

Metal–Metal Bonding in $(C_5H_5V)_2C_8H_8$: A New Interpretation of ab Initio Results

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Abstract: Ab initio MO calculations including correlation have been carried out on $(C_5H_5V)_2C_8H_8$. Important nondynamic correlation effects lead to a new interpretation of the V–V bonding in terms of a weak, antiferromagnetic metal–metal interaction involving the weakly overlapping 3d π and, mainly, 3d δ orbitals. The computed singlet–triplet energy separation is 1122 cm^{-1} in agreement with the experimental evidence for a thermally populated triplet state. Several delocalized metal–ligand–metal interactions stabilize the C_8H_8 ligand in its $\eta^2:\eta^5$ coordination mode. These delocalized interactions have a net V–V bonding character and contribute more than half to the computed bond order of 1.10.

In a recent work, the electronic structure of $(C_5H_5V)_2C_8H_8$ (Figure 1) has been investigated by C.W.B. through ab initio SCF calculations.¹ This molecule is characterized by a short V–V distance of 2.44 Å.² This bond length can be a priori interpreted either in terms of a multiple metal–metal bond or in terms of a weak V–V bonding, the short distance resulting from the metal–ligand interactions. The magnetic properties of this molecule indicate a singlet ground state with a low-lying, thermally populated triplet state.³ In order to determine the nature of the V–V bond, the SCF energies have been computed for various configurations, namely the following: (i) A closed-shell configuration referred to as (1) corresponds to the coupling of the six 3d electrons

$$^1A_1 \quad \dots 30a_1^2 14a_2^2 25b_1^2 17b_2^2 \quad (1)$$

through a triple V–V bond (one mixed σ – δ bond and one π bond in the a_1 representation and another π bond in b_2). (ii) Another closed-shell configuration referred to as (2) contains two orbitals

$$^1A_1 \quad \dots 29a_1^2 14a_2^2 26b_1^2 17b_2^2 \quad (2)$$

with π -bonding character (29 a_1 and 17 b_2) and one π -antibonding MO (26 b_1). The configuration (2) was 3.75 eV lower in energy than (1)¹ and has been therefore considered to provide a correct representation of the singlet ground state, characterized by a V–V bond order between 0.58 and 1.86.¹ (iii) A triplet configuration as shown in (3) is assigned to the thermally populated triplet state.

$$^3B_1 \quad \dots 30a_1^1 14a_2^2 26b_1^1 17b_2^2 \quad (3)$$

Due to the difference in pair correlation energies, the RHF open-shell calculation carried out for the triplet state yielded an energy 1.09 eV lower than that of the reported singlet ground state.¹

A thorough investigation of the obtained wave functions however suggests that including the correlation of the d metal electrons could yield an alternative description of the V–V bonding:

(i) The characterization of the singlet ground state in our previous work relies on the energy comparison between SCF closed-shell configurations corresponding to different metal–metal bond multiplicities. Former calculations on the multiple Cr–Cr bond have shown that the weak overlap between 3d orbitals yields large nondynamic correlation effects dramatically increasing with the considered metal–metal bond order.⁴ The symmetry-adapted SCF calculations artificially favor the configuration with low metal–metal bond order.⁵

(ii) An analysis of the 29 a_1 and 30 a_1 MOs in the configuration (1) shows that the V–V bonding interactions in the a_1 irreducible representation consist in (a) a π interaction involving d_{xz} orbitals⁶ and (b) an interaction between d orbitals with mainly $2y^2-x^2-z^2$ character, i.e. with predominant δ character. The 3d δ –3d δ overlap is known to be extremely weak beyond 2.0 Å,⁷ and a

Table I. Energy (Hartrees) of the Lowest Closed-Shell and Open-Shell Configurations Computed at the SCF and CI Levels^a

config.	SCF			CI		
	state	energy	es, eV	state	energy	es, cm^{-1}
(1)	1A_1	-2573.1441	+3.51	1A_1	-2573.5002	0
(2)	1A_1	-2573.2730	0			
(3)	3B_1	-2573.3347	-1.68	3B_1	-2573.4951	1122
(4)	5A_1	-2573.4619	-5.14	5A_1	-2573.4834	3696

^aEnergy separations (es) are indicated with respect to the lowest singlet state.

single-determinant description of this interaction does not seem appropriate.

We have therefore carried out ab initio calculations including correlation effects⁸ in order to reinvestigate the nature of the metal–metal bond in the singlet ground state. The main results are displayed in Table I.

SCF Results

Although the basis sets selected for the present study are different from those used in our previous work,^{8,10,11} the SCF calculations carried out on the configurations (1)–(3) yield energy separations and population analyses in excellent agreement with those previously reported. However, the poor overlap between metal π and δ orbital combinations suggests that a high-spin coupling of the metal electrons could be energetically favored at the SCF level. The quintet state corresponding to the configuration

(1) Lüthi, H. P.; Bauschlicher, Ch. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2046.

(2) Elschenbroich, Ch.; Heck, J.; Massa, W.; Nun, E.; Schmidt, R. *J. Am. Chem. Soc.* **1983**, *105*, 2905.

(3) Heck, J.; Baltzer, Ph.; Elschenbroich, Ch.; Massa, W.; Schmidt, R., unpublished results.

(4) Benard, M. *J. Chem. Phys.* **1979**, *71*, 2546.

(5) (a) Garner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. W. *Chem. Phys. Lett.* **1976**, *41*, 91. (b) Guest, M. F.; Hillier, I. H.; Garner, C. D. *Ibid.* **1977**, *48*, 587. (c) Benard, M.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 97.

(6) The reference system used in the present work is consistent with the notations used in ref 1: Ox is collinear with the V–V axis, and the xz plane bisects the C_8H_8 and C_5H_5 ligands (see Figure 1).

(7) Trogler, W. C. *J. Chem. Educ.* **1980**, *57*, 424.

(8) The LCAO–MO–SCF CI calculations were carried out with the IBM version of the ASTERIX program system.⁹ Basis sets (9,5) and (4) were used for C and H¹⁰ and contracted to split-valence ([3,2] and [2]). For V, we used the (13,7,5) set of Hyla-Kryspin et al.¹¹ incremented with one p (exp 0.15) function and one diffuse d (exp 0.065) function and contracted to [5,3,3].

(9) *ASTERIX, Reference Manual*; Laboratoire de Chimie Quantique: Strasbourg, France, 1985.

(10) Huzinaga, S. Technical Report, 1971; University of Alberta: Edmonton, Canada.

(11) Hyla-Kryspin, I.; Demuyck, J.; Strich, A.; Benard, M. *J. Chem. Phys.* **1981**, *75*, 3954.

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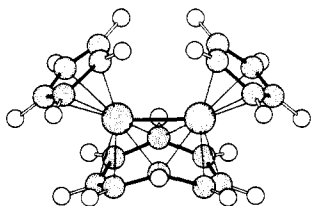
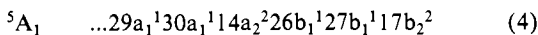


Figure 1. Geometry of the $(C_5H_5V)_2C_8H_8$ molecule.

(4) was effectively found lower by 5.15 eV than the configuration (2) (Table I).



The nature of the frontier orbitals of b_1 symmetry appears as the key point for a correct understanding of the V–V bonding. As a matter of fact, the relatively small energy gap between the closed-shell configurations (2) and (3) was interpreted in our previous work in terms of a competition between the stabilization brought in by the triple V–V bond in the configuration (2) and by the metal–ligand interaction occurring through molecular orbital $26b_1$ in the configuration (3).

The simultaneous optimization of the $29a_1$, $30a_1$, $26b_1$, and $27b_1$ MOs through the open-shell SCF calculation of the quintet state (4) provides a more balanced description of these frontier orbitals. At variance from the analysis carried out from the closed-shell results, each of the four semioccupied MOs displays *almost pure metal character* (between 96 and 98%), and orbitals $26b_1$ and $27b_1$ are the respective antibonding counterparts (with δ^* and π^* character) of orbitals $30a_1$ and $29a_1$.

From these results emerges an alternative view of the V–V bonding, reminiscent of the weak interactions encountered in V_2 , Cr_2 ,¹² and other complexes of the first transition series with multiple metal–metal bonds.¹³ It is well established that for such complexes the closed-shell configuration describing the multiple bond generates large nondynamic correlation effects due to the presence of several metal-bonding orbitals with low overlap.¹⁴ Since the associated correlation energy cannot be obtained from the plain closed-shell SCF treatment,¹⁵ this would account in the present case for the relatively high SCF energy of the triply bonding configuration (1). If we now consider the lowest closed-shell singlet (2), most of the nondynamic correlation vanishes due to the presence of only one remaining V–V bond (π_{xy}), thus explaining the low energy of this configuration *at the SCF level*. A similar artifact occurring in the closed-shell SCF description of the quadruple Cr–Cr bond in $Cr_2(O_2CH)_4$ resulted in a misleading interpretation of the early theoretical results concerning this molecule: A nonbonding configuration was found to be lower in energy than the expected quadruply bonding configuration.⁵

A confirmation of these hypotheses should be provided by evaluating the correlation energy of the metal d electrons.

CI Calculations and Results

The best possible description of the nondynamic correlation of the metal d electrons should be obtained from a complete active

(12) (a) Walch, S. P.; Bauschlicher, Ch. W., Jr.; Roos, B. O.; Nelin, C. *J. Chem. Phys. Lett.* **1983**, *103*, 175. (b) Goodgame, M. M.; Goddard, W. A., III *J. Phys. Chem.* **1981**, *85*, 215. (c) Goodgame, M. M.; Goddard, W. A., III *Phys. Rev. Lett.* **1985**, *54*, 661.

(13) For example, see: (a) Kok, R. A.; Hall, M. B. *Inorg. Chem.* **1985**, *24*, 1542, and references therein. (b) Corrêa de Mello, P.; Edwards, W. D.; Zerner, M. C. *Int. J. Quantum Chem.* **1983**, *23*, 425. (c) Wiest, R.; Strich, A.; Demuyneck, J.; Benard, M.; Siegbahn, P. E. M. *Chem. Phys. Lett.* **1985**, *122*, 453.

(14) Walch, S. P.; Bauschlicher, Ch. W., Jr. *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules*; Bartlett, R. J., Ed.; Reidel: Dordrecht, The Netherlands, 1985; pp 17–51.

(15) A large part of the nondynamic correlation energy could be accounted for in a so-called “broken-symmetry SCF solution” obtained by relieving the space-symmetry constraints acting on the LCAO coefficients.^{4,16}

(16) (a) Wiest, R.; Benard, M. *Theor. Chim. Acta* **1984**, *66*, 65. (b) Hall, M. B. *Quantum Chemistry, the Challenge of Transition Metals and Coordination Chemistry*; Veillard, A., Ed.; Reidel: Dordrecht, The Netherlands, 1986; pp 391–401.

Table II. Distribution of the Most Important Configurations in the CI Expansion Describing the Singlet Ground State^a

$\bar{\pi}^2 \pi^2 \delta^2$	0.33	$\bar{\pi}^2 \pi^* \delta^* \delta^* 2$	0.09
$\bar{\pi}^2 \pi^2 \delta^* 2$	0.17	$\bar{\pi}^1 \pi^1 \delta^2 \pi^* \pi^* 1$	0.01
$\bar{\pi}^2 \pi^1 \delta^1 \pi^* \delta^* 1$	0.18	$\bar{\pi}^1 \pi^2 \delta^1 \delta^* \pi^* 1$	0.01
$\bar{\pi}^2 \delta^2 \pi^* 2$	0.13	$\pi^2 \delta^2 \pi^* 2$	0.005

^a π and δ are the bonding MOs of the a_1 representation; π^* and δ^* stand for their antibonding counterparts in b_1 ; $\bar{\pi}$ represents $17b_2$, a metal–ligand MO with π -bonding character. The values represent the sum of the square of the coefficients corresponding to different spin components of the same configuration.

space SCF (CASSCF) calculation¹⁷ involving $29a_1$, $30a_1$, $26b_1$, and $27b_1$ as active orbitals. A CASSCF calculation on such a large molecule could unfortunately not be carried out for technical reasons. We rather considered that a configuration interaction (CI) expansion correlating the metal d electrons could yield a result close to the CASSCF quality *provided it is carried out using the MO set of the quintet state* (4). As a matter of fact, (i) all four orbitals involved in the V–V direct interaction are variationally optimized in the same subspace, thus yielding a balanced description of the active set, and (ii) in case the CI expansion confirms the hypothesis of a weak V–V double bond involving the four active MOs, the population of each of these MOs should be relatively close to one electron, and this would a posteriori justify our initial choice.

Since we also intend to correlate the two electrons involved in the third component of the V–V bond ($17b_2$), we have included in the MO basis of the CI expansion this MO and its two unoccupied counterparts, namely, (i) the V–V bonding, V– C_8H_8 antibonding MOs (b_2 symmetry) and (ii) the V–V antibonding MOs with π^*_{xy} character (a_2 symmetry). The corresponding active space was composed of 12 molecular orbitals populated with 6 electrons. Three complete CI expansions (including all excitations up to sextuples) were carried out on this active space, in order to characterize the 1A_1 , 3B_1 , and 5A_1 states. The respective numbers of generated configurations are 4000, 5814, and 2160. The energies of the ground-state singlet and of the lowest triplet and quintet states obtained from these expansions are displayed in Table I. The computed singlet–triplet energy separation is 1122 cm^{-1} , in agreement with the reported thermal population of the triplet state. The 5A_1 quintet state is only 3700 cm^{-1} above the ground state. The ground state is a covalent singlet corresponding to a mixture of configurations, as listed in Table II. In terms of the π_{xz} and δ/σ orbitals (a_1 symmetry) and of their antibonding counterparts (b_1 symmetry),¹⁸ the leading configuration is $\pi^2 \delta^2$, corresponding to a triple V–V bond (in all configurations with major weights, the π_{xy} orbital $17b_2$ remains doubly occupied). The weight of the leading term of the CI expansion is only 32.5%. The weighted distribution of configurations displayed in Table II involving a large amount of nonbonding and even antibonding configurations with respect to π_{xz} and δ/σ is characteristic of a weak metal–metal interaction of the antiferromagnetic type.

The orbital populations obtained from the CI expansion for the singlet state are as follows:

$$\delta, 1.21; \pi_{xz}, 1.28; \pi^*_{xz}, 0.70; \delta^*, 0.80; \pi_{xy}, 1.89$$

The populations obtained for δ and π_{xz} are in keeping with those similarly computed for the δ and individual π components of the quadruple metal–metal bond of $Cr_2(O_2CH)_4$ at $d(Cr-Cr) = 2.20 \text{ \AA}$.¹⁹

These results confirm the hypothesis of a weak antiferromagnetic interaction involving the four frontier orbitals of a_1 and b_1 symmetry. The V–V bond order, assumed to be half the difference between the metal–metal bonding and antibonding populations,

(17) Siegbahn, P. E. M.; Heiberg, A.; Roos, B. O.; Levy, B. *Phys. Scr.* **1980**, *21*, 323.

(18) Unitary transformations have been carried out in the semioccupied set of MOs in order to keep apart the π and the δ/σ character in both the a_1 and the b_1 irreducible representations.

(19) Mitschler, A.; Rees, B.; Wiest, R.; Benard, M. *J. Am. Chem. Soc.* **1982**, *104*, 7501.

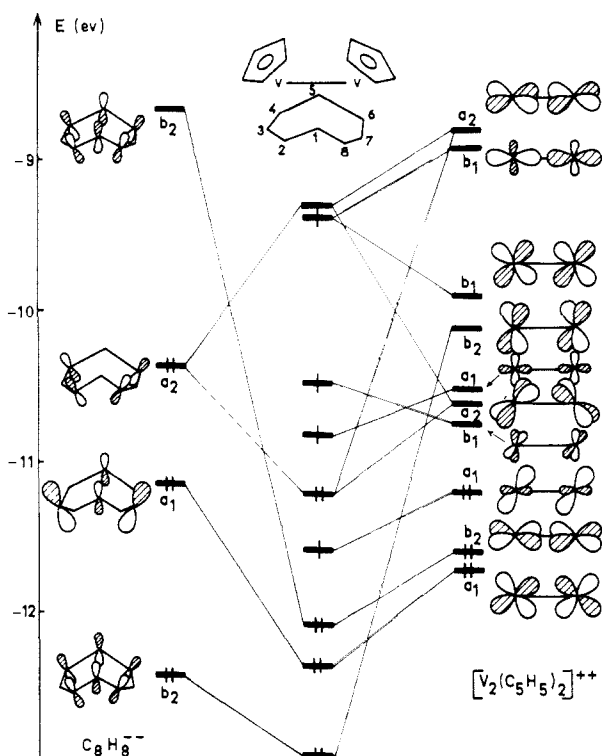


Figure 2. Orbital interaction diagram between the $(C_5H_5V)_2$ and the C_8H_8 fragments (from extended Hückel calculations). The orbital populations of the $(C_5H_5V)_2C_8H_8$ molecule are those of the 5A_1 state characterized from the ab initio SCF calculations.

is computed to be 1.10 from the CI expansion describing the singlet state. This estimate is not so different from the one obtained from closed-shell SCF calculations.¹ From the populations of the four frontier MOs of a_1 and b_1 symmetry, the contribution of the weak double bond to the bond order can be estimated to 0.49. More than half of the V–V bond order is therefore due to delocalized metal–ligand–metal interactions with overall metal–metal bonding character. The most important of these interactions occurs through orbital $17b_2$, which contributes 0.56 to the V–V bond order.

Metal–Ligand–Metal Interaction

A detailed analysis of the interaction stabilizing the C_8H_8 ligand in its $\eta^5:\eta^5$ conformation can be obtained from extended Hückel calculations.²⁰ As previously mentioned,¹ such calculations are not expected to accurately delineate the nature of the metal–metal bond, and as a matter of fact, important changes in the sequence of the frontier orbitals and in their energy separation can be ascertained with respect to the ab initio results concerning the 5A_1 state (Figure 2). Furthermore, the metal orbital combinations seem to be systematically shifted to low energies with respect to the C_8H_8 orbitals. The qualitative nature of the orbital interactions between the $C_8H_8^{2-}$ and the $[V(C_5H_5)]_2^{2+}$ fragments (Figure 2) can however be analyzed with confidence and in agreement with the ab initio results.

The frontier π orbitals of the C_8H_8 cycle in its planar form are well-known.²¹ The puckering of the C_8H_8 cycle (Figure 1)

abolishes the separation between the σ and the π subsets of MOs and breaks the degeneracy between the (b_1, b_2) and (a_1, a_2) orbital pairs. In the folded C_8H_8 ring four MOs with mainly π character are responsible for the most important interactions with the $(VCp)_2$ dimer. The lowest in energy, $1b_2$, is characterized by a π -bonding character connecting atoms 1, 2, and 8 on the one hand and 4–6 on the other hand (Figure 2). Much higher in energy, the antibonding counterpart of this orbital, $2b_2$, remains unoccupied. In between the two b_2 orbitals, two nonbonding orbitals, $1a_1$ and $1a_2$, respectively, display π character on the odd- and even-numbered carbon atoms (Figure 2). Both $1a_1$ and $1a_2$ are doubly occupied in $C_8H_8^{2-}$. The sequence of the 10 metal orbital combinations occupied with 6 electrons in the $(VCp)_2$ fragment is also displayed in Figure 2.

The bonding between V_2Cp_2 and C_8H_8 results from stabilizing interactions in the a_1 , a_2 , and b_2 irreducible representations. Two distinct interactions are present in the b_2 symmetry. The $1b_2$ orbital of C_8H_8 is stabilized by the appropriate combination of metal d orbitals through a bonding interaction involving the π lobes on carbons 2, 4, 6, and 8. In the ab initio calculation, this interaction gives rise to molecular orbital $15b_2$, with 15% metal character. The other (occupied) metal combination is globally nonbonding with respect to $1b_2$. This latter bonding metal combination is however strongly stabilized by the empty ligand orbital $2b_2$. The resulting MO is $17b_2$, which has 56% metal character and as much as 42% C_8H_8 weight (from the population analysis of the ab initio quintet wave function).

From the three metal orbital combinations belonging to the a_1 representation (all with metal–metal bonding character), the lowest one only has a significant overlap with the ligand π orbital of same symmetry (Figure 2). It must be noted however that the resulting MO has predominant C_8H_8 character, with 16% metal weight only. Finally, we find in the a_2 irreducible representation two metal orbital combinations both with V–V π_{xy} and δ_{yz} antibonding character. Both combinations and particularly the one of lowest energy, with metal orbitals oriented parallel to the ligands, strongly stabilize the C_8H_8 orbital with appropriate symmetry. The corresponding MO, $14a_2$, corresponds for 70% to the HOMO of $C_8H_8^{2-}$ (Figure 2) with 29% metal weight.

The extended Hückel calculations confirm that the four open-shell orbitals in the quintet state are only slightly affected by interactions with C_8H_8 . This can be attributed to the large energy gap between the cluster of metal levels and (a) the underlying occupied orbitals of C_8H_8 with b_1 symmetry and (b) the high-lying unoccupied ligand orbitals with a_1 symmetry.

Conclusion

The present study shows that the V–V bond in $(C_5H_5V)_2C_8H_8$ involves two contributions of distinct nature. One contribution comes from a weak double bond of π and δ/σ character. These interactions are free of any significant ligand contribution and are reminiscent of the multiple antiferromagnetic coupling occurring in weakly bonded dichromium tetracarboxylates. As in these multiply bonded molecules, the weak metal–metal coupling is responsible for the small singlet–triplet energy separation experimentally observed and computed in the present work. This weak double bond contributes less than half to the computed bond order of 1.10. The other contribution to the V–V bond comes from delocalized interactions through the C_8H_8 ligand. One of these interactions stabilizes the metal–metal bonding combination with π character ($17b_2$), which contributes 0.56 to the V–V bond order. Other stabilizing interactions with C_8H_8 introduce in the wave function significant contributions of both metal–metal bonding ($28a_1$, $d_{xz} - d_{xz}$; $16b_2$, $d_{yz} + d_{yz}$) and antibonding ($14a_2$) characters.

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