inseparable mixture of many compounds, as evidenced by the ^{19}F NMR spectrum. Reaction with CsF in CH_3CN led to the uptake of 1 equiv of CsF, but the fluorine spectrum showed the presence of at least two C(O)F groups. Separation was not attempted.

While the esters $SF_5CH(SO_2F)C(O)OR$ (R = CH_3, $CH(CH_3)_2$), when treated with the base $F_3B{\cdot}N(C_2H_5)_3$, gave compound **1**, similar treatment of the ester $SF_5CH_2C(O)OCH_3$ resulted in decomposition; only residual material and SF_4 were observed in the ^{19}F NMR spectrum.

Experimental Section

All experiments were done on a conventional Pyrex glass vacuum line equipped with a mercury manometer. $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ was made as described earlier.[5] Infrared spectra were measured from capillary films on KBr plates with a Nicolet 20DX spectrometer, and NMR spectra were obtained on a Varian Model EM-390 spectrometer at 90.0 (^1H) or 84.67 (^{19}F) MHz. Tetramethylsilane and CCl_3F were used as external standards. The mass spectra were taken on a VG-7070 HS mass spectrometer at 70 eV. Elemental analyses were determined by Microanalytisches Laboratorium Beller, Göttingen, West Germany.

1. $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$ + $F_3B{\cdot}N(C_2H_5)_3$. A 50-mL round-bottom flask equipped with a magnetic stirring bar and containing the ester (5.00 g, 16.1 mmol) and the base $F_3B{\cdot}N(C_2H_5)_3$[6] (6.10 g, 36.1 mmol) was connected via a vacuum transfer line that was attached to another vacuum line with a cold trap held at −196 °C. The pressure in the entire system was lowered to ≈300 mmHg, and heating of the reaction vessel commenced. When the oil bath had reached a temperature of 71 °C, a vigorous reaction occurred. Heating was continued for another 15 min; the reaction vessel was then chilled (−196 °C), the compartment was evacuated, and the remaining volatile materials were transferred at room temperature into a cold trap for containment. A total of 0.4960 g was collected. The high-boiling product was distilled directly from the reaction flask, bp 44.5–45 °C/4–5 mmHg (1.40 g). The foreshot (0.22 g) and the contents of the cold trap (0.23 g) had identical infrared spectra as the main fraction. Yield: 1.40 g (38.1%).

^{19}F NMR spectrum (neat sample): $[F^2{}_2S(O){=}C(SO_2F^3)C(O)F^1]$ $\phi_1 = 31.3$ ppm (d-t), intensity = 1.00 (C(O)F); $\phi_2 = 59.7$ ppm (d-d), intensity = 2.04 ($=SOF_2$); $\phi_3 = 72.3$ ppm (d-t), intensity = 1.08 (SO_2F); $J_{12} = 12.8$ Hz; $J_{13} = 7.2$ Hz; $J_{23} = 9.5$ Hz.

IR spectrum (cm^{-1}): 1825 (vs), 1448 (vs), 1419 (vs), 1241 (sh, vs), 1226 (vs), 1138 (s), 1099 (m), 1050 (m–w), 986 (w), 875 (vs), 801 (vs), 739 (m), 725 (m), 715 (m–w), 622 (s), 568 (vs), 534 (m–s), 529 (m–s), 482 (m), 473 (m–w), 463 (m–w).

Mass spectrum (electron impact; *m/e*, species, % abundance): 228, $M(^{32}S)^+$, 100.0; 209, $(M - F)^+$, 13.1; 149, $CF_3OS_2{}^+$, 3.5; 126, $C_2F_2O_2S^+$, 6.3; 123, $C_2FOS_2{}^+$, 5.3; 107, $C_2FO_2S^+$, 1.5; 105, $SOF_3{}^+$ (rearr), $(MH - SOF_4)^+$, 31.5; 91, C_2FOS^+, 5.1; 89, $SF_3{}^+$ (rearr), $(MH - SO_2F_4)^+$, 2.6; 86, $SOF_2{}^+$, 4.6; 83, SO_2F^+, 4.1; 72, C_2SO^+, 1.3; 70, $SF_2{}^+$, 12.9; 67, FOS^+, 94.5; 64, $SO_2{}^+$, 18.1; 63, CFS^+, 10.5; 60, COS^+, 3.2; 59, C_2FO^+, 4.4; 51, SF^+, 7.5.

Anal. Calcd for $C_2F_4O_4S_2$: C, 10.53; F, 33.3; S, 28.11. Found: C, 10.71; F, 33.1; S, 27.95.

The infrared spectrum of the gaseous products showed a band of medium size at 1664 cm^{-1} ($\nu(C{=}C)$ in $CH_3CH{=}CH_2$ = 1647 cm^{-1})[7] and another strong one at 1139 cm^{-1}, assigned to a C–F stretch vibration. There was also a very strong band centered at 2990 cm^{-1} and several weaker ones.

2. $F_5SCH(SO_2F)C(O)OCH_3$. Into 7.20 g (26.7 mmol) of $F_5SCH{-}CF_2OSO_2$ in a 50-mL reaction vessel equipped with a Kontes Teflon valve was condensed 2.00 g (62.5 mmol) of anhydrous CH_3OH at −196 °C. The mixture was warmed to room temperature, and after 20 min with stirring, the product was transferred to a 25-mL flask and the reaction vessel was rinsed twice (0.5 mL) with CH_3OH. The rinse solution was combined with the bulk of the product. Distillation (15–18 mmHg) yielded 1.69 g of a fraction boiling from 65 to 68 °C. The foreshot (0.54 g) was also pure ester. Additional product could be collected from the cold trap after precipitating the ester with water (20 mL) and distillation (0.40 g). Total product: 2.63 g (35%).

^1H NMR ($CDCl_3$): $\delta_1 = 4.45$ ppm (s), intensity = 3.3 (CH_3); $\delta_2 = 6.26$ ppm (m, br), intensity = 1.0 ($CHSF_5$).

^{19}F NMR ($CFCl_3$): $\phi_1 = 71.7$ ppm (m), intensity = 5.0; $\phi_2 = 59.7$ ppm (m), intensity = 1.0 (SO_2F).

IR spectrum (cm^{-1}): 2971 (m), 1767 (vs), 1443 (vs), 1305 (s), 1277 (s), 1223 (s), 1200 (m–s), 1157 (m–s), 1053 (m–w), 1019 (m), 996 (w, sh), 916 (vs), 869 (vs), 804 (s), 773 (m, sh), 749 (m), 692 (m), 648 (m), 612 (m–s), 571 (vs), 490 (m), 458 (m–w), 417 (w).

Mass spectrum (electron impact; *m/e*, species, % abundance): 262, $(M - HF)^+$, 0.8; 253, $(MH - CH_2O)^+$, 1.6; 251, $(M - OCH_3)^+$, 10.4; 250, $(M - CH_3OH)^+$, 1.7; 231, $(M - HF - CH_3O)^+$, 5.4; 168, $(M - SO_2F - OCH_3)^+$, 3.6; 155, $(M - SF_5)^+$, 6.4; 143, $(M - 4F - OCH_3 - 2O)^+$, 4.7; 139, $(M - SO_2F - C(O)OCH_3 - H)^+$, 2.5; 135, $(M - HF - SF_5)^+$, 3.4; 129, $(MH - 5F - C(O)OCH_3)^+$, 2.9; 127, $SF_5{}^+$, 48.0; 125, $(MH - SF_5 - OCH_3)^+$, 18.7; 124, $(M - SF_5 - OCH_3)^+$, 2.9; 122, $(MH - SO_2F - F - C(O)OCH_3)^+$, 6.4; 105, $(M - SF_5 - OCH_3 - F)^+$, 9.8; 91, C_2FOS^+, 2.3; 89, $SF_3{}^+$, 42.2; 79, $CFOS^+$, 3.8; 70, $SF_2{}^+$, 3.3; 67, FSO^+, 27.4; 64, $SO_2{}^+$, $CHFS^+$, 2.4; 61, $CHOS^+$, 3.8; 60, COS^+, 3.9; 59, $C(O)OCH_3{}^+$, 100.0.

Anal. Calcd for $C_3H_4F_6O_4S_2$: C, 12.77; H, 1.43; F, 40.4; S, 22.72. Found: C, 12.83; H, 1.30; F, 40.7; S, 22.58.

3. $F_5SCH(SO_2F)C(O)OCH_3$ + $F_3B{\cdot}N(C_2H_5)_3$. The reaction was conducted as described above for the isopropyl ester derivative with the exception that the volatile materials were collected in a preweighed 50-mL Pyrex glass vessel equipped with a Kontes Teflon valve. $F_5SCH(SO_2F)C(O)OCH_3$ (1.52 g, 5.4 mmol) and 1.12 g of $F_3B{\cdot}N(C_2H_5)_3$ (6.60 mmol) were heated under a pressure of 270 mmHg. At 85 °C (oil bath temperature) a reaction occurred, while at 89 °C foaming had ceased, but heating was continued to a final temperature of 108 °C (12 min). After collection and recondensation (at 0 °C) of the volatile material into another vessel, 0.1600 g was obtained. The infrared spectrum (band positioning) coincided with that of CH_3F.[8] Yield: 87.3%. The spectrum was also identical with that obtained from the product of the reaction of CH_3I + KF in sulfolane at 125 °C/2 days.

The title compound (**1**) was isolated from the reaction mixture by vacuum transfer. The infrared spectrum of this material (1.05 g) was identical with that of the product obtained from $F_5SCH(SO_2F)C(O)OCH(CH_3)_2$. Yield: 85.4%.

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(5) Winter, R. H.; Gard, G. L. *Inorg. Chem.* **1988**, *27*, 4329.

(6) Kraus, C. A.; Brown, E. H. *J. Am. Chem. Soc.* **1929**, *51*, 2690.

(7) Herzberg, G. Infrared and Raman Spectra. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold Co.: New York, 1945; Vol. II, p 354.

(8) Herzberg, G. Infrared and Raman Spectra. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold Co.: New York, 1945; Vol. II, p 315.

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The Vanadium–Vanadium Double Bond in $(C_5H_5{-}V)_2(C_8H_8)_2$: An Antiferromagnetic Coupling. An ab Initio SCF/CI Study

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Previous work on (cyclooctatetraene)bis(cyclopentadienylvanadium) has proved that the electronic structure of this dinuclear complex of V(II) with a short metal–metal bond was not straightforward. A first study carried out at the ab initio SCF level by Lüthi and Bauschlicher[1] concluded that the two Cp–V moieties were connected through a single metal–metal bond, whereas the four remaining metal electrons were kept localized on the vanadium atoms and involved in stabilizing interactions with the cyclooctatetraene ligand. A subsequent ab initio study[2] including nondynamic correlation completely reversed this picture and showed that all six metal d electrons are involved in a triple metal–metal coupling. One of these bonds, with π character, is delocalized through the C_8H_8 ligand. The two other bonds, with respective σ/δ and π characters, are weak antiferromagnetic V–V couplings with no significant contribution from the ligands. As

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

(2) Mougenot, P.; Demuynck, J.; Bénard, M.; Bauschlicher, Ch. W., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 4503.

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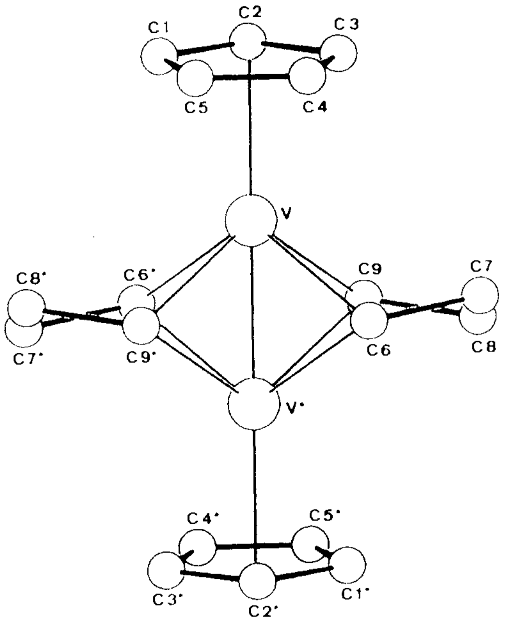

Figure 1. Structure of the $(C_5H_5-V)_2(C_4H_8)_2$ complex (reproduced with permission from ref 3. Copyright 1986 VCH Publishers).

noticed by Lüthi and Bauschlicher, the existence of two distinct configurations for $(C_5H_5-V)_2C_8H_8$, one with a single V–V bond and the other one with a triple bond, illustrates a competition between the stabilizing potentialities respectively offered by the metal–ligand and by the metal–metal interactions. In order to investigate the effect of this competition on other binuclear complexes of electron-deficient transition metals, we are planning to carry out ab initio SCF/CI calculations on a series of metal-metal-bonded complexes of divanadium recently characterized by Jonas, Krüger, et al.[3,4] We now report on such calculations concerning the dimer of cyclopentadienylvanadium complexed by two butanediyl ligands: $(C_5H_5-V)_2(C_4H_8)_2$ (Figure 1).[3]

Computational Details

The SCF calculations have been carried out with the ASTERIX-CRAY2 system of programs,[5] assuming the metal–metal axis to be collinear with Oz. The geometrical parameters used for the calculations, including the V–V distance of 2.315 Å, were taken from the X-ray characterization of the crystal structure,[3] slightly modelized in order to retain a perfect C_{2h} symmetry. The carbon chain of the butanediyl ligands was assumed to be twisted as in the crystal structure (Figure 1). All C–H distances were scaled to 1.09 Å. The Gaussian basis sets were the same as those used in ref 2, that is minimal for the inner shells and the 4p shell of vanadium and double-ζ for the other valence shells, except for the vanadium 3d shell, which is of triple-ζ quality.

Results and Discussion

The metal–metal and metal–butanediyl interactions in the $(CpV)_2(C_4H_8)_2$ complex involve 12 valence electrons, eight of them originating in the lone pair of the C_4H_8 ligands and the four remaining ones coming from the vanadium(III) atoms. The electronic structure of the complex is conditioned by the way these 12 electrons will be distributed among 14 frontier orbitals. The stabilization prevails, and at variance from the other MOs of subset 4. These frontier orbitals can be classified into four subsets:

(i) Subset 1 is composed of four combinations of the C_4H_8 lone pairs, stabilized through bonding interactions with metal d-orbital combinations of proper symmetry. These four molecular orbitals are represented in Figure 2. One can notice that all four combinations display metal–metal bonding character. They will be respectively referred to as BB_σ, BB_π, BB_π, and BB_δ, the first capital designating the *metal–ligand* bonding character, the second capital, the *metal–metal* bonding character, and the subscript, the type of the metal–metal bond.

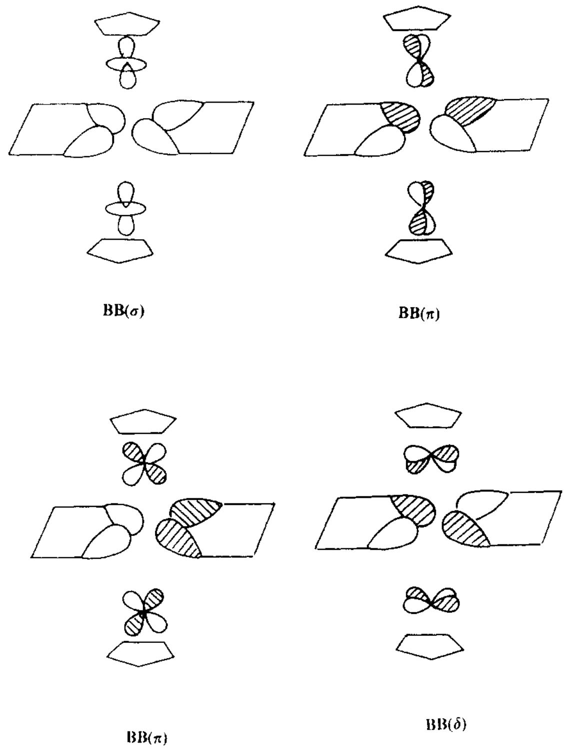

Figure 2. Scheme of the four combinations of the $(C_4H_8)_2$ lone pairs stabilized through interactions with metal–metal bonding orbital combinations. The orbital contributions from the Cp rings are omitted for clarity.

Table I. EHT Energies (eV) of the 14 Valence Orbitals Involved in the V–V and in the V–(C_4H_8) Interactions

identification	EHT orbital energy, eV	identification	EHT orbital energy, eV
AB_δ	-5.55	NB_δ	-10.74
	-6.87	$NA_{\delta*}$	-10.78
AB_π	-7.66	AB_σ	-11.20
AB_π	-7.69	BB_δ	-12.33
$NA_{\pi*}$	-8.31	BB_σ	-13.22
$NA_{\pi*}$	-8.36	BB_π	-13.32
$NA_{\sigma*}$	-8.90	BB_π	-13.35
$NA_{\delta*}$	-9.60		

(ii) Subset 2 contains two orbitals. These are the bonding and antibonding combinations of the metal $d_{x^2-y^2}$ orbitals, which can interact with none of the ligand lone-pair combinations because of symmetry. These MO's will be referred to as NB_δ and $NA_{\delta*}$ (N for nonbonding). It is well-known that 3d–3d interactions of the δ type at a distance of 2.3 Å correspond to very weak bonds.[6] It is therefore not surprising that these two levels are found quasi-degenerate from extended Hückel calculations (Table I).

(iii) Subset 3 is composed of four *metal–metal antibonding* orbital combinations. It is easy to deduce from Figure 2 that the symmetry of these combinations, $NA_{\sigma*}$, $NA_{\pi*}$, $NA_{\pi*}$, and $NA_{\delta*}$, prevents any combination with the ligand lone pairs.

(iv) Finally, we find in subset 4 the metal–ligand antibonding counterparts of the orbitals represented in Figure 2, namely AB_σ, AB_π, AB_π, and AB_δ. These orbitals, which have their major weights on vanadium, are in fact the real metal–metal bonding MOs, but they are rejected to high energies, except for AB_σ, because of their antibonding interaction with $(C_4H_8)_2$.

An extended Hückel calculation carried out on $(CpV)_2(C_4H_8)_2$ shows that the order of the four MO subsets given above corre-

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(3) Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 925.

(4) (a) Jonas, K.; Rüsseler, W.; Krüger, C.; Raabe, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 928. (b) Jonas, K.; Wiskamp, V.; Tsay, Y. H.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5480.

(5) Rohmer, M.-M.; Ernenwein, R.; Demuynck, J.; Wiest, R.; Bénard, M. *Comput. Phys. Commun.*, in press.

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

sponds to increasing values of the energy, with a unique, but important, exception concerning the AB_σ orbital. This MO belongs to subset 4, the highest in energy, but corresponds to the weakest (antibonding) metal–ligand interaction[7] and to the strongest (bonding) metal–metal coupling. The stabilization prevails, and at variance from the other MOs of subset 4, AB_σ is found rather low in energy, between subsets 1 and 2. It is unusual to notice however that two π and one δ metal–metal bonding orbitals are found *higher* in energy than their metal–metal antibonding counterparts. Table I displays the ordering of the 14 orbitals, according to EHT calculations.

According to the aufbau principle, eight electrons should be accommodated into the four MOs of the BB subset; then the AB_σ orbital should be doubly occupied, giving rise to a V–V σ bond, and the two remaining electrons should be attributed to the quasi-degenerate NB_δ and $NA_{\delta*}$ orbitals of subset 2, thus giving rise to a probable triplet ground state. One must notice the existence of a destabilizing four-electron interaction due to the presence of both the BB_σ and the AB_σ orbitals in the doubly occupied set.

It is well-established—and the ab initio calculations on $(CpV)_2C_8H_8$ have confirmed—that the ground state of a binuclear complex can seldom be expressed in terms of a unique closed-shell configuration. If it is forced to do so, and if more than one electron pair is available for metal–metal bonding, the preferred configuration often corresponds to the localization of an even number of electrons on each metal atom, thus reducing to 0 or 1 the number of delocalized M–M bonds.[1,2,9] This is again verified for the butanediyl complex, since the ab initio SCF closed-shell configuration of lowest energy (−2577.9576 hartrees) corresponds to localizing the four metal electrons on the atomic $d_{x^2-y^2}$ orbitals, the V–V bonding AB_σ orbital being rejected into the virtual space. As in the EHT wave function, the eight remaining electrons are accommodated into the four MOs of subset 1.

Since this configuration violates Hund's rule on both metal atoms, it was expected that an open-shell quintet state in which the four metal electrons are accommodated into distinct space orbitals should lead to an improved energy value. This was corroborated by a calculation carried out on the configuration $(NB_\delta)^1\ (NA_{\delta*})^1\ (AB_\sigma)^1\ (NA_{\sigma*})^1$, which yielded an energy of −2578.1296 hartrees. Note that this configuration is formally nonbonding with respect to the V–V interaction, except for the minor metal–metal bonding contributions included in the underlying orbitals of subset 1.

The ground state of our complex has however little chance to be a quintet. The real nature of the ground state mainly depends upon the relative populations of orbitals AB_σ and $NA_{\sigma*}$, knowing that an increase of the AB_σ population will enhance both the stabilization resulting from the V–V σ bond and the destabilization originating in the four-electron interaction between AB_σ and BB_σ.

The nature of the ground state was determined through CI expansions generating all singlet and all triplet configurations from the set of four singly occupied orbitals optimized in the SCF open-shell calculation carried out on the $(NB_\delta)^1\ (NA_{\delta*})^1\ (AB_\sigma)^1\ (NA_{\sigma*})^1$ configuration. The ground state was found to be a singlet (E_S = −2578.146 51 hartrees) corresponding to the natural orbital population $(AB_\sigma)^{1.32}\ (NB_\delta)^{1.01}\ (NA_{\delta*})^{0.99}\ (NA_{\sigma*})^{0.68}$. The δ and δ^* orbitals are practically equally populated. In spite of that, the lowest triplet state was found higher in energy by 926 cm^{-1} (E_T = −2578.142 29 hartrees), due to the strong coupling with configurations involving σ and σ^*. The quintet state optimized from SCF open-shell calculations is predicted to lie about 3700 cm^{-1} above the ground state. A much larger multireference SDCI expansion was also carried out, leading to minor quantitative changes with respect to these results. This CI expansion was designed to correlate eight electrons, including the BB_σ and the BB_δ electron pairs, with respect to the complete virtual space (180 MOs). The reference space included all configurations (five for the singlet state, four for the triplet) occurring with a coefficient larger than 0.06 in the small CI. The total energies obtained for the singlet and for the triplet states (respectively −2578.159 26 and −2578.154 79 hartrees) and the singlet–triplet energy separation (983 cm^{-1}) are no more than marginally affected by the account of dynamic correlation.

As for $(CpV)_2C_8H_8$,[2] the present study predicts for $(CpV)_2(C_4H_8)_2$ an antiferromagnetic V–V coupling involving four electrons, reflecting the trend toward localization of the 3d metal electrons.[9,10] As was previously done to check the electronic structure predicted for metal phthalocyanines and porphyrins,[11] we are planning to complete the present study by a joint experimental and theoretical investigation of the electron density distribution of short-bonded divanadium complexes.[12]

Acknowledgment. The calculations have been carried out on the CRAY-2 computer of the CVVR (Palaiseau, France) through a grant of computer time from the Conseil Scientifique du Centre de Calcul Vectoriel pour la Recherche.

Registry No. $(CpV)_2(C_4H_8)_2$, 104462-69-3.

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(7) The relative strengths of the various metal–ligand interactions are illustrated by the AB_x and BB_x energy differences that can be obtained from Table I. The large splitting between the two pairs of BB_π and AB_π orbitals and the BB_δ and AB_δ orbitals indicates that the metal–ligand interaction is stronger than the metal–metal; i.e., these are mostly metal–ligand bonds. As suggested by a reviewer, the small splitting between the BB_σ and AB_σ orbitals implies that the interaction here should be interpreted as one ligand–ligand bond and one metal–metal bond. Note that the twisting of the butanediyl ligands (Figure 1) contributes to strengthening the metal–ligand stabilizing interaction in the BB_π and BB_δ MOs, but not in the BB_σ one. In this latter case, the bonding lobes of the metal orbitals are directed toward the center of symmetry of the molecule and overlap mainly with the most diffuse part of the ligand orbital combination (Figure 2).

(8) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; *37*, 2872. EHT parameters for vanadium are taken from: Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(9) (a) Garner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. W. *Chem. Phys. Lett.* **1976**, *41*, 91. (b) Bénard, M.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 97. (c) Guest, M. F.; Hillier, I. H.; Garner, C. D. *Chem. Phys. Lett.* **1977**, *48*, 587. (d) Bénard, M. *J. Chem. Phys.* **1979**, *71*, 2546. (e) Wiest, R.; Bénard, M. *Theoret. Chim. Acta* **1984**, *66*, 65. (f) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.

(10) (a) Bénard, M. *Theoret. Chim. Acta* **1982**, *61*, 379. (b) Bénard, M. *Chem. Phys. Lett.* **1983**, *96*, 183. (c) Newton, M. D. *Chem. Phys. Lett.* **1982**, *90*, 291. (d) Messmer, R. P.; Caves, T. C.; Kao, C. M. *Chem. Phys. Lett.* **1982**, *90*, 296.

(11) (a) Li, N.; Coppens, P.; Landrum, J. *Inorg. Chem.* **1988**, *27*, 482 and references therein. (b) Bénard, M. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 868. (c) Rohmer, M.-M. *Inorg. Chem.* **1989**, *28*, 4574.

(12) Krüger, C.; Goddard, R.; Poumgba, C.; Daniel, C.; Bo, C.; Bénard, M. Work in progress.

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Valence Localization in Triangular Trimanganese(II,2III) Complexes[1]

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Mixed-valence trinuclear complexes of the general type $[M^{III}_2M^{II}O(OOCR)_6L_3]$ (Figure 1) are expected to show either trigonal or lower symmetry depending on the rate of intramolecular electron transfer in relation to the time scale of the measurement. For most complexes of this class, X-ray crystallography indicates

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