond-order scales as the overlap and not as the number of bonding pairs. This would imply that bond-order numbers in excess of the valence simply indicate a more effective (more bonding and less antibonding character) use of the valence electrons than occurs in the elemental reference compounds from which the $D(1)$ values were obtained.

With these intentions in mind, Mulliken overlap populations (MOP) and Pauling bond orders (PBO) were calculated for the metal-metal interactions in Ta_2S and both the monoclinic and triclinic structure of Ta_6S. In a third step the stability and structural differences as seen from the point of metal-metal interactions are discussed.

STRUCTURES AND CALCULATIONS

The basic building blocks for all three structures Ta_2S, Ta_6S (monoclinic) and Ta_6S (triclinic) are Ta-centered pentagonal antiprisms of Ta. These antiprisms are fused together in the basal plane, thus forming chains which run along the short crystallographic axis of the corresponding unit cell. Each central Ta atom is surrounded by 12 Ta-neighbors in a compressed icosahedral arrangement. The compression is associated with short Ta-Ta distances between the central atoms of adjacent icosahedra. These distances are 2.62 Å in Ta_6S (t), 2.64 Å in Ta_6S (m) and 2.79 Å in Ta_2S compared to 2.63 Å in the elemental Ta. The central-Ta to Ta interactions inside the icosahedra are compiled in Table I.

TABLE I

Interatomic distances/Å: central Ta to Ta inside the icosahedra

Ta_6S (t)[a]		Ta_6S(m)[b]		Ta_2S[c]	
Central atom: Ta(1) + Ta(2)		Central atom: Ta(1)		Central atom: Ta(3)	
Bonded atom*	dist./Å	Bonded atom*	dist./Å	Bonded atom*	dist./Å
Ta(1)	2.621	Ta(1)	2.643	Ta(3)	2.790
Ta(1)	2.621	Ta(1)	2.643	Ta(3)	2.790
Ta(4)	2.830	Ta(5)	2.794	Ta(1)	2.840
Ta(4)	2.830	Ta(5)	2.826	Ta(1)	2.840
Ta(3)	2.851	Ta(3)	2.870	Ta(2)	2.898
Ta(3)	2.851	Ta(3)	2.888	Ta(2)	2.898
Ta(5)	2.975	Ta(6)	2.952	Ta(4)	2.909
Ta(5)	2.975	Ta(2)	2.962	Ta(2)	2.923
Ta(7)	2.992	Ta(6)	2.978	Ta(2)	2.923
Ta(7)	2.992	Ta(4)	3.000	Ta(1)	2.942
Ta(6)	2.998	Ta(4)	3.003	Ta(1)	2.942
Ta(6)	2.998	Ta(2)	3.008	Ta(4)	2.996

* Atom numbering according to structure reference.

[a] See Ref. 4

[b] Ref. 3

[c] Ref. 5

Structural differences arise from the interchain connectivities *i.e.*, the orientation of the Ta-chains with respect to each other as well as the sulfur linkage. In the monoclinic form of Ta_6S, metal-atoms on corners of the icosahedra are bonded to corners on the adjacent chains with metal-metal distances of 3.01 Å and 3.06 Å. Thus, the waist edges of each icosahedron are parallel to the correesponding ones of the neighboring icosahedra (for a pictorial presentation of the three structures see Figures 1 and 2). The triclinic structure of Ta_6S can be derived from the monoclinic form by an imaginary rotation of the neighboring chains around an axis through the central Ta-atoms perpendicular to the pentagons, so that the closest triangular faces of icosahedra of two adjacent chains are eclipsed. In the monoclinic form the

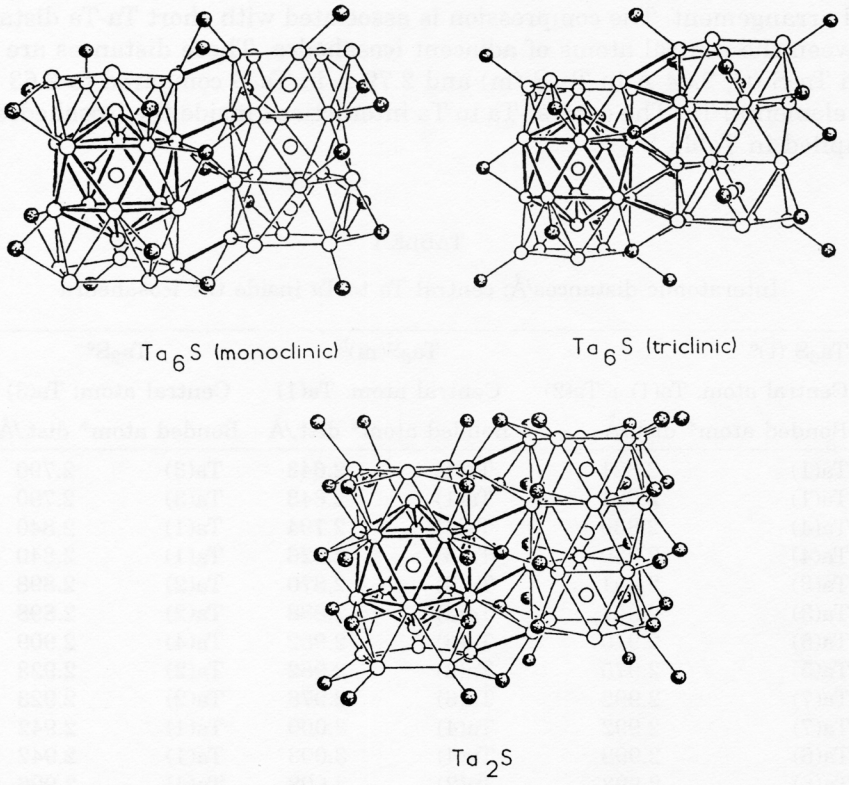

Figure 1. Segments of two adjacent Ta-chains in the structure of Ta_6S (monoclinic), Ta_6S (triclinic) and Ta_2S projected perpendicular to the fused and centered metal icosahedra (Ta: open circles, S: dotted circles). The bonds of the central Ta-atoms are omitted far clearity. One icosahedron is highlighted as well as the interchain Ta-Ta bonds.

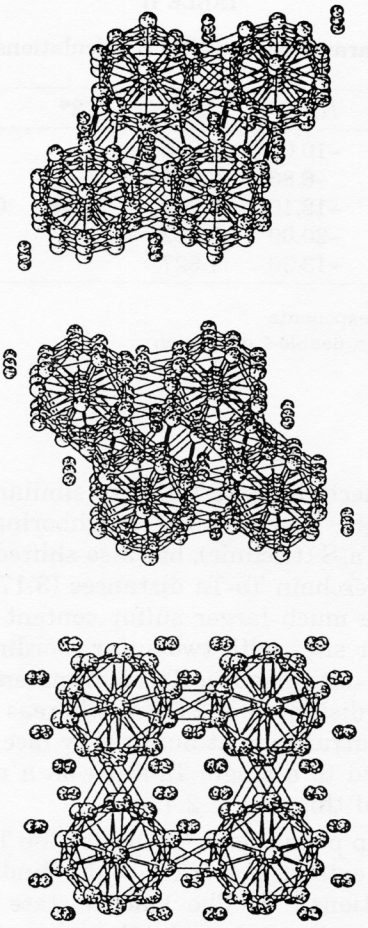

Figure 2. View along the icosahedral chain axes (tilted by 5°) of Ta_2S (botttom), Ta_6S(t) (middle) and Ta_6S(m) (top).

triangular faces are staggered and slightly shifted away from each other. As a result the chains in the triclinic form have slightly shorter Ta-Ta interchain connections (2.89 Å, 3.07 Å and 3.19 Å), and this is reflected in a slightly higher density for the triclinic form (15.61 g/cm^3 compared to 15.18 g/cm^3).

The sulfur atoms in both modifications of Ta_6S are bridging Ta-atoms of three different chains and are coordinated in a monocapped trigonal fashion. The Ta-S distances in the triclinic form range from 2.410 to 2.557 Å, whereas the range spans 2.466 to 2.532 Å in the monoclinic one.

TABLE II

Parameters for EHTB calculations

Atom	Orbital	H_{ii}/eV	$\zeta 1$*	$\zeta 2$*	$c1$**	$c2$**
Ta[a]	6s	−10.00	2.280			
	6p	−6.86	2.241			
	5d	−12.10	4.762	1.938	0.61061	0.61061
S[b]	3s	−20.00	2.122			
	3p	−13.30	1.827			

* Slater-type orbital exponents
** Coefficients used in double-ζ expansion
[a] See Refs. 21,22
[b] Ref. 22

The interchain connectivities in Ta_2S are similar to those found in the monoclinic form of Ta_6S. However, the neighboring chains are not only slightly rotated like in Ta_6S (triclinic), but also shifted away from each other giving rise to larger interchain Ta-Ta distances (3.17 and 3.31 Å). This difference also reflects the much larger sulfur content of the compound. The structure has two sulfur sites with two sufur coordination modes. One site has a distorted trigonal antiprismatic Ta environment around the sulfur-atoms with average Ta-S distances of 2.56 Å, whereas the other S-atom is in a distorted tetrahedral arrangement built-up by face bridging a Ta-triangle with one additional bond to a single Ta-atom on a neighboring chain. The average Ta-S distance of this site is 2.47 Å.

The Mulliken overlap populations (MOP) for the Ta-Ta-interactions were obtained by means of extended Hückel Tight-Binding (EHTB) electronic band structure calculations.[17–20] The valence-state ionization energy parameters (H_{ii}) used as well as the orbital exponents and coefficients are listed in Table II. The computer program employed was EHMACC, adapted for use on an IBM compatible PC. The calculations were carried out using a triclinic 48 k-point mesh, with the monoclinic Ta_6S being reduced to the corresponding primitive triclinic setting. The MOP's were calculated for each Ta-atom in the unit cell taking all the Ta-Ta interactions up to 3.5 Å into account. PBO's were obtained using the same bond distances.

RESULTS AND CONCLUSIONS

The results of the Mulliken overlap population calculations for Ta_2S and monoclinic and triclinic Ta_6S are given in Table III. The overlap population calculated for *bcc* Ta is 3.70. The conclusions reached from these calculated results are in good agreement with the following intuitive conclusions: *1.* the

TABLE III

Mulliken overlap populations (MOP) and Pauling bond orders (PBO) for the metal-rich sulfides of Ta

Atom*	No. of Ta-Ta bonds	Total Ta-Ta MOP	PBO
Ta_6S monoclinic			
Ta(1)	12	4.31	6.47
Ta(2)	11	2.89	2.50
Ta(3)	11	3.00	2.95
Ta(4)	11	3.14	2.74
Ta(5)	11	3.23	3.63
Ta(6)	12	3.43	3.55
Ta_6S triclinic			
Ta(1)	12	4.28	6.84
Ta(2)	12	4.31	6.65
Ta(3)	11	3.32	3.67
Ta(4)	11	3.13	3.13
Ta(5)	12	3.13	2.61
Ta(6)	13	3.43	2.97
Ta(7)	13	3.57	3.49
Ta_2S			
Ta(1)	10	2,50	2.31
Ta(2)	9	2.49	2.38
Ta(3)	12	4.29	5.62
Ta(4)	10	2.67	2.30

* Atom numbering according to structure reference.

metal-metal bonding in these complex structures is site dependent. *2.* the strongest metal-metal bonded atom is in all cases the central, icosahedrallly coordinated Ta atom. *3.* this atom has an overlap population that is significantly greater than that calculated for elemental *bcc* Ta. *4.* the overall metal-metal bonding in these metal-rich sulfides is less than that of the elemental metal. As was expected, the icosahedral cluster plays an important role in stabilizing the compound principally through enhanced metal-metal bonding character of the central tantalum atom relative to *bcc* Ta.

The fact that the overlap population in a compound can exceed that in the elemental metal calls into question the meaning of bond order as it was used to obtain the Pauling $D(1)$ values for metals. It is well known,[17] however, that the solutions to single electron wave functions in the band-theory approach yield wave functions that vary in their bonding character continuously throughtout the Brillouin zone. Thus it seems reasonable to propose

that PBO's scale as MOP's as opposed to the number of valence electron pairs, and Figure 3 shows that to a first approximation that proposal holds for the compounds under discussion here. Furthermore, the question of whether a particular compound and structure is observed at equilibrium is the question of whether it is stable relative to disproportionation into adjacent phase or transformation into an alternative structure. The energetic component of the relative stabilization, is, in this model, determined by the total electron energy as determined by the electronic wave functions. Thus, one can address the question, is Ta_6S energetically stable with respect of disproportionation into Ta_2S and Ta by examining the distribution of electronic energy eigenvalues in Ta_6S relative to those of the stoichiometric mixture 4Ta and Ta_2S. Viewed in this way, »antibonding« for Ta_6S means having an energy eigenvalue greater thant that of the average for 4Ta and Ta_2S.

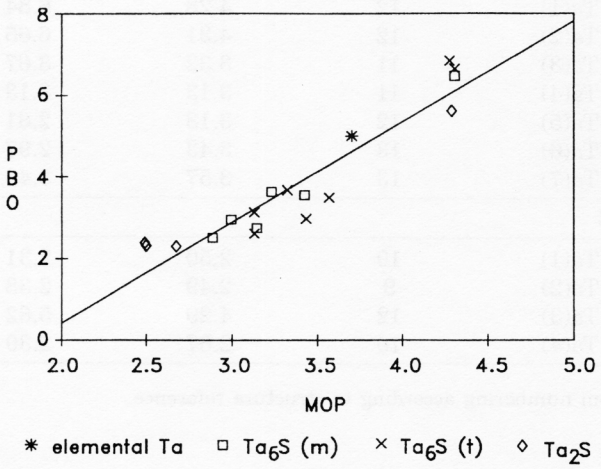

Figure 3. Correlation of Pauling Bond Order numbers and Mulliken Overlap Populations for the metal-metal interactions in Ta_6S (monoclinic), Ta_6S (triclinic), Ta_2S and the Ta-metal.

Thus, the quantity relevant to structural stability in the thermodynamic sense is not just the number of valence electrons, nor the number involved in bonding pairs, but rather the distribution of valence electrons in the eigenfunctions relative to the weighted average of those of the stable decomposition products. The overlap populations provide a way of evaluating the single atom contributions to the overall bonding, in particular when they are used in the relative sense described above, for in this case errors inherent in the band-structure method will tend to cancel. At the same time the Cou-

lomb part of the total energy, which is not taken into account in Extended Hückel calculations, can be considered as being close enough to the same absolute value for each one in this series of compounds to allow for disregard. For example bands that are bonding (antibonding) at the zone center and antibonding (bonding) at a zone boundary (*i.e.*, bands that »run up«[17] (»run down«) along the Brillouin zone direction illustrate that increased antibonding character increases with the electron energy, *i.e.*, the bond-energy decreases with decreased overlap.

It is then a question of whether in one compound (*e.g.*, Ta_6S) the correlation between bond-energy and overlap is, to a sufficient approximation, the same as for the decomposition products, and the fact that wavefunctions centered on Ta are involved in both cases gives cause for hope that this will be so.

Many years ago Linus Pauling discovered that bond distance correlates well with bond energy and, particularly in simple molecules such as those involving single, double and triple bonded carbon, that the correlation is also with bond-order. He generalized this concept to include metallic bonding and provided a set of »single bond« radii for the metallic elements based upon

$$D(n) = D(1) - 0.6 \log n$$

and the assumption that Σn_i for a given atom is equal to the valence for that atom. However, based upon the discussion presented above, it is more reasonable, now that such values are available, to assume that Σn_i is proportional to the overlap population in a metal, *i.e.*, that the bond-order depends both upon the number of electrons involved and their bonding and antibonding character.

Using the data from Table III the changes in MOP and PBO for the chemical reactions

$$Ta_6S \text{ (tri)} = Ta_2S \text{ (s)} + 4Ta \text{ (s)} \quad (1)$$

and

$$Ta_6S \text{ (tri)} = Ta_6S \text{ (mono)} \quad (2)$$

can be evaluated. For (1) ΔMOP = –0.428, *i.e.*, there is a small (relative to the average MOP of Ta in any of the compounds) loss of metal-metal bonding upon reaction. Thus, according to the discussion above, it is expected on the basis of the metal-metal interactions alone (*i.e.*, assuming essentially unchanged metal-sulfur interactins before and after reaction) that Ta_6S is slightly stable with respect to disproportionation. This is what has been found experimentally.[23] For reaction (2) ΔMOP = –0.148 which is consistent with the fact that this reaction must be endothermic, because the monoclinic form is the high temperature form.[4]

Thus, the changes in the MOP values with reaction are consistent with what is known about the energetics of reactions (1) and (2) and prove the useful result that the icosahedral-chain sulfides of Ta are stabilized by the strong Ta-Ta bonding of the central Ta atoms, and weakly destabilized by the smaller (relative to *bcc*) Ta-Ta bonding of the other Ta atoms.

The results of the PBO changes with chemical reaction are less satisfying. Although the PBO-MOP correlation is quite good to a first approximation (Figure 3), this correlation is not so precise that the POB's provide a rational for reaction energetics similar to that given above based upon the MOP's. In future work this approach will be extended to the metal-rich niobium sulfides and the mixed Ta-Nb sulfides stabilized by DFSO.

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SAŽETAK

Na granici Paulingove koncepcije reda veze: veza metal-metal u ikozaedarskim lancima klustera tantalova sulfida

Martin Köckerling i Hugo F. Franzen

Veza metal-metal u ikozaedarskim tantalovim sulfidima razmotrena je sa stajališta proširene Hückel-ove metode preko Mullikan-ove populacijske i Pauling-ova reda veze. Ustanovljena je podudarnost tih pristupa, ali je populacijska analiza osjetljivija kod određivanja reakcijskih energija. Rezultati su u skladu s jakom stabilizacijom ikozaedarskih klustera vezama centralnih atoma Ta-Ta i blagom destabilizacijom (u odnosu na produkte raspada) ostalim vezama Ta-Ta.