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Electronic Structures of $(\mu\text{-}\eta^5{:}\eta^5)$-Cyclooctatetraene)bis(($\eta^5$-cyclopentadienyl)vanadium) and Its Radical Anion

Jacques Weber* and Henry Chermette[1]

Laboratoire de Chimie Théorique Appliquée, Université de Genève, 30 quai Ernest Ansermet,
CH-1211 Genève 4, Suisse

Jürgen Heck

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, D-3550 Marburg, Deutschland

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The electronic structures of the organometallic compound (μ-η^5:η^5-cyclooctatetraene)bis((η^5-cyclopentadienyl)vanadium) and its radical anion have been investigated by using the multiple-scattering Xα molecular orbital (MO) method. It is found that the ordering of MOs principally concerned with V–V bonding is $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$, the energy difference between the δ HOMO and the δ^* LUMO being 0.5 eV, which leads to a $^1A_1$ closed-shell ground state for the neutral complex. In agreement with both ^{1}H NMR data and previous ab initio calculations, the present study concludes to the presence of a low-energy $\delta\delta^*$ triplet state that may be easily thermally populated. Finally, the ^{51}V isotropic hyperfine coupling constant is calculated for the radical anion of this complex, and, in order to describe the properties of related derivatives with bridged C_5H_5 ligands, the results of the calculations performed with various V–V distances are presented.

Introduction

According to both theoretical[2,3] and experimental[4-8] studies, it is now firmly established that vanadium may form some types of compounds in which multiple bonds are found between metal atoms. However, contrasting with the case of chromium, these compounds are rather uncommon and a detailed study of their electronic structure and related properties is undoubtedly of considerable interest. Elschenbroich et al.[8] have recently prepared the complex (μ-η^5:η^5-cyclooctatetraene)bis((η^5-cyclopentadienyl)vanadium) (1) (Figure 1), which, according to their single-crystal X-ray diffraction study, contains a bridging C_8H_8 ring connecting two C_5H_5 units. Though, for this synfacial compound, it may be difficult to unambiguously assign a bond order to the V–V bond because of the presence of a bridging ligand,[6] it is reasonable to postulate that it is a triple bond, i.e. involving a pair of d^3 V(II) atoms, which allows us to describe complex 1 by two resonance structures. Indeed each of the resonance forms allows one vanadium atom to reach the 18-valence-electron configuration, which contributes to the stability of the complex.

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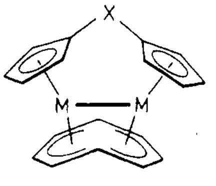
In view of the interest presented by compound 1, the radical anion 1^- and their Cr–Cr and V–Cr analogues, one of us (J.H.) decided to perform an extensive experimental investigation of their structural, NMR, EPR, and redox properties.[9] In particular, attempts to clarify important questions regarding the structural features of complex 1, such as some plausible reasons for the bending of the C_8H_8 ligand or the possibility of synthesizing an antifacial analogue to 1, have already been previously reported.[9,10] In this paper, we present and discuss the results of a theoretical study carried out for 1 and 1^-, using the multiple scattering (MS) Xα molecular orbital method, in order to rationalize and interpret the vast amount of experimental data collected for these compounds. In addition to the ground-state electronic structure and singlet–triplet splitting of 1, the Fermi contact parameter of the hyperfine tensor on metal is reported for 1^-. The results of calculations performed for 1 and 1^- with various V–V distances are then presented in an attempt to describe the behavior of 1 and 1^- derivatives wherein the C_5H_5 ligands are linked via an X-bridging group,[9] which may obviously modify the metal–metal distance.



Finally, a discussion is made of the influence the bridging of C_5H_5 ligands may have on their structural and chemical properties.

Computational Details

The standard version of the SCF MS Xα method[11] is used. The geometry of complex 1 is taken from the previously reported X-ray diffraction study[8] and slightly modified so as to exhibit the ideal C_{2v} symmetry, but the initial V–V distance is kept unchanged as 2.439 Å (called case A thereafter). Then, the structural changes accompanying the presence of bridging C_5H_5 ligands are simulated by inducing symmetric rotations on the left and right moieties (assumed to be rigid) of the compound around the C11–C15 axis. In other words, one rotates simultaneously the left moiety by an

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[1] Permanent address: Laboratoire de Chimie Nucléaire, Université Claude Bernard Lyon I, F-69622 Villeurbanne Cedex, France.

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Table I. Upper Valence Ground-State Molecular Orbitals of Compound 1

		charge distribution,[b]										
		V					C		H			
orbital[a]	energy, eV	s	p	dσ	dπ	dδ	C_8H_8	C_5H_5	C_8H_8	C_5H_5	inter sphere	outer sphere
$13b_2$	−3.67				6	49	11	12			19	3
$20a_1$	−4.02			12	10	30	18	12			17	1
$11a_2$	−5.04		1		68	2	12	6			11	
$17b_1$	−5.21			3	84	1	4	2			6	
$16b_1$	−6.44	2		14		66	5	2			11	
$19a_1$	−6.93	1	1	6	29	46	2	2	1	1	11	
$10a_2$	−7.97		3		13	19	38	4			23	
$18a_1$	−8.25	4	10	12	27	6	1	20			20	
$12b_2$	−8.27		4		13	26	7	24	1		25	
$15b_1$	−8.40		4	13		6	1	48			28	
$9a_2$	−8.43		2		6	19	3	43			27	
$11b_2$	−8.50		2		40	1	11	22			24	
$17a_1$	−8.55		3	16	11	3	20	20	1		26	
$16a_1$	−9.90	2	6	37	2	6	23	10	2		12	
$14b_1$	−10.72	2	3	1	5	1	56	4			28	
$10b_2$	−10.77		7		7	12	48	2	5		22	
$15a_1$	−11.48	1	4			1	34	26	3		28	
$13b_1$	−12.08	6			1		4	54		1	30	
$14a_1$	−12.68	15		3	1		20	30	5		26	
$12b_1$	−12.78	1			1		51	14	21	4	8	

[a] The HOMO is the $19a_1$ level. [b] The V, C, and H charge distributions refer to the charge contained in all the respective spheres of that type.

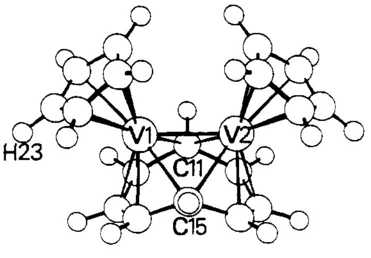

Figure 1. Structure of complex 1.

angle of +θ (counterclockwise) and the right one by −θ (clockwise). In regard to the V–V distance, the choice of θ = +5° (case B) leads thus to an elongation (d_{V-V} = 2.642 Å) whereas the case θ = −5° (C) leads to shrinking (d_{V-V} = 2.235 Å). In all cases, the geometry of 1^- is assumed to be the same as that of 1.

The radii of atomic spheres characteristic of the MS Xα model have been chosen as follows. In accordance with previous calculations performed on octahalodimetalate complexes,[12,13] a moderate amount of spheres overlapping (15%), leading to a sphere radius of R_V = 2.651 au, was used for vanadium spheres. This is somewhat smaller than the value of 30% used in a recent theoretical study of the V_2 molecule,[3] but the presence of bulky ligands limits somewhat the amount of overlapping to be chosen for the spheres of vanadium atoms. Then, the radii of carbon and hydrogen spheres have been uniformly taken at 1.603 and 1.250 au, respectively. These values, which lead to overlaps of atomic spheres amounting to 16–28% and 37–41% for C–C and C–H bonds, respectively, correspond to averages of the atomic sphere radii obtained by using the procedure suggested by Norman[14] with a criterion of 90% of the atomic number radii. An externally tangent (to the H23 sphere) outer sphere, centered in the middle of the V–V bond, is used. All these sphere radii are kept constant in cases B and C, except for the outer sphere whole radius is modified so as to remain tangent to the H23 sphere.

The values of atomic exchange parameters α are taken from the compilation of Schwarz[15] for V (0.715 56) and C (0.759 28) and from Slater[16] for H (0.777 25). A weighted average of the atomic values (0.765 49) is chosen for the α value in interatomic (intersphere) and extramolecular (outer sphere) regions. For 1^-, the effect of an external stabilizing electrostatic field is taken into account by use of a Watson sphere of the same radius as the outer sphere and bearing a charge of 1+. The calculations of the electronic structure of 1 have been performed by using the nonspin-polarized (NSP) version of the MS Xα computer programs, whereas for the excited states of 1 and all the calculations on 1^- the SP version has been used.

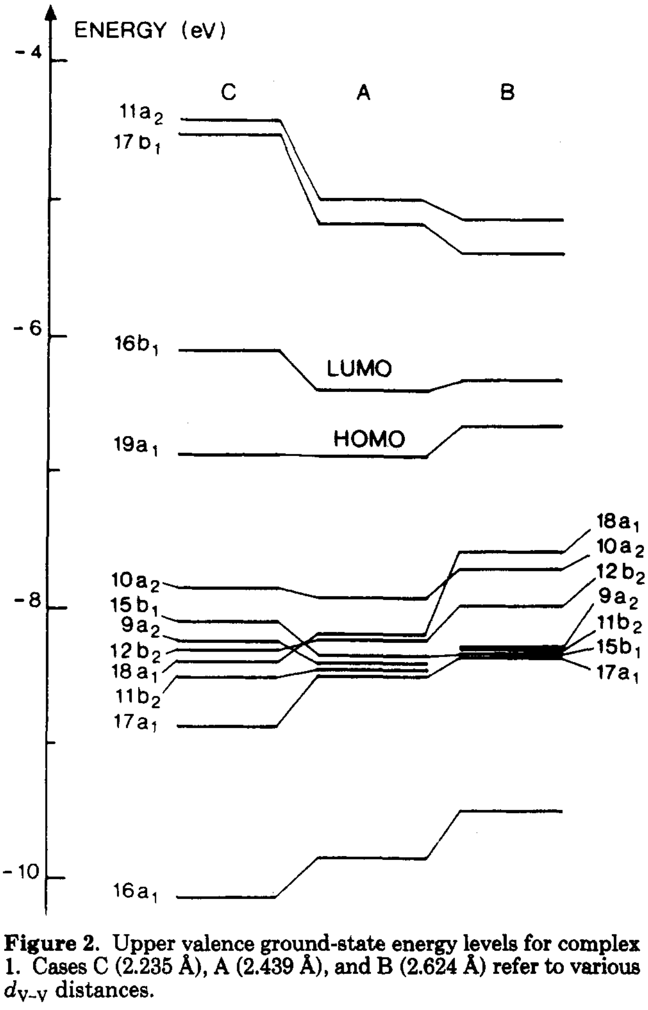

Figure 2. Upper valence ground-state energy levels for complex 1. Cases C (2.235 Å), A (2.439 Å), and B (2.624 Å) refer to various d_{V-V} distances.

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Table II. Gross Bonding (N_B) and Antibonding (N_A) Populations of the Various Components[a] of Vanadium Orbitals in 1

	orbital					
	4s	4pσ	4pπ	3dσ	3dπ	3dδ
N_B	0.58	0.44	0.50	1.58	2.78	2.18
N_A	0.28	0.12	0.36	0.38	0.56	1.08
$N_B - N_A$	0.30	0.32	0.14	1.20	2.22	1.10

[a] Components are labeled σ, π, and δ with respect to the V–V bond axis. The populations reported refer to two vanadium atoms.

Results and Discussion

The ground-state electronic structure of 1 is presented in Table II and Figure 2, which displays an energy level diagram of the upper valence MOs of the complex. Both the $19a_1$ HOMO and $16b_1$ LUMO have a predominantly metal character, with vanadium charge distributions amounting to 83% and 82%, respectively. However, whereas $19a_1$ is δ bonding with a strong admixture of π component, $16b_1$ is essentially δ^* antibonding with a smaller admixture of σ^* component (Figure 3).[17] The (δ, δ^*) character predicted for the (HOMO, LUMO) pair of orbitals of 1 is in complete agreement with the results obtained by Cotton et al.,[2] using the Fenske–Hall model, for both $V_2(DMP)_4$ and $V_2(PMePh_2)_4(H_2ZnH_2BH_2)_2$ and seems thus to be a characteristic of such compounds exhibiting a triple bond between V(II) atoms. The energy difference between HOMO and LUMO is seen to be small ($\approx$0.5 eV in case A), and its dependence upon V–V distance will be discussed further in the text. The small ligand contributions to both HOMO and LUMO are confirmed experimentally by the dependence of redox potentials upon the electronic characteristics of the X bridging group between the C_5H_5 systems.[9]

As the π and δ components of 3d orbitals belong simultaneously to all the irreducible representations of the C_{2v} point group, it is not suprising that most of the upper valence MOs of 1 exhibit within their metal charge distribution a considerable (π, δ) mixing. This is specially true for $10a_2$ (Figure 3), $18a_1$, and $12b_2$ which are important contributors to metal–ligand bonding ($10a_2$, M–C_8H_8; $18a_1$, $12b_2$, M–C_5H_5). At the same time, $10a_2$ is V–V (δ + π) antibonding, whereas $18a_1$ and $12b_2$ are V–V (δ + π) bonding; in addition, $18a_1$ shows a significant amount of p–d hybridization. At lower energies, one finds the $15b_1$ and $9a_2$ MOs which have predominant C_5H_5 character; however, both of them receive important contributions from the metal atoms and display metal–ligand bonding and metal–metal antibonding interactions. The $11b_2$ orbital is typically V–V π bonding with significant admixtures of both types of ligands, whereas $17a_1$ (Figure 3) is considerably delocalized over the whole complex while exhibiting both metal–metal and metal–ligand bonding interactions. As expected, the $16a_1$ orbital, which is predominantly V–V σ bonding, is the lowest in energy of the metal-based 3d MOs, though the distinction between metal and ligand orbitals is sometimes difficult to make for those lying between −7.0 and −10.0 eV because of the considerable covalent metal–ligand interactions they exhibit.

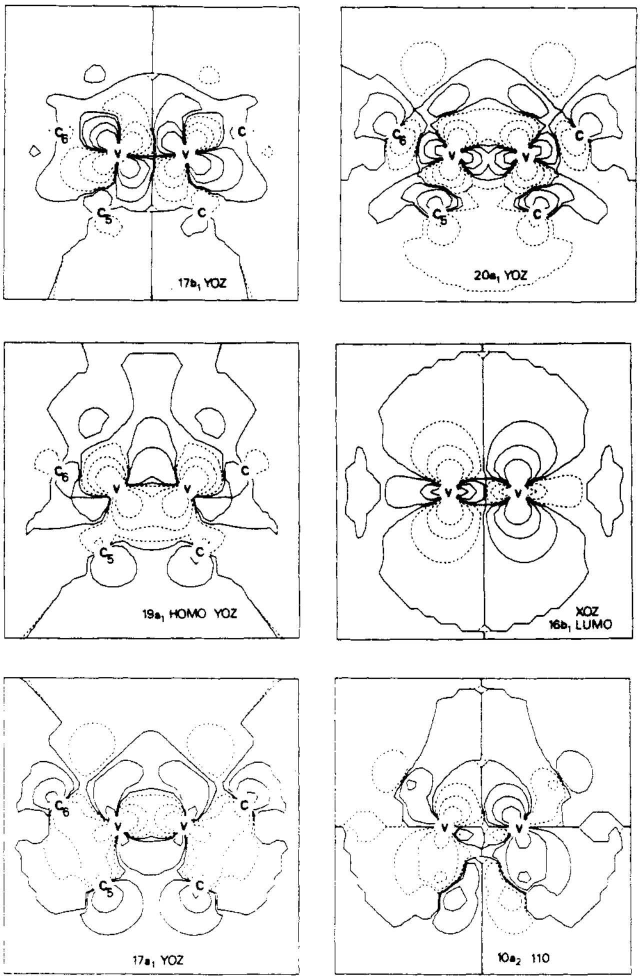

Figure 3. Wave function contours of some important MOs of complex 1, plotted in the indicated plane. Positive contours are represented by a solid line and negative ones by a dashed line.

Examination of Table I shows that, below −10.0 eV, the $14b_1$–$12b_1$ orbitals are all ligand-based MOs, though some of them exhibit significant contributions from the metal atoms, such as $10b_2$ or $14a_1$. Turning now to the virtual orbitals of 1, it is seen that the low-lying ones, which have a predominant metal character, are in the ordering $\delta^* < \pi^* < \sigma^*$. Taken as a whole and considering that, as pointed out by Cotton et al.,[18] the strong metal–ligand interaction observed in 1 may result in difficulties when the bonding is discussed in terms of idealized pure metal orbitals, the ordering of MOs principally concerned with V–V bonding is $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$. With the exception of the $\pi^* < \sigma^*$ ordering, this is in agreement with the currently accepted picture of the electronic structure of metal–metal complexes characterized by a triple or quadruple bond.[2,19] In addition, our ordering of metal–metal d orbitals is the same as that deduced from MS Xα calculations by Norman et al. for the $Mo_2(O_2CH)_4$ and $Mo_2Cl_8^{4-}$ complexes.[20,21]

It is interesting to study now in more detail the description of the V–V bond which emerges from our calculations, in an attempt to estimate the bond order and its formulation in terms of σ, π, and δ occupancies. However, the isolation of the V_2 unit as a conceptual entity within the complex is complicated and the difficulties encountered in this analysis are real: the C_5H_5 ligands strongly tailor the metal-centered orbitals and, in addition to "through-space" V–V interactions, there are important "through-bond" effects via the C_8H_8 ligand. The dissection

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(17) In C_{2v} symmetry, the in-phase (bonding) mixing of the dσ, dπ, and dδ orbitals of the two metal atoms gives raise to MOs of a_1, $a_1 + b_2$, and $a_1 + b_2$ symmetries, respectively; similarly, their out-of-phase (antibonding) mixing leads to b_1, $a_2 + b_1$, and $a_2 + b_1$ MOs, respectively.

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of V–V interactions into σ, π, and δ components then becomes somewhat arbitrary and, moreover, it is both method and basis set dependent. However, keeping these restrictions in mind, we feel that an approximate analysis of the V–V bond order deserves to be performed as it could help in describing one of the most intriguing features of this complex. To this end, because of the considerable (σ, π, and δ) mixing exhibited by most MOs with predominantly metal character, it is necessary to evaluate the total gross populations of all orbital components on the metal, much in the same way as already performed in previous calculations on metallocene[22-24] or tetraperoxometalate[25] complexes. This may be readily achieved by summing up the partial charge distributions on the metal over all orbitals with at least 1% metal character. The results, obtained as previously described[22-25] by fully attributing to the ligands both inter-sphere and outer-sphere charges, are presented in Table II. One should note again that these results are to be taken "cum grano salis" since atomic populations depend, of course, on calculation parameters such as the radii of muffin-tin spheres in the MS Xα model.

The population analysis presented in Table II has been made so as to estimate separately the contributions of bonding and antibonding electrons, which can be easily performed by examining the nature of each orbital involved. It is seen that indeed there is a significant amount of antibonding electrons located on metal atoms, and they have to be accounted for when estimating the bond order. As to 4s and 4p populations, they are found to be nonnegligible, as already pointed out from MS Xα calculations performed for other transition-metal complexes.[22-25] Turning to 3d populations, their relative proportion is primarily dictated by the structure of the complex and the symmetry of the ligand-based MOs which contribute the most to ligand to metal charge donation. In the present case, the overall (bonding + antibonding) populations in 3d orbitals are 2.0, 3.3, and 3.3 e for σ, π, and δ components, respectively. With the assumption that the V–V triple bond in a complex such as 1 might be formulated as $(\sigma)^2(\pi)^2(\delta)^2$ in terms of idealized pure metal orbitals,[2] these figures reveal an important charge donation from the ligands to metal dπ and dδ orbitals. Referring to the X-ray crystal structure of 1, it has been pointed out that the distance of 2.44 Å for the V–V bond may probably be interpreted as a long triple bond.[8] On the other hand, it is possible to evaluate approximately this bond order from our calculations by using the well-known definition formulated as "the difference between the number of pairs of electrons in bonding MOs minus the number of pairs in antibonding MOs".[26] In our case, the large delocalization of the upper valence MOs suggests that the N_B and N_A populations of Table II should be used instead of the number of electrons in pure bonding and antibonding MOs. Thus, when the various contributions to $N_B - N_A$ reported in Table II are summed up, the bond order is approximately 2.6, i.e. somewhat intermediate between a triple and a double bond, which is in good agreement with the assumption of a long triple bond. In addition, when attempting to rationalize these populations in terms of pure metal orbitals, the configuration $(\sigma)^{1.2}(\pi)^{2.2}(\delta)^{1.1}$ is obtained, which compares well with the two possible standard formulations $(\sigma)^2(\pi)^2(\delta)^2$ and $(\sigma)^2(\pi)^4$. This is a further justification of the qualitative MO picture reported for complex 1 in ref 9 by assuming that it originates from a combination of two bent metallocenes.

Two ab initio studies of complex 1 have been reported recently,[27,28] and it is interesting to compare their main conclusions with the present Xα results. In a first study,[27] performed at the SCF level, Lüthi and Bauschlicher (LB) conclude that the singlet ground state of 1 corresponds to the $^1A_1$ $(\sigma)^2(\pi)^2(\pi^*)^2$ configuration, but surprisingly they report the presence of a triplet state, $^3B_1$ $(\sigma)^2(\pi)^2(\pi)^1(\pi^*)^1$, with a total energy 1.09 eV *lower* than that of the $^1A_1$ singlet. However, LB suggest that this SCF result would probably be modified by introduction of electron correlation in the sense of a larger energy lowering for the singlet than for the triplet, with the final result that both states would be very close in energy. Though this would explain the experimental finding of a low-lying triplet state in 1 (see below), it is a bit surprising that it would originate from a ππ* configuration as the energy difference between $2\pi_u$ and $2\pi_g$ MOs is predicted to be of the order of 15 eV for the V_2 molecule at a V–V distance of 2.44 Å.[3] Similarly, the presence of an antibonding π* doubly occupied MO in the ground-state configuration of 1, as predicted by LB, might be questionable as all previous theoretical descriptions of multiple bonding between vanadium atoms suggest that the occupied MOs with predominant metal 3d character are all of the σ, π, or δ bonding type.

The other ab initio study of 1 has been performed by Mougenot, Demuynck, Benard, and Bauschlicher[28] (MDBB). At the SCF level, the results of MDBB are in good agreement with those of LB as far as the $^1A_1$ and $^3B_1$ states are concerned. However, due to the "poor overlap metal π and δ orbital combinations" reported by MDBB, a $^5A_1$ $(\pi)^2(\delta)^1(\pi)^1(\delta^*)^1(\pi^*)^1$ high-spin configuration is predicted to be the ground state at the SCF level, the energy difference between this quintet and the $^1A_1$ singlet being 5.14 eV. Clearly, this result is again questionable in view of the diamagnetic character of the ground state of 1 previously reported on experimental grounds.[8,9] Among other things, this disagreement has prompted MDBB to perform a configuration interaction (CI) expansion correlating the 3d electrons, whose results lead indeed to a $^1A_1$ ground state, the $^3B_1$ and $^5A_1$ high-spin configurations lying at slightly higher energies by 1122 and 3696 cm^{-1}, respectively. The leading configuration in the $^1A_1$ ground state is $(\pi)^2(\pi)^2(\delta)^2$, with a weight of 0.33, whereas a large number of nonbonding and antibonding configurations are present in the CI expansion of this state with nonnegligible coefficients. The predominantly 3dδ doubly occupied MO (a_1 symmetry) exhibits a significant 3dσ contribution, which allows us to roughly classify the leading term of the ground-state configuration as $(\sigma/\delta)^2(\pi)^4$, in agreement with the present results. Finally, according to the CI calculations of MDBB, the V–V bond order is 1.1, which is significantly less than the 2.6 value we report in the present study. However, the bond order of 1.1 has been obtained: (i) by taking account of 3d electrons only (no contribution from 4s and 4p electrons); (ii) by using *net* 3d orbital populations instead of the *gross* populations we have employed here. These reasons, together with the ambiguity mentioned above concerning the definition of the V–V bond order, lead us to conclude that a meaningful com-

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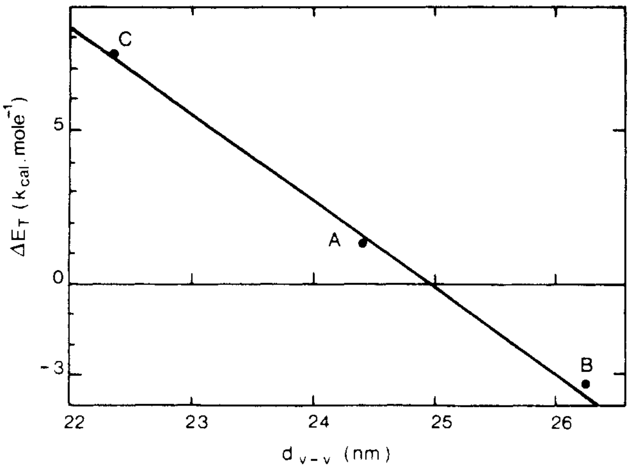

Figure 4. Dependence of ground-state δ^2 singlet to $\delta\delta^*$ triplet excitation energy as a function of V–V distance (SP MS Xα calculations).

parison of the metal–metal interactions deduced from both theoretical models is practically impossible.

Before turning to the calculation of the first triplet excited state of 1, let us briefly describe the dependence of the electronic structure of 1 upon the V–V distance. Whereas one notices small variations in the charge distributions of upper valence MOs when going from case A to cases B and C, which are not reported here, it is interesting to focus on the behavior of energy levels (Figure 2). As expected, and in agreement with the calculations of Andrews and Ozin[3] performed for V_2, the δ – δ^* (i.e. HOMO – LUMO) energy difference is found to be very sensitive upon d_{V-V}, reducing drastically from 0.76 to 0.34 eV when going from case C to case B, i.e. when increasing d_{V-V} from 2.235 to 2.624 Å. Compared with experiment,[9] a slight decrease in the δ – δ^* energy difference may indeed be deduced from the cyclovoltammetric measurements when d_{V-V} increases by roughly 0.04–0.05 Å.[9] There is no doubt that this effect will in turn strongly influence the energy separation between the $(\delta)^2$ ground state and the $(\delta\delta^*)$ triplet excited state. Simultaneously, one notices when going from case C to case B an overall decrease of the $19a_1$ – $16a_1$ energy separation, i.e. a narrowing of the energy splitting of the predominantly metal orbitals. However, this decrease is in proportion much smaller than that of the δ – δ^* energy separation, again in agreement with the V_2 case.[3] Concerning the ordering of the $10a_2$–$17a_1$ levels, it is seen in Figure 2 that these levels display several crossings when going from case C to case B, which is not surprising as they all lie at very close energies.

A temperature-dependent NMR study of the ground state of complex 1 has shown that it may be described by a singlet–triplet equilibrium, with a thermally populated low-lying triplet state,[9] which may be compared with the similar finding of Cotton et al.[18] for dimolybdenum(II) compounds. Actually, this low-lying triplet state has been interpreted as resulting from the $\delta\delta^*$ configuration, the singlet–triplet splitting being of the order of 5–6 kcal/mol.[9] Our theoretical results are consistent with these observations, as they show indeed the presence of a low-energy LUMO with δ^* character, giving rise after a HOMO – LUMO electronic excitation to a $^3B_1$ $(\delta)^1(\delta^*)^1$ triplet state. It is therefore interesting to evaluate the energy separation between the $^1A_1$ ground state and this $^3B_1$ excited state. It is well-known[29] that the accurate calculation of singlet–triplet excitation energies ΔE_T requires the use of the SP formalism, and the results reported here (Figure 4) have been obtained in this approximation, using the transition-state procedure.[30] The calculated ΔE_T energies are indeed very small and depend strongly upon V–V distance, their values being 0.333 (case C), 0.055 (A), and –0.146 eV (B). Because of the large value of the Coulombic $J_{\delta\delta^*}$ integral,[31] ΔE_T is actually much smaller than the HOMO – LUMO energy difference in the ground-state calculation. At the V–V equilibrium distance of 2.44 Å, ΔE_T is thus predicted to be 1.3 kcal/mol, in reasonable agreement with both the experimental value (5–6 kcal/mol) and the CI result reported by MDBB (3.2 kcal/mol). It is seen in Figure 4 that the variation of ΔE_T as a function of d_{V-V} is practically linear in the range 2.2–2.6 Å and that at approximately 2.5 Å the $\delta\delta^*$ triplet configuration becomes the ground state of the complex; i.e., its total energy is lower than that of the δ^2 singlet configuration. Again, because of the approximation inherent to the model, these results should be considered as of semiquantitative value, but they are consistent with the experimental facts on two important points: (i) the energy separation between ground state and first triplet excited state is so small that the latter can be easily thermally populated; (ii) at the V–V distance determined by the X-ray crystal study, the compound is diamagnetic; however, it could exhibit paramagnetic properties at larger distances. The experimental singlet–triplet energy separations obtained for compounds in which the C_5H_5 ligands are linked via different groups, X = CH_2, $SiMe_2$, and $GeMe_2$, show little variation. According to the theoretical results presented in Figure 4, this may be interpreted in the sense of a little dependence of d_{V-V} upon ligand substitution. From X-ray studies of several X-bridged complexes, the metal–metal distance varies by only 0.04–0.05 Å, which should result in a change of roughly 1 kcal/mol for ΔE_T. This is probably too small of an energy change to be observed by the ^1H NMR technique employed in ref 9.

Table III. Contributions to the Fermi Contact Parameter A_F of the ^{51}V Hyperfine Tensor of 1^- for Various Metal–Metal Distances[a] (d_{V-V})

	contributions to the Fermi contact parameter		
	d_{V-V} = 2.235 Å	d_{V-V} = 2.439 Å	d_{V-V} = 2.642 Å
4s	+0.162 55	+0.151 55	+0.140 00
3s	+0.046 20	+0.045 63	+0.046 31
2s	–0.152 67	–0.159 83	–0.166 12
1s	–0.002 05	–0.002 74	–0.002 94
total	+0.054 03	+0.034 61	+0.017 25
A_F,[b] G	22.7	14.6	7.3

[a] Unless otherwise stated, the values reported are the spin density at each *V* nucleus, i.e. $\rho^\uparrow(0)-\rho^\downarrow(0)$, in au. [b] $A_F = 8\pi/3C_N[\rho^\uparrow(0)-\rho^\downarrow(0)]$, where $8\pi/3C_N$ = 420.45 G/au (see ref 31). Experimental value: A_F = 10.5 G.[8]

Finally, we are going to present some results obtained for the radical anion 1^-. Elschenbroich et al.[8] have previously reported on the ease of formation of 1^- when attempting to reduce the neutral compound 1. Leading to a low-energy $16b_1$ LUMO, the present calculations suggest indeed that 1 may be characterized as a Lewis acid, and, as such, it should be easy to reduce to 1^-. The electronic structure of 1^-, which is not reported here in detail, may easily be inferred from that of 1 by adding an extra electron to the LUMO, little rearrangement being observed in upper valence MOs during the reduction. However, as the ^{51}V isotropic hyperfine coupling constant has been

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(29) Weber, J. *Chem. Phys. Lett.* **1977**, *45*, 261.

(30) Slater, J. C. *Adv. Quantum Chem.* **1972**, *6*, 1.

(31) In a frozen-orbital model taking electron repulsion into account, $\Delta E_T = \epsilon_{\delta^*} - \epsilon_\delta - J_{\delta\delta^*}$.

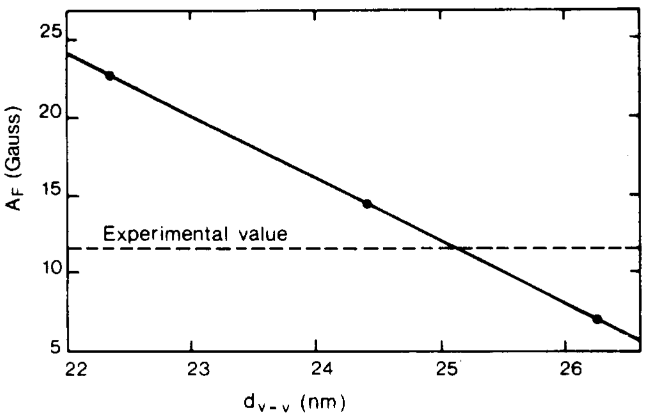

Figure 5. Dependence of Fermi contact parameter of ^{51}V hyperfine tensor of 1^- as a function of V–V distance (SP MS Xα calculations).

deduced from ESR measurements performed on 1^-,[8] it was interesting to evaluate this quantity within the MS Xα framework and to study its dependence as a function of d_{V-V}. Indeed, previous studies have shown that this model is generally appropriate for the prediction and interpretation of the magnetic properties of transition-metal complexes.[24,25,32,33] The results are presented in Table III and Figure 5. Inspection of the individual shell contributions (Table III) shows that the resultant spin density at vanadium nucleus is due to a competition of different terms of opposite sign, none of them being negligible. However, as expected,[24] the most important contributions are due to 2s, 4s (arising mainly through the 4s partial character of the $16b_1$ open-shell MO), and, to a smaller extent, 3s orbitals. It is easy to understand why the calculation of isotropic hyperfine coupling constants is by no means a straightforward task, as this property results from the competition of large numbers with opposite signs. It is therefore gratifying to see that the agreement between the calculated Fermi contact term A_F (14.6 G, case A) and the experimental one (10.5 G) is reasonable, which underlines the good quality of the MS Xα wave functions. The dependence of A_F as a function of d_{V-V} (see Figure 5) is again practically linear with, as expected, a negative slope since bringing the metal atoms closer one another increases the overlap of the wave functions and therefore the spin density at metal nuclei. However, it is difficult to use the linear dependence exhibited by Figure 5 in order to deduce the geometry of X-bridged derivatives of 1^-. Indeed, we have reported above that the variations in the V–V distance arising from the presence of different X groups are of the order of 0.04–0.05 Å only, which leads according to Figure 5 to a change in A_F amounting roughly to 2 G. As the modifications in the electronic structure of 1^- induced by the different X-bridging groups lead probably also to small variations of A_F, of the order of a few gauss, it is not possible to discriminate between these two effects and to use the linear relationship between A_F and d_{V-V} only in order to deduce structural information concerning 1^- derivatives. An accurate description of the influence of X-bridging groups on the chemical properties of 1 and 1^- derivatives would therefore require additional calculations performed for the bridged complexes themselves.

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Registry No. 1, 107201-40-1; 1^-, 85234-88-4.

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