DALTON
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The coloring problem in $Ba_2Cu_3VS_6$ †

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The relative stabilities of the different arrangements of Cu(I) and V(V) cations in $Ba_2Cu_3VS_6$ estimated through plane wave density functional calculations show a preference for structures which maximize the number of Cu···V contacts that involve $d^{10}\cdots d^0$ interactions.

During the last years an increasing interest has been devoted to the metal···metal interactions between transition metals with closed shell electronic configurations.[1] Especially, the analysis has focused on the interactions in homonuclear d^{10} or d^8 complexes showing that the participation of the empty p orbitals allows a donor–acceptor interaction between a filled d orbital of one metal atom and an empty p orbital of another one and *vice versa*.[2–5] Recently, we have analyzed a similar kind of closed shell interaction between d^{10} and d^0 transition metals in some extended structures with edge-sharing tetrahedral Cu(I) and V(V) ions by using semiempirical calculations.[6] In this case, due to the different electronic configuration of both transition metals, the donor–acceptor interaction appears only between filled d orbitals of the Cu(I) atom and empty d orbitals of V(V). Our conclusion was that the most stable structures are those that maximize the number of Cu···V contacts. Although a variety of d^{10}–d^0 combinations can be found in molecular[7–10] or extended structures,[11–19] we have focused our study on the extended structures of ternary copper(I) thiovanadates. One of the most interesting cases is that of $Ba_2Cu_3VS_6$, a compound that adopts a double chain structure[12] (Fig. 1) for which several distributions of the cations in the unit cell (colorings) can be foreseen, as sketched in Chart 1. In this communication we report an *ab initio* theoretical study of the coloring problem in the $Ba_2Cu_3VS_6$ compound to complement the results obtained from previous semiempirical calculations and to extend the understanding of the relationship between the crystal structure and the metal···metal interactions in such compounds.

The calculations presented in this work have been performed using the pseudo-potential plane wave approach as implemented in the CASTEP code.[20] This method,[21] based on density functional theory (DFT)[22] has been applied using the Becke[23] and Perdew[24] expressions for the exchange and correlation functionals, respectively. To optimize the geometry, the electronic wavefunctions are employed to calculate the ionic forces and a minimization algorithm (BFGS)[25–28] performs the relaxation of the ions to the ground state. The ions and lattice parameters have been freely relaxed, without imposing symmetry restrictions, in order to facilitate the comparison between structures that belong to different space groups. In the optimization process, the electronic wavefunctions have been expanded in plane waves up to a 320 eV cut-off and the nuclei and core electrons are represented by ultrasoft Vanderbilt pseudo-potentials.[29] For integration of k-dependent magnitudes in reciprocal space a 14 k-point mesh following the Monkhorst–Pack scheme[30] has been adopted. Extended-Hückel tight-binding (EHTB)[31] calculations for the optimized structures have been done with the CASSANDRA code[32] using the same computational parameters as in our previous study.[6]

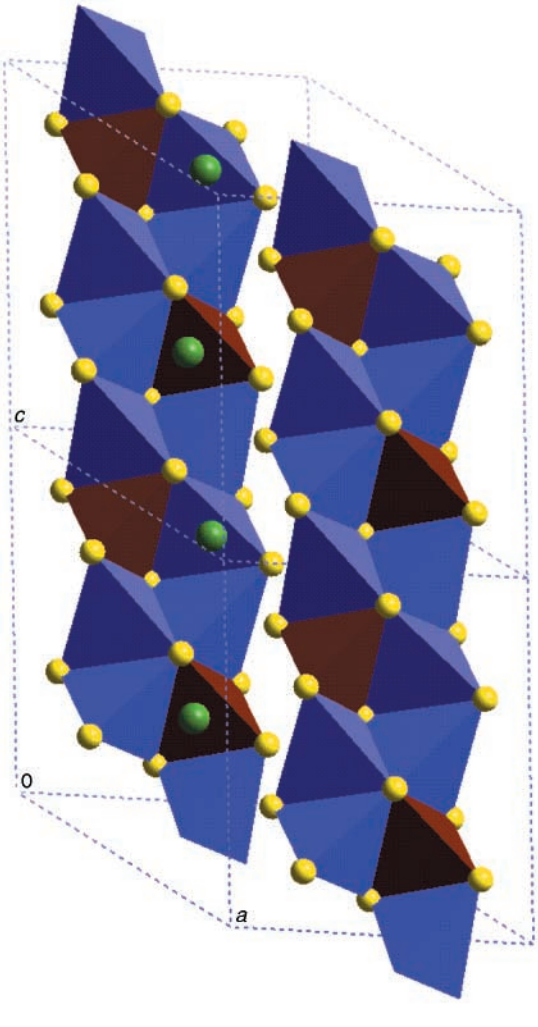

Fig. 1 Polyhedral representation of the crystal structure of $Ba_2Cu_3VS_6$. The blue and brown tetrahedra correspond to the CuS_4 and VS_4 units, respectively. The yellow and green spheres represent the S and Ba atoms, respectively.

The relative energies corresponding to the optimized structures are indicated in Table 1 (optimized cell parameters and

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† Electronic supplementary information (ESI) available: a listing of the unit cell parameters and crystallographic coordinates for the five structures **1a**–**e** optimized using plane wave density functional calculations. See http://www.rsc.org/suppdata/dt/a9/a909517i/

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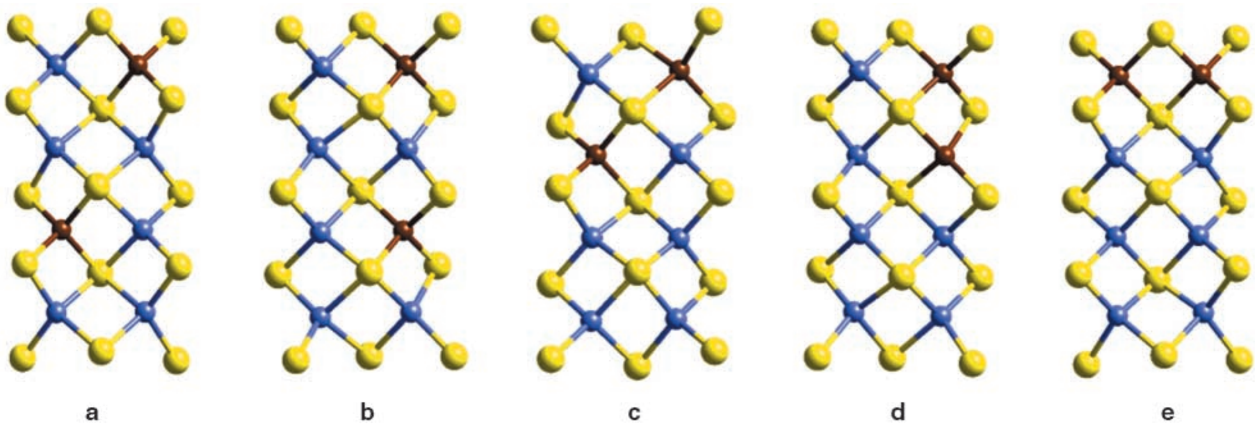

Chart 1

Table 1 Relative energy per unit cell (kcal mol^{-1}) for the five different arrangements of the Cu(I) and V(V) cations (Chart 1) in the lattice of $Ba_2Cu_3VS_6$. These values have been calculated with the PW-DFT method and also using the EHTB method with the DFT optimized structure. The previously reported EHTB results[6] obtained with frozen structures having all M–S distances of 2.3 Å are given in parentheses

	PW-DFT	EHTB
a	0.0	0.0 (0.0)
b	+13.4	+9.2 (−1.1)
c	+33.4	+19.2 (+2.4)
d	+39.5	+32.2 (+17.2)
e	+37.9	+38.9 (+17.2)

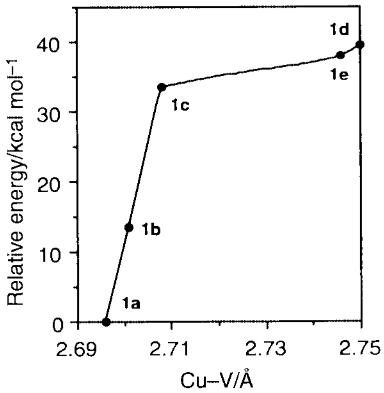

Fig. 2 Relative energies of the five optimized structures as a function of their average Cu···V distances.

atomic coordinates are included as ESI). The most stable structure corresponds to the distribution of metal cations **1a**, with three Cu···V contacts for each vanadium atom, two along the chain direction and one between the parallel chains, in agreement with the crystal structure reported by Mujica *et al.*[12] Interestingly, trends in the total energies obtained for the optimized structures with the semiempirical EHTB method are very similar, even at a semiquantitative level, to those obtained using the PW-DFT method. These results indicate that the EHTB method can correctly handle the interactions involved in this kind of compound, thus confirming the conclusions of our previous qualitative molecular orbital and electronic band study.[6]

The deviation of the calculated Cu···V and Cu···Cu bond lengths in the most stable structure from the experimental values is less than 3%. It is worth stressing that the chains tend to adopt structures with alternating short and long interchain contacts (Table 2). Short distances are favored for pairs of tetrahedra incorporating a vanadium atom, due to the shorter V–S distances compared to the Cu–S ones. We note, however, that the interchain Cu···V distances are as short as the V···V distance in **1e**, probably reflecting the weak d^{10}–d^0 bonding in the former case.

The calculated energy for each arrangement of the anionic sublattice is apparently related to the Cu···V distances, as seen in Fig. 2: the shorter the average Cu···V distance is, the lower the calculated energy. Two types of behavior can be detected in Fig. 2, corresponding to the two sets of topologies. One set corresponds to structures **1a**–**c**, all having six Cu···V and four Cu···Cu contacts, for which a dependence of the calculated energy on the Cu···V distance is found. The other set, formed by structures **1d** and **1e**, with four Cu···V, seven Cu···Cu and one V···V contacts, presents longer Cu···V distances and larger energies, but their energies are less sensitive to such distances. These results are also consistent with the qualitative rule that structures that maximize the number of Cu···V interactions are more stable, as stated in our previous qualitative study, and might be attributed to the stronger stabilizing effect of the d^{10}–d^0 interactions compared to the d^{10}–d^{10} ones.

A related result is observed in the optimized Cu···V and Cu···Cu distances. For compounds **1a**–**c**, a strong decrease of the Cu···Cu average distance on increasing the Cu···V one is observed. The second set of structures, **1d** and **1e**, present longer Cu···V and shorter Cu···Cu distances, but within that set the trend is not respected. This could be due to the strain required to adopt a structure with two short consecutive interchain Cu···V bonds to maximize the d^{10}–d^0 interactions in the case of **1d**.

We have performed a study of the tetrahedral continuous symmetry measures[33,34] for the MS_4 groups in the optimized structures. In short, the symmetry measure $S(T_d)$ should be zero for a perfect tetrahedron and increase for increasingly distorted tetrahedra. Although the symmetry values (Table 2) are rather small in all cases, consistent with a tetrahedral coordination of the metal atoms, the results indicate that the coordination spheres of the vanadium atoms are significantly less distorted than those of the copper atoms. The $S(T_d)$ values obtained for the experimental structure are consistent with those of the calculated structures. As for the CuS_4 tetrahedra, it is interesting to note that the lowest $S(T_d)$ correspond to those Cu atoms with interchain Cu···V contacts. Although there is no clear correlation between the degree of distortion of the metal tetrahedra and the calculated energy of each structure, it seems clear that the most stable structures are those with the most symmetric vanadium atoms. This fact, together with the influence of the Cu···V distance on both the Cu···Cu distances and the calculated energies for the structures with similar topologies, suggests that the fine structural details and the calculated stabilities are mostly governed by the Cu···V contacts.

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Table 2 Interchain metal · · · metal distances for structures **1a**–**e** (values involving V atoms given in boldface) and average values of the tetrahedral continuous symmetry measures $S(T_d, M)$ for the MS_4 polyhedra (M = Cu, V)

Structure	Interchain M · · · M distances/Å	Average distances/Å		$S(T_d, Cu)$	$S(T_d, V)$
		Cu · · · V	Cu · · · Cu		
a	**2.754**, 3.028, **2.754**, 3.028	2.696	2.793	0.33	0.03
Exp.[a]	**2.736**, 2.979, **2.736**, 2.979	2.733	2.763	0.31	0.12
b	**2.744**, 2.968, **2.728**, 2.968	2.701	2.782	0.36	0.05
c	**2.834**, **2.728**, 2.957, 2.748	2.708	2.757	0.25	0.14
d	**2.823**, **2.755**, 2.949, 2.806	2.750	2.738	0.32	0.07
e	**2.740**, 2.860, 2.747, 2.867	2.746	2.702	0.32	0.12

[a] Experimental values corresponding to structure **a**.

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