

# Ab Initio Calculation of the Magnetic Exchange Coupling in Linear Oxo-Bridged Binuclear Complexes of Titanium(III), Vanadium(III), and Chromium(III)

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Received April 6, 1994<sup>®</sup>

Quantum chemical ab initio calculations have been performed for linear oxo-bridged binuclear transition metal complexes of the form  $L_5Me(III)-O-Me(III)L_5$  with  $Me = Ti, V, Cr$ . The rather bulky ligands used in the experiments have been replaced in the present theoretical study by He-like model ligands. Different basis sets and two levels of sophistication have been employed: The first step are CASSCF (complete active space SCF) and valence CI (configuration interaction) calculations in the space of the active  $3d(t_{2g})$  orbitals at the metal ions, the second step are large-scale multireference CI calculations with all single and double excitations from all valence orbitals, including 2s, 2p at the bridging  $O^{2-}$  ion, into the full virtual space. The CASSCF calculations can already reproduce the experimental magnetic properties of these compounds: no coupling of the spins at the two transition metal ions in the binuclear Ti(III) complex, ferromagnetic and antiferromagnetic coupling in the V(III) and Cr(III) complexes, respectively. The mechanism of the spin coupling is the famous “superexchange”, which can be described by a phenomenological exchange integral  $J$ . At the CASSCF level, the calculated values for  $J$  are too small. It needs the multireference CI to bring the exchange integrals into reasonable agreement with experiment. The analysis of the wave functions shows that it is the balance of covalent (“neutral”) and charge-transfer (“ionic”) configurations that causes the differences in the magnetic behavior of the three compounds.

## I. Introduction

Linear  $\mu$ -oxo-bridged homo-binuclear transition metal complexes of the form  $L_5Me-O-MeL_5$  with early transition metals  $Me = Ti, V, Cr$  in the oxidation state +3 show an intriguing magnetic behavior: In Ti(III)-O-Ti(III) complexes the two unpaired electrons on the Ti(III)( $d^1$ ) ions are uncoupled<sup>1–3</sup> or weakly antiferromagnetically coupled;<sup>4</sup> in the corresponding V(III)-O-V(III) complexes the spins of the two V(III)( $d^2$ ) ions are strongly ferromagnetically aligned, giving rise to a quintet ( $S = 2$ ) ground state,<sup>5–7</sup> whereas in the Cr(III)-O-Cr(III) complexes the spins of the Cr(III)( $d^3$ ) ions are antiferromagnetically coupled to a singlet ( $S = 0$ ) ground state.<sup>8–11</sup> In complexes with the same transition metal ions but different ligands  $L$ , the spin multiplicity of the ground state does not depend on the ligands, as long as they are  $\sigma$ -donors and form an approximately octahedral surrounding for the metal ion; the energy difference between different spin states, e.g., the singlet–triplet splitting in the chromium complexes is only slightly

influenced by the ligands. Upon deviation from the linearity of the  $Me(III)-O-Me(III)$  moiety, on the other hand, the spin coupling may change considerably.

Generally, the magnetic interaction between two spins  $\vec{S}_1$  and  $\vec{S}_2$  on weakly coupled metal ions can be described by means of a spin-only Heisenberg–Hamiltonian

$$H = -2J\vec{S}_1 \cdot \vec{S}_2 \quad (1)$$

which contains a single exchange integral  $J$ . In eq 1 we have used the convention that  $J$  is positive if the spins are parallel, i.e., ferromagnetically coupled, and negative if they are antiparallel, i.e., antiferromagnetically coupled. For two spins with equal quantum numbers  $S_1 = S_2$  the total spin can have the values  $S = 0, 1, 2, \dots, 2S_1$  and the eigenvalues of  $H$  are given by

$$E(S) = -J[S(S+1) - 2S_1(S_1+1)] \quad (2)$$

hence the difference between adjacent energy levels with spin quantum numbers  $S$  and  $S-1$  corresponds to a simple Landé pattern

$$E(S) - E(S-1) = -2JS \quad (3)$$

In particular, two spins with  $S_1 = S_2 = 1/2$  can be coupled to a singlet ( $S = 0$ ) or a triplet ( $S = 1$ ), the triplet–singlet splitting amounts to

$$E(1) - E(0) = -2J \quad (4)$$

If the two spins are so far separated from each other that the direct exchange integral  $J$  is zero, there is still the possibility of an indirect exchange coupling through an intermediate nonmagnetic atom or ion. Such a coupling is called superexchange and has been proposed by Kramers<sup>12</sup> and discussed in

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, November 15, 1994.

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detail by Anderson<sup>13</sup> in order to explain the magnetic properties of ionic crystals of transition metal compounds, e.g., of MnO, FeO, CoO, NiO. This indirect interaction is attributed to the overlap between the 3d AOs of the transition metal cations and the 2p AOs of the bridging O<sup>2-</sup> anion and leads in general to an antiferromagnetic ground state, i.e., to a negative value of  $J$ .

In solid state physics, the Mott–Hubbard Hamiltonian is generally used for the derivation of a general formula for the exchange integral  $J$ . Following the ideas of Anderson<sup>13</sup> which have been later extended by various authors, e.g., by Zaanen and Sawatzky<sup>14</sup> or Geertsma,<sup>15</sup> one gets

$$J = K - 2b^2 \left( \frac{1}{U} + \frac{1}{\Delta} \right) \quad (5)$$

$$b = \frac{V^2}{\Delta} \quad (6)$$

where  $K$  is the direct ferromagnetic (positive) exchange integral involving only the d AOs of the two transition metal ions,  $V$  is the 3d – 2p hybridization matrix element (proportional to the 3d – 2p overlap),  $U$  is the 3d Coulomb energy, and  $\Delta$  is the 3d – 2p charge transfer energy, i.e., the difference between the 3d and 2p orbital energies of the isolated ions. (In Anderson's original formula the term with  $1/\Delta$  in eq 5 is missing since it is assumed that  $\Delta \gg U$ .) Similar formulas have also been obtained in the quantum chemical treatments of the superexchange by Hay et al.,<sup>16</sup> Noodleman,<sup>17</sup> Hart et al.<sup>18–20</sup> and others.

For the discussion of the magnetic properties of complexes such as the above oxo-bridged binuclear transition metal compounds, generally the Dunitz–Orgel<sup>21</sup> molecular orbital diagram is invoked in the chemically oriented literature. However, it is not possible to predict the energetic order of the lowest spin states of such complexes only from orbital energies and Hund's rule. In particular, the antiferromagnetic coupling in the chromium complexes cannot be explained in this manner. The reason is that the simple MO picture does not correctly describe the balance between covalent ("neutral") and charge-transfer ("ionic") terms in the wave functions for the different spin states. Generally, in MO-type wave functions the ionic terms have too high weights, in Heitler–London-type wave functions too low weights. It needs some sort of configuration interaction (at least within the subspace of the active orbitals, i.e., the "active-orbital approximation"<sup>22</sup>) based either on MO configurations or on AO configurations to provide enough flexibility to adjust the weights of ionic versus neutral configurations. Several approaches in this direction have been proposed in the literature, e.g., UHF (unrestricted Hartree–Fock) broken symmetry treatments,<sup>17,19,20</sup> perturbation expansions in terms of "natural magnetic orbitals",<sup>23</sup> and very few large-scale CI calculations.<sup>24</sup>

In this paper we present the results of a series of ab initio CASSCF, valence CI, and MC-CEPA calculations for the low-lying electronic states of the above complexes. Since the experiments have been mostly performed with quite bulky ligands which can hardly be treated accurately with quantum chemical methods, we have first tried to design a model ligand which generates the same ligand field as a real ligand. The valence CI and CASSCF calculations are performed in an active space that corresponds to Kahn's active-orbital approximation;<sup>22</sup> in the MC-CEPA calculations dynamic correlation and relaxation effects are added which turn out to have a very large influence on the numerical values of the exchange integrals, but do not alter the energetic order of the low-lying electronic states.

## II. Method of Calculation

**II.1. Quantum Chemical Treatment.** All calculations in the present paper have been performed with the Bochum ab initio open-shell program package which consists of a restricted open-shell Hartree–Fock (ROHF or SCF) program, a complete active space SCF (CASSCF) program<sup>25</sup> with a conventional graphical CI part,<sup>26</sup> and a single-reference CEPA (coupled electron pair approximation)<sup>27</sup> as well as a multireference CEPA (MC-CEPA) program<sup>28</sup> to take care of dynamic correlation effects.

In a first step we have generated molecular orbitals being equally appropriate for all low-lying electronic states of the complexes. For the chromium complex this can be easily achieved by a ROHF calculation for the septet (<sup>7</sup>A<sub>2u</sub>) state in which each of the six valence orbitals which are constructed essentially from the three t<sub>2g</sub> components of the 3d AOs on either metal ion is singly occupied, and all unpaired spins are parallel. For the titanium and vanadium complexes, similar orbitals were obtained by CASSCF calculations with the six t<sub>2g</sub> orbitals in the active space and for an energy expression averaged over several of the low-lying states such that all valence orbitals are nearly equally occupied.

In the second step we have performed either full valence CI (VCI) calculations for all low-lying states simultaneously with the above six valence orbitals in the active space and the orbitals taken unchanged from the ROHF or the CASSCF calculation of the first step. Alternatively, we have performed separate CASSCF calculations for each individual state, also with the six valence orbitals in the active space. For the manifold of the energetically closely spaced low-lying electronic states with energy differences of only a few hundred cm<sup>-1</sup>, the two procedures differ so little that it was sufficient to use only the simpler VCI variant. However, this might not hold true for charge-transfer states such as for instance L<sub>5</sub>Cr(IV)–O–Cr(II)L<sub>5</sub> which exhibit quite large relaxation effects.

The VCI and CASSCF calculations yield already the correct ordering of the low-lying electronic states and can be used for an analysis of the superexchange mechanism, but the numerical values obtained for the exchange integral  $J$ , i.e., for energy differences between the electronic states, are too small. For the calculation of reliable values for  $J$  it is necessary to include dynamic correlation effects. This has been done as the third step by means of our MC-CEPA program.<sup>28</sup> This contains as one possibility a large-scale multireference CI calculation, abbreviated by MR-CI, in which all singly and doubly excited configurations from the VCI or CASSCF reference are included.

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Table 1

(a) Gaussian Basis Sets for the Constituent Atoms in the  $L_5Me-O-MeL_5$  Complexes

atom	type	reference	primitive and contracted basis set
ligand	TZ	this work	6s(25.0, 7.0, 2.5, 0.6, 0.2, 0.05) → [4,2*1]
metal	DZ	30	9s5p3d → [4,5*1;2,3*1;2,1]
	TZ	32	15s9p5d → [10,5*1;6,3*1;3,2*1] <sup>a</sup>
O	DZ <sup>b</sup>	31	7s3p → [4,3*1;2,1]
	TZdiff	31	9s5p → [4,5*1;2,3*1] + 1s(0.15) + 2p(0.1,0.05)
N <sup>c</sup>	DZ	31	7s3p → [4,3*1;2,1]
H <sup>c</sup>	DZ	31	3s → [2,1]
F <sup>c</sup>	DZdiff	31	7s3p → [4,3*1;2,1] + 2p(0.2,0.08)

(b) Gaussian Basis Sets for the  $L_5Me-O-MeL_5$  Complexes

complex	basis	metal ion	oxygen	ligand
Ti-O-Ti	I	DZ + 1d(0.2)	TZdiff + 1d(0.5)	TZ
V-O-V	I	DZ + 1d(0.25)	TZdiff + 1d(1.0)	TZ
	II	TZ + 1f(1.0)	TZdiff + 2d(1.3,0.4)	TZ
Cr-O-Cr	I	DZ + 1d(0.3)	TZdiff + 1d(0.5)	TZ
	II	TZ	TZdiff + 1d(1.0)	TZ
	III	TZ + 1f(1.2)	TZdiff + 1d(1.0)	TZ
	IV	TZ + 1d(0.15) + 1f(1.2)	TZdiff + 1d(1.0)	TZ

<sup>a</sup> General contraction: ten s functions contracted to minimal basis sets for 1s, 2s, and 3s, six p functions for 2p and 3p. <sup>b</sup> Used for some test calculations which are not documented here. <sup>c</sup> Used only for the determination of the model ligands, see section II.2.

The size consistency errors of such a MR-CI can be corrected in an approximate way by means of different recipes. In our program the MC-CEPA (multiconfiguration coupled electron pair approach)<sup>28</sup> and the ACPF (averaged coupled pair functional)<sup>29</sup> recipes are implemented. In most cases we will use the ACPF scheme since it yields more consistent results for the energy differences between close-lying electronic states than does the MC-CEPA scheme.

In general, we have correlated all valence electrons of the Me-O-Me part of the compounds, i.e., the 3d electrons at the two metal ions and the 2s,2p electrons of the bridging O<sup>2-</sup>. The electrons at the ligands as well as the core electrons of Me(III) and O<sup>2-</sup> were left uncorrelated. Since the superexchange coupling does not depend much on the ligands themselves and since our ligands are model ligands anyway (section II.2), it seemed unnecessary to correlate also the electrons of the ligands. Some test calculations on (NH<sub>3</sub>)<sub>3</sub>CrOCr(NH<sub>3</sub>)<sub>3</sub> have indeed confirmed that the inclusion of orbitals at the terminal ligands into the correlation treatment has virtually no effect on *J*. On the other hand, the orbitals at the bridging ligands, in our case at O<sup>2-</sup>, have to be correlated for a quantitative estimate of *J*, as has been also stressed by de Loth et al.<sup>23</sup> for the cupric acetate hydrate dimer. In some cases, in particular for the V(III) complex, it turned out to be necessary to localize the valence orbitals before starting the MC-CEPA calculation in order to separate the Me-O-Me moiety from the ligand orbitals.

Spin-orbit coupling effects have not been included in the present work and will be the subject of a forthcoming study.

The Gaussian basis sets used in our calculations are given in the Table 1. Mostly, we employed two different sets, denoted by I and II: Basis I consists of the small 9s5p3d basis of Roos et al.<sup>30</sup> for the metal ion, contracted to double  $\zeta$  quality (DZ) and augmented by one further semidiffuse d function, and a triple  $\zeta$  (TZ) Huzinaga<sup>31</sup> basis for the bridging oxygen. In order to better represent the Me-O-Me interaction and to account

for the larger spatial extent of the O<sup>2-</sup> ion in the bridging position as compared to a neutral O atom, the basis for O was augmented by diffuse s and p functions and by one set of d functions. Basis II contains the basis set of Wachters<sup>32</sup> for the metal ion, contracted to TZ quality, and the same set as basis I for the bridging oxygen. For the calculation on the vanadium complexes, additional polarization functions both on V and O were added. The model ligands (compare section II.2) were always described by a TZ basis.

Since our results for *J* depend only weakly on the size of the basis sets and since the main goal of the present paper is the analysis of the different behavior of the magnetic coupling in the three complexes, we do not document the results obtained with several further basis sets different from those in the Table 1.

**II.2. Model Ligands.** In order to reduce the necessary computer time, in particular for the MC-CEPA calculations which require rather flexible basis sets for the Me-O-Me moiety, our calculations have not been performed for real ligands, as used in the experiments,<sup>1-11</sup> but for model ligands as described below. Even for ligands as small as NH<sub>3</sub>, a reasonable representation of for instance DZ quality would require 10 × 16 = 160 functions only for the ligand shell and would render the CI and MC-CEPA calculations extremely time consuming. Most experiments<sup>1-11</sup> have been performed with much more complicated ligands which can be hardly correctly included in an ab initio calculation. On the other hand, there is experimental evidence<sup>8,11</sup> that the energetic ordering of the states and the values of *J* are insensitive to the precise form of the ligands, provided that they are  $\sigma$ -donors and the surrounding of the metal ions is approximately octahedral.

The model ligands that we have used are pseudo He atoms, i.e., closed-shell atoms with a doubly occupied 1s orbital, but with a reduced nuclear charge *Z*. The value of *Z* and the distance between the metal ion and the model ligands were determined by the requirements that (a) the orbital energy of the model ligand should be similar to that of the lone pair orbital of a typical  $\sigma$ -donor ligand such as NH<sub>3</sub>, (b) the 3d occupation and the net charge on the metal ion should be comparable to those in NH<sub>3</sub> or F<sup>-</sup> complexes, and (c) the strength of the octahedral ligand field, i.e., the  $e_g - t_{2g}$  energy difference 10Dq in Me(III)L<sub>6</sub> complexes should be similar for the model ligand L and real ligands NH<sub>3</sub> or F<sup>-</sup>.

Table 2 contains the results of several test calculations for Cr(III)L<sub>6</sub> complexes. After some experimentation we have fixed the charge *Z* of the model ligand to 1.6 for all metal ions. This value seems slightly too high as indicated by the rather low orbital energy but has the advantage of rendering the L<sub>5</sub>-MeOMeL<sub>5</sub> complex charge neutral. The Me(III)-L distance has to be chosen smaller for the model ligand than for, for example, NH<sub>3</sub>, otherwise the ligand field would be too weak. Table 2 shows that the quartet excitation energies, i.e., the  $e_g - t_{2g}$  energy splitting, become larger upon decrease of the Cr(III)-L distance, a value of 1.9 Å for this distance would correspond to a weak ligand as for instance F<sup>-</sup>, a value of 1.6 Å to a strong ligand such as NH<sub>3</sub>. The 3d occupation and the net charge on Cr(III) have reasonable values and do not change much for Cr(III)-L distances in the range between 1.9 and 1.6 Å.

In all subsequent calculations we have chosen a Cr(III)-L distance of 1.903 Å (=3.6a<sub>0</sub>). For Ti(III) and V(III) the Me-L distances were scaled to the Cr(III)-L distance by the formula

$$R(\text{Me-L})R(\text{Cr-N}) = R(\text{Me-N})R(\text{Cr-L})$$

using experimental values for the metal-nitrogen distances.<sup>2,5,33</sup>

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**Table 2.** Properties of the Model Ligands L as Compared to NH<sub>3</sub> and F<sup>-</sup> Ligands in the Octahedral Complexes Cr(III)L<sub>6</sub>, Cr(III)(NH<sub>3</sub>)<sub>6</sub>, and Cr(III)F<sub>6</sub><sup>3-</sup>

property	NH <sub>3</sub>		F <sup>-</sup>		L (3.6)	L (3.0)
	CASSCF	exp	CASSCF	exp	CASSCF	CASSCF
nuclear charge/au					1.6	1.6
orbital energy <sup>a</sup> /eV	-11.05				-12.22	-12.22
Cr-L distance/Å	2.08 <sup>b</sup>	2.07 <sup>c</sup>	1.903 <sup>b</sup>	1.907 <sup>d</sup>	1.903 <sup>b</sup>	1.588 <sup>b</sup>
3d orbital occupation			3.47		3.33	3.56
net charge of Cr/au	2.55		2.64		2.66	2.41
excitation energies/cm <sup>-1</sup>						
<sup>4</sup> A <sub>g</sub> (t <sub>2g</sub> <sup>3</sup> ) → <sup>4</sup> T <sub>2g</sub> (t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>1</sup> )	31400	21500 <sup>e</sup>	14300	15200 <sup>f</sup>	9900	23900
→ <sup>4</sup> T <sub>1g</sub> (t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>1</sup> )	41000	28500 <sup>e</sup>	22600	21800 <sup>f</sup>	16900	34200
→ <sup>2</sup> <sup>4</sup> T <sub>1g</sub> (t <sub>2g</sub> <sup>1</sup> e <sub>g</sub> <sup>2</sup> )	71100		36000	35000 <sup>f</sup>	29800	54000

<sup>a</sup> 1s orbital of the ligand and lone pair orbital of NH<sub>3</sub>, respectively. <sup>b</sup> Fixed distance, not optimized. <sup>c</sup> Experimental Cr-N distance; average value for a number of Cr(III)(NH<sub>3</sub>)<sub>6</sub> ions in different crystal environments; references to the experimental work are given in ref 33. <sup>d</sup> Experimental Cr-F distance in the Na<sub>3</sub>Cr(III)F<sub>6</sub> complex.<sup>34</sup> <sup>e</sup> Reference 35. <sup>f</sup> Reference 36.

We have used  $R(\text{Ti(III)}-\text{L}) = 2.05 \text{ \AA} (=3.88a_0)$  and  $R(\text{V(III)}-\text{L}) = 2.11 \text{ \AA} (=3.99a_0)$ .

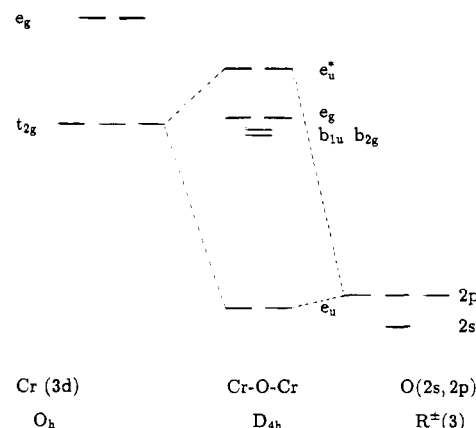
It has to be emphasized that the use of model ligands as well as the choice of the parameters  $Z$  and  $R(\text{Me}-\text{L})$  have only a small influence on the value of  $J$ . For instance, if  $R(\text{Cr(III)}-\text{L})$  is varied between 1.9 and 1.6 Å, the value of  $J$  in the L<sub>5</sub>-Cr(III)-O-Cr(III)L<sub>5</sub> complex is altered by only 5 cm<sup>-1</sup> (in the VCI calculation, which yield  $J \approx 60 \text{ cm}^{-1}$ , see Table 6). Similarly, test calculations<sup>37</sup> on (NH<sub>3</sub>)<sub>5</sub>CrO-Cr(NH<sub>3</sub>)<sub>5</sub> showed that the  $J$  value for the NH<sub>3</sub> complex is about 10 cm<sup>-1</sup> lower than for the complexes with model ligands. This means that our qualitative conclusions are not changed if the model ligands are replaced by real ligands, while the quantitative values for  $J$  might be subject to small changes. Be-type model ligands have been used in a similar way by Simpson et al.<sup>38</sup> in SCF and CI calculations for the singlet-triplet splitting in mononuclear Ti(II) complexes.

**III.3. Geometry of the Complexes.** Throughout the following sections the Me-O-Me bridge was taken as linear and symmetric with the Me-O distances fixed to their experimental values: Ti-O, 1.872 Å; V-O, 1.806 Å;<sup>5</sup> Cr-O, 1.821 Å.<sup>39,40</sup> Of course, there is no "experimental" Me-O distance for our model complex, but the Me-O distances in complexes with different ligands and linear symmetric Me-O-Me bridges vary by no more than 0.02-0.03 Å; therefore, we can safely use one of the experimental values.

The distances between the metal ion and the adjacent five model ligands were chosen equal, the two octahedral moieties were eclipsed; thus the whole binuclear model complex has  $D_{4h}$  symmetry. In the following we will characterize both the molecular orbitals and the many-electron states by the irreducible representations of  $D_{4h}$ .

### III. Qualitative Analysis of the Superexchange Coupling

**III.1. Molecular Orbitals.** Figure 1 contains a molecular orbital (Dunitz-Orgel<sup>21</sup>) diagram for the valence orbitals of the Me-O-Me moiety, as obtained from the ROHF calculation



**Figure 1.** MO diagram for the valence orbitals of Cr(III)-O-Cr(III). To avoid confusion, the unoccupied 3d(e<sub>g</sub>) orbitals and the O<sup>2-</sup> σ-orbitals (2s, 2p<sub>z</sub>) are not plotted for the Cr-O-Cr complex.

**Table 3.** Orbital Energies (eV, Relative to b<sub>2g</sub>) of the Valence Orbitals in the L<sub>5</sub>Me-O-MeL<sub>5</sub> Complexes

	Ti(III)	V(III)	Cr(III)	
	I <sup>a</sup>	I <sup>a</sup>	I <sup>a</sup>	IV <sup>a</sup>
e <sub>u</sub> *	1.58	1.31	1.79	1.72
e <sub>g</sub>	0.16	0.09	0.18	0.15
b <sub>1u</sub>	0.008	0.007	0.005	0.006
b <sub>2g</sub>	0.0	0.0	0.0	0.0
b <sup>b</sup>	1.42	1.22	1.61	1.57

<sup>a</sup> Basis; compare Table 1b. <sup>b</sup> Energy difference between the e<sub>u</sub>\* and e<sub>g</sub> orbitals; compare eqs 12 and 13 in the text.

for the <sup>7</sup>A<sub>2u</sub> state of the chromium complex in which all MOs originating from the 3d t<sub>2g</sub> AOs of the Cr(III) ions are singly occupied. The corresponding orbital energies are given in Table 3. Obviously, there is no serious difference between the two basis sets; several other basis sets that we have also exploited gave more or less identical results.

The detailed analysis of the orbitals and the orbital energies by means of population analysis, orbital plots, etc. yields the well-known Dunitz-Orgel interpretation<sup>21</sup> of the chemical bond in Me-O-Me complexes: From the three pairs of AOs belonging to e representations (3d<sub>xz</sub> and 3d<sub>yz</sub> on either Cr(III) ion, 2p<sub>x</sub> and 2p<sub>y</sub> on the bridging O<sup>2-</sup> ion) a bonding, a nonbonding, and an antibonding linear combination can be formed. These orbitals are plotted on Figure 2. The bonding orbitals, e<sub>u</sub>, are predominantly localized on O<sup>2-</sup>, the nonbonding orbitals, e<sub>g</sub>, have—for symmetry reasons—no admixture of the 2p AOs, and the antibonding orbitals, e<sub>u</sub><sup>\*</sup>, are mainly localized on the metal ions with a small contribution of the 2p AOs. The

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two  $3d_{xy}$  AOs on the metal ions, on the other hand, cannot mix through the intermediate  $O^{2-}$  ion, since  $O^{2-}$  has no AO of the proper symmetry. Since the distance between the metal ions is rather large, the overlap between the two  $3d_{xy}$  AOs is nearly zero. Therefore, they form two nonbonding linear combinations of  $b_{2g}$  and  $b_{1u}$  symmetry, respectively, which are not exactly degenerate but have virtually identical orbital energies.

If we use simple Hückel theory and neglect all overlap integrals, we obtain for the frontier orbitals the following linear combinations of the AOs

$$\varphi(b_{2g}) = \frac{1}{\sqrt{2}}(d_{xy}(1) + d_{xy}(2)) \quad (7a)$$

$$\varphi(b_{1u}) = \frac{1}{\sqrt{2}}(d_{xy}(1) - d_{xy}(2)) \quad (7b)$$

$$\varphi(e_{ux}) = N \left( -\frac{V}{\Delta} d_{xz}(1) + p_x - \frac{V}{\Delta} d_{xz}(2) \right) \quad (8a)$$

$$\varphi(e_{gx}) = \frac{1}{\sqrt{2}}(d_{xz}(1) - d_{xz}(2)) \quad (8b)$$

$$\varphi(e_{ux}^*) = \frac{N}{\sqrt{2}} \left( d_{xz}(1) + \frac{2V}{\Delta} p_x + d_{xz}(2) \right) \quad (8c)$$

$$N = \left( 1 + 2 \frac{V^2}{\Delta^2} \right)^{-1/2} \quad (9)$$

where the serial numbers 1 and 2 denote the two metal ions. (For the e-type orbitals in eqs 8a,b,c only the x component is given explicitly.) The coefficients in the  $e_{ux}$  orbitals in eqs 8a,c as well as the normalization constant  $N$  in eq 9 are given in first-order perturbation theory with the assumption that the (negative) resonance (or hybridization) integral  $V$  is small compared to

$$\Delta = \epsilon(3d, t_{2g}) - \epsilon(O^{2-}, 2p) \quad (10)$$

The full expressions are slightly more lengthy. The orbital energies are in this approximation

$$\epsilon(b_{2g}) = \epsilon(b_{1u}) = \epsilon(e_g) = \epsilon(3d, t_{2g}) \quad (11)$$

$$\epsilon(e_u^*) = \epsilon(3d, t_{2g}) + b \quad (12)$$

i.e.,  $b$  is the energy difference between the antibonding orbital  $e_u^*$  and the  $t_{2g}$  component of  $3d$ . In Hückel theory,  $b$  is given by

$$b = \frac{\Delta}{2} \left( -1 + \sqrt{1 + 2(2V/\Delta)^2} \right) \approx \frac{2V^2}{\Delta} \quad (13)$$

in agreement with eq 6. Glerup<sup>41</sup> denotes the quantity  $b$  by  $2\Delta(t_2)$ .

Table 3 shows that the four nonbonding orbitals are indeed very close in energy. Further calculations with the other basis sets always gave  $b_{1u}$  and  $b_{2g}$  degenerate within 0.01 eV; however, the energetic order of  $b_{1u}/b_{2g}$  and  $e_g$  might be reversed. The antibonding orbitals,  $e_u^*$ , are 1.5 eV higher in energy, i.e., the numerical value of  $b$  is about 1.5 eV  $\approx$  12 000  $\text{cm}^{-1}$ . For the titanium and vanadium complexes the values for  $b$  are slightly smaller than for chromium.

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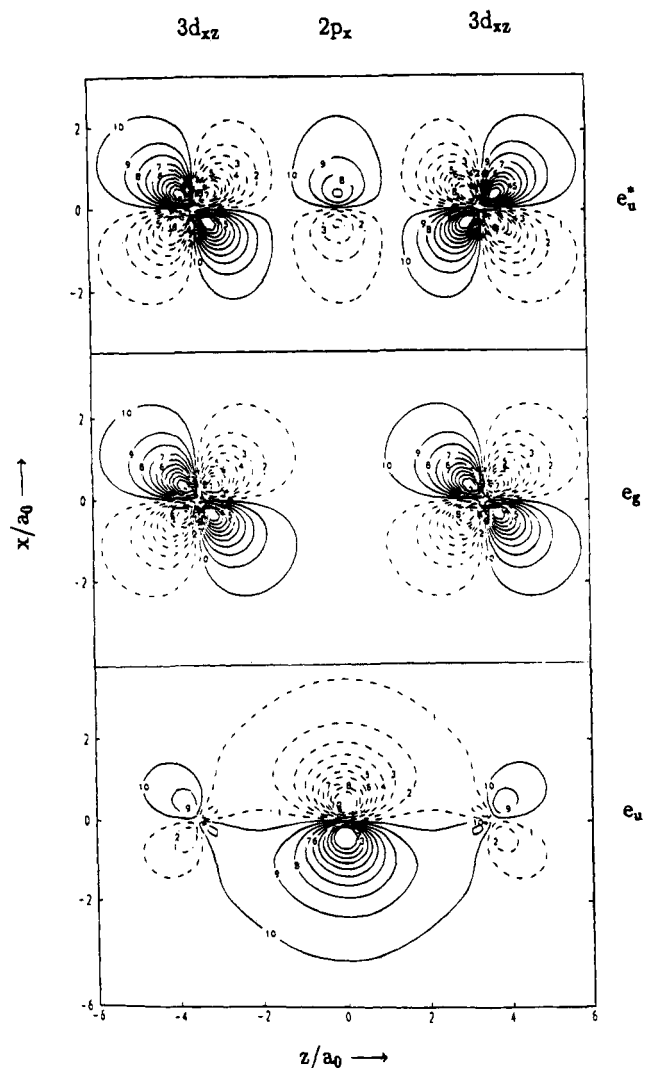


Figure 2. Contour plots of the valence orbitals  $e_{ux}$ ,  $e_{gx}$ ,  $e_{ux}^*$  of the  $L_5Cr-O-CrL_5$  complex.

Since the  $2p_z$  and  $2s$  AOs of the  $O^{2-}$  ion as well as the two  $e_g$  AOs ( $3d_{x^2-y^2}, 3d_{z^2}$ ) at the metal ions do not enter into the discussion of the magnetic properties of the early transition metals, they are not included in the present analysis. However, they play a decisive role for complexes containing late transition metals.<sup>42</sup>

**III.2. Valence CI and CASSCF Results.** As a second step, valence CI(VCI) and CASSCF calculations have been performed for the  $L_5Me-O-MeL_5$  complexes, with the six valence orbitals  $e_g$ ,  $b_{1u}$ ,  $b_{2g}$ ,  $e_u^*$  in the active space. The results for the three metal ions and for different basis sets are summarized in the Tables 4–6.

For the titanium complex with two Ti(III) ( $d^1$ ) ions in spatially triply degenerate  ${}^2T_{2g}$  ground states (in octahedral symmetry) one would expect nine low-lying singlet and nine low-lying triplet states, since the ionic configurations with  $d^0/d^2$  occupations, i.e., the Ti(IV)/Ti(II) charge-transfer states, are very high in energy. However, Table 4 shows that there are only two low-lying states, one singlet and one triplet, which are even degenerate. The next eight states are about 5000  $\text{cm}^{-1}$  higher in energy (i.e., about  $b/2$ ), the remaining eight states follow at about 10000  $\text{cm}^{-1}$  (about  $b$ ).

For the vanadium complex the situation is much more complicated. Again, one would expect nine quintets, nine

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**Table 4.** Valence CI and CASSCF Results for the Excitation Energies (cm<sup>-1</sup>) of L<sub>5</sub>Ti—O—TiL<sub>5</sub>

	basis I		$\Delta E^{(1)d}$ <i>b</i>	$\Delta E^{(2)d}$ <i>b</i> <sup>2</sup> / <i>U</i>
	VCI <sup>a,b</sup>	CASSCF <sup>b,c</sup>		
<sup>1</sup> A <sub>1g</sub>	0	0	0.0	0.0
<sup>3</sup> A <sub>2u</sub>	0	0.2	0.0	0.0
<sup>3</sup> E <sub>g</sub>	5194		0.5	-0.25
<sup>3</sup> E <sub>u</sub>	5195		0.5	-0.25
<sup>1</sup> E <sub>g</sub>	5238		0.5	-0.25
<sup>1</sup> E <sub>u</sub>	5272		0.5	-0.25
<sup>3</sup> A <sub>2g</sub>	9940		1.0	-1.0
<sup>1</sup> B <sub>2g</sub>	10279		1.0	-1.0
<sup>1</sup> B <sub>1g</sub>	10287		1.0	-1.0
<sup>1</sup> A <sub>1g</sub>	10580		1.0	-1.0
<sup>1</sup> A <sub>1u</sub>	11284		1.0	0.0
<sup>3</sup> B <sub>1u</sub>	11345		1.0	0.0
<sup>3</sup> B <sub>2u</sub>	11348		1.0	0.0
<sup>3</sup> A <sub>2u</sub>	11409		1.0	0.0

<sup>a</sup> The orbitals are optimized for the average energy expectation value containing all nine triplet states given in this table. <sup>b</sup> Energy of the <sup>1</sup>A<sub>1g</sub> ground state is -1786.840 001 au for VCI and -1786.841 726 au for CASSCF, respectively. <sup>c</sup> Separate CASSCF calculations for each state. <sup>d</sup> First-order and second-order perturbation energies (see text).

**Table 5.** Valence CI and CASSCF Results for the Excitation Energies (cm<sup>-1</sup>) of L<sub>5</sub>V—O—VL<sub>5</sub>

	basis I		$\Delta E^{(1)c}$ <i>b</i>	$\Delta E^{(2)c}$ <i>b</i> <sup>2</sup> / <i>U</i>
	VCI <sup>a</sup>	CASSCF <sup>b</sup>		
<sup>5</sup> A <sub>1u</sub>	-1975.426007	-1977.347551		
<sup>5</sup> A <sub>1u</sub>	0	0	1.0	-1.0
<sup>1</sup> B <sub>2g</sub>	705	754	1.0	-0.75
<sup>3</sup> A <sub>2g</sub>	707	793	1.0	-0.5
<sup>1</sup> B <sub>1g</sub>	712	761	1.0	-0.75
<sup>3</sup> B <sub>1u</sub>	925	1002	1.0	-0.5
<sup>3</sup> B <sub>2u</sub>	931	1007	1.0	-0.5
<sup>1</sup> A <sub>1g</sub>	958	993	1.0	-0.75
<sup>1</sup> A <sub>1u</sub>	1102	1198	1.0	-0.25
<sup>3</sup> A <sub>2u</sub>	1121	1186	1.0	-0.5
<sup>5</sup> B <sub>2g</sub>	1407	1489	1.0	0.0
<sup>3</sup> B <sub>1g</sub>	1409	1488	1.0	0.0
<sup>5</sup> A <sub>1g</sub>	1470	1548	1.0	0.0

<sup>a</sup> The orbitals are optimized for the average energy expectation value containing the two highest quintet states (<sup>5</sup>B<sub>1g</sub>, <sup>5</sup>A<sub>1g</sub>) since in these states the valence orbitals are similarly occupied (b<sub>2g</sub>, b<sub>1u</sub> singly occupied, each component of e<sub>g</sub>, e<sub>u</sub>\* with the occupation 0.5). <sup>b</sup> Separate CASSCF calculations for each state. <sup>c</sup> First-order and second-order perturbation energies (see text).

triplets, and nine singlets originating from the two V(III) (d<sup>2</sup>) ions with <sup>3</sup>T<sub>1g</sub> ground states. But the VCI and CASSCF calculations (Table 5) yield only four low-lying states of each of the three spin multiplicities within about 1500 cm<sup>-1</sup> and with a rather irregular spacing. The ground state is clearly a quintet, separated by about 700 cm<sup>-1</sup> from the next states, i.e., the coupling is ferromagnetic. The next bunch of states after those in Table 5 follows at about 5000 cm<sup>-1</sup>, i.e., about *b*/*2* higher in energy. The CASSCF results for the lowest excitation energies are consistently 50–100 cm<sup>-1</sup> higher than the VCI results but show qualitatively the same pattern and, except for nearly degenerate levels, also the same order of the states.

Finally, Table 6 contains VCI and CASSCF results for the chromium complex. For the coupling of two Cr(III) (d<sup>3</sup>) ions with spatially nondegenerate <sup>4</sup>A<sub>2g</sub> ground states one expects one septet, one quintet, one triplet, and one singlet, and exactly these are the low-lying states obtained both in the VCI and CASSCF calculation. The next states are by about 22000 cm<sup>-1</sup> higher in energy. Three points should be particularly emphasized: (a) The spin coupling is antiferromagnetic, the ground state is a singlet, in agreement with all experiments<sup>8–11</sup> for L<sub>5</sub>CrOCrL<sub>5</sub> complexes with different ligands. (b) The spacing between the

different spin states shows a very regular 3:2:1 Landé pattern which can be described by one exchange integral *J*. This holds nearly exactly for the VCI calculation which uses a common set of orbitals for all states, but to a very good approximation also for the CASSCF calculation in which each of the states has been optimized separately. (c) The excitation energies and the value of *J* do not depend markedly on the basis set (as soon as it is beyond the DZ quality) or on the method of calculation. But the calculated value of *J* is considerably lower than the experimental value of ca. -225 cm<sup>-1</sup>.<sup>8</sup>

**III.3. Analysis of the Wave Functions: First-Order Perturbation Theory.** If one uses the simple MO theory as advocated by Dunitz and Orgel<sup>21</sup>—the MO diagram of Figure 1 together with the Aufbau and Pauli principles and Hund's rule—one is led to the following prediction for the lowest electronic states of the Ti—O—Ti complex with its two d electrons: There are several low-lying electronic states with configurations b<sub>2g</sub><sup>2</sup>, b<sub>1u</sub><sup>2</sup>, b<sub>2g</sub>b<sub>1u</sub>, e<sub>g</sub><sup>2</sup>, e<sub>g</sub>b<sub>2g</sub>, etc., both singlets and triplets, with very similar energies. Since the orbital energies of the four nonbonding orbitals b<sub>1u</sub>, b<sub>2g</sub>, e<sub>gx</sub>, e<sub>gy</sub> are nearly identical, it cannot be uniquely decided which of these states is the true ground state; Hund's rule will probably favor a triplet. Obviously, our valence CI results in Table 4 are completely different from this prediction.

The reason for this discrepancy is of course that simple MO theory does not correctly describe the proper balance of covalent and ionic terms in the wave function. This is no serious deficiency for normal closed-shell molecules in the vicinity of their equilibrium geometries, but leads to qualitatively wrong predictions in the present situation of weakly coupled transition metal ions at rather large separations.

Let us consider the configurations b<sub>2g</sub><sup>2</sup>, b<sub>1u</sub><sup>2</sup>, b<sub>2g</sub>b<sub>1u</sub> as the simplest example. If we use the explicit form (7a,b) of the orbitals b<sub>2g</sub> and b<sub>1u</sub>, we can easily show that

$$\frac{1}{\sqrt{2}}(b_{2g}\bar{b}_{2g} - b_{1u}\bar{b}_{1u}) \quad (14a)$$

$$\frac{1}{\sqrt{2}}(b_{2g}\bar{b}_{1u} - b_{1u}\bar{b}_{2g}) \quad (14b)$$

represent purely covalent (neutral) states while

$$\frac{1}{\sqrt{2}}(b_{2g}\bar{b}_{2g} + b_{1u}\bar{b}_{1u}) \quad (15a)$$

$$\frac{1}{\sqrt{2}}(b_{2g}\bar{b}_{1u} + b_{1u}\bar{b}_{2g}) \quad (15b)$$

represent purely ionic (charge-transfer) states. ( $\beta$ -spin is indicated by an overhead bar, all wave functions belong to M<sub>S</sub> = 0.) The "simple" MO configurations b<sub>2g</sub><sup>2</sup>, b<sub>1u</sub><sup>2</sup>, b<sub>1u</sub>b<sub>2g</sub>, b<sub>1u</sub>b<sub>2g</sub>, however, are mixtures of covalent and ionic contributions with equal weights. That means, if one wants to get rid of the ionic terms in the wave functions—which is necessary in the present situation of metal ions at large separations since the charge transfer states d<sup>2</sup>/d<sup>0</sup> and d<sup>0</sup>/d<sup>2</sup> are much higher in energy than d<sup>1</sup>/d<sup>1</sup>—one has to use the linear combinations given in eqs 14a,b instead of the simple MO configurations.

The wave functions (14a,b) are exactly the valence CI wave functions belonging to the two lowest states, <sup>1</sup>A<sub>1g</sub> and <sup>3</sup>A<sub>2u</sub>, in Table 4. Their energies are separated by the direct exchange integral

$$2J_F = 2(d_{xy}(1)d_{xy}(2)|d_{xy}(2)d_{xy}(1)) \quad (16)$$

**Table 6.** Valence CI and CASSCF Results for the Excitation Energies (cm<sup>-1</sup>) of L<sub>5</sub>Cr–O–CrL<sub>5</sub>

	DZ <sup>a</sup> VCI	basis I <sup>b</sup> VCI	basis I VCI	basis I CASSCF	basis II <sup>c</sup> VCI	basis II CASSCF	basis IV VCI
<sup>7</sup> A <sub>2u</sub> , E <sup>d</sup>	-0.699875	-0.815158	-0.919324	-0.919324	-0.104128	-0.112148	-0.135295
<sup>1</sup> A <sub>1g</sub>	0	0	0	0	0	0	0
<sup>3</sup> A <sub>2u</sub>	77	110	112	142	111	120	112
<sup>5</sup> A <sub>1g</sub>	232	331	336	407	334		335
<sup>7</sup> A <sub>2u</sub>	465	664	672	767	667		670
J <sup>e</sup>	-39	-55	-56	-64	-56	-60	-56

<sup>a</sup> DZ without polarization functions for Cr(III) and O<sup>2-</sup>, TZ for model ligands. <sup>b</sup> Basis I without d(0.5) at O<sup>2-</sup>. <sup>c</sup> Basis II without d(1.0) at O<sup>2-</sup>. <sup>d</sup> SCF energy in au relative to -2175.0 for basis I, DZ or relative to -2178.0 for basis II, IV. <sup>e</sup> Average value: (E(<sup>7</sup>A<sub>2u</sub>) - E(<sup>1</sup>A<sub>1g</sub>))/12.

which is small because of the large distance between the two metal ions. For a Cr(III) dimer without oxygen bridge and with a distance of 2 × 1.821 Å, we have calculated the direct exchange integral (16) and found that it was smaller than 1 cm<sup>-1</sup>. The direct ferromagnetic coupling can be safely neglected for all binuclear complexes considered here. (Of course, J<sub>F</sub> is also zero in Hückel theory where the overlap between the metal ions is neglected.) It is important that in those configurations (b<sub>1u</sub><sup>2</sup>, b<sub>1u</sub>b<sub>2g</sub>) which are necessary to eliminate the ionic terms from configurations that contain only nonbonding orbitals (b<sub>2g</sub><sup>2</sup>, b<sub>2g</sub>b<sub>1u</sub>) also only nonbonding orbitals are occupied.

Let us now turn to a slightly more complicated case: In order to eliminate the ionic terms from the configuration e<sub>g</sub><sup>1</sup>b<sub>2g</sub><sup>1</sup>, <sup>3</sup>E<sub>g</sub>, one has to mix in the configuration e<sub>u</sub><sup>\*</sup>b<sub>1u</sub><sup>1</sup>, <sup>3</sup>E<sub>g</sub>, in the same way as this has been done in (14a,b). In this case, the purely covalent wave function is given by

$$\Psi_{\text{cov}} = \frac{1}{\sqrt{2}}(b_{2g}e_g - b_{1u}e_u^*) \quad (17a)$$

while the purely ionic state is represented by

$$\Psi_{\text{ionic}} = \frac{1}{\sqrt{2}}(b_{2g}e_g + b_{1u}e_u^*) \quad (17b)$$

The covalent wave function (17a) contains one of the antibonding orbitals, e<sub>u</sub><sup>\*</sup>, singly occupied; thus the elimination of the ionic terms costs energy. The raise in energy can be easily estimated by first-order perturbation theory: In the MO representation, the perturbation is simply a diagonal operator

$$\hat{V} = b\hat{n}_{eu} \quad (18a)$$

where  $\hat{n}_{eu}$  is the occupation number operator of the e<sub>u</sub><sup>\*</sup> orbitals. Therefore the energy change in first-order perturbation theory is simply given by

$$\Delta E^{(1)} = (\Psi|\hat{V}|\Psi) = bn_{eu} \quad (18b)$$

n<sub>eu</sub> now being the occupation number of the e<sub>u</sub><sup>\*</sup> orbitals in the wave function Ψ.

For the covalent wave function (17a) ΔE<sup>(1)</sup> is b/2 since e<sub>u</sub><sup>\*</sup> is singly occupied in the configuration b<sub>1u</sub>e<sub>u</sub><sup>\*</sup> which has the weight 1/2. The same first-order energy contribution ΔE<sup>(1)</sup> = b/2 is found for e<sub>g</sub><sup>1</sup>b<sub>2g</sub><sup>1</sup>, coupled to a singlet, and for e<sub>g</sub><sup>1</sup>b<sub>1u</sub><sup>1</sup>, singlet and triplet, hence for all states with E symmetry at about 5000 cm<sup>-1</sup> in Table 4. The energies of these four states are equal in this order of perturbation theory.

Finally, the elimination of the ionic terms from the configuration e<sub>g</sub><sup>2</sup> is only possible by the admixture of e<sub>u</sub><sup>\*</sup>2, which costs the energy of 1b in first-order perturbation theory. Likewise, the covalent states from e<sub>g</sub>e<sub>u</sub><sup>\*</sup> are by the amount of b higher than the purely covalent ground states (14a,b). Indeed, all these states

have excitation energies of about 10000 cm<sup>-1</sup> in the VCI calculations presented in Table 4.

Thus we can summarize the situation in the binuclear Ti–O–Ti complex as follows: The elimination of the ionic terms from the simple MO configurations has no effect for the two lowest states but raises the energies of the four states with E symmetry by b/2 and those of the next eight states by b. This is indicated in the fourth column of Table 4. The further energy splitting between these states cannot be explained in first-order perturbation theory.

Of course, instead of starting from the delocalized MOs of eqs 7 and 8 and the MO configurations which can be constructed from them, one can also start from purely covalent AO configurations built up from the localized (and possibly orthogonalized) 3d AOs on the metal ions. This procedure is generally adopted in the derivation of the superexchange coupling<sup>13–15,41</sup> since it enables a comparably simple construction of the covalent states. However, since the perturbation is a simple diagonal operator in the MO basis, but an off-diagonal operator in the AO basis,<sup>41</sup> we prefer the simpler description (18a,b) in the MO representation.

For the V–O–V complex with four d electrons, first-order perturbation theory does not lead to a definite answer concerning the spin multiplicity of the lowest states: All states with two electrons in b<sub>2g</sub> or b<sub>1u</sub> and the other two electrons in e<sub>g</sub> or e<sub>u</sub><sup>\*</sup> orbitals have ΔE<sup>(1)</sup> = b; these are exactly the 12 states given in Table 5. (As for Ti–O–Ti, the elimination of the ionic contributions for two electrons in b<sub>2g</sub>/b<sub>1u</sub> costs no energy, that for two electrons in e<sub>g</sub>/e<sub>u</sub><sup>\*</sup> costs b.) The VCI and CASSCF results in Table 5 show that these 12 low-lying states are quite irregularly spaced, but all of them are within about 1500 cm<sup>-1</sup>. On the other hand, if more than two or less than two electrons occupy the pair b<sub>2g</sub>/b<sub>1u</sub> of orbitals, the elimination of the ionic contributions raises the energy by 3/2b or 2b.

If the two metal ions contain more than one d electron each, it is not only necessary to get rid of the ionic terms, but one has also to take care of the correct spin coupling in the isolated metal ions, i.e., <sup>3</sup>T<sub>1g</sub> for the ground state of V(III) and <sup>4</sup>A<sub>2g</sub> for Cr(III). This requirement will further reduce the number of the low-lying states of the complex.

For the Cr–O–Cr complex, in which each Cr(III) ion has a spatially nondegenerate <sup>4</sup>A<sub>2g</sub> ground state in an octahedral environment with the configuration d<sub>xy</sub>d<sub>yz</sub>d<sub>xz</sub>, exactly one covalent septet, quintet, triplet, and quartet state can be constructed. The wave functions of these four states have been given explicitly by Glerup<sup>41</sup> in terms of AO configurations. For the septet state with M<sub>S</sub> = 3, the wave function consists of just one configuration

$$|d_{xy}(1)d_{yz}(1)d_{xz}(1)d_{xy}(2)d_{yz}(2)d_{xz}(2)| = |b_{2g}b_{1u}e_{gx}e_{gy}e_{ux}e_{uy}| \quad (19)$$

both in the AO and MO description. Its perturbation energy

$\Delta E^{(1)}$  is  $2b$  according to eq 18b since  $e_u^*$  is doubly occupied. The wavefunctions for the other three states contain many more determinants, however the occupation of  $e_u^*$  is always 2, such that all four states have identical energies in first order. This is again in accord with the small splittings in the VCI and CASSCF calculations given in Table 6.

**III.4. Second-Order Perturbation Theory.** As we have shown in the previous section, the elimination of the ionic terms in the wave functions raises the energy since the unfavorable antibonding orbital  $e_u^*$  has to be partly occupied. In some cases, this increase in energy can be reduced if the occupation of  $e_u^*$  can be lowered below that in the zeroth order covalent wave functions such as eqs 14a,b or 17a. Such an effect can be achieved by a small admixture of ionic terms to the pure covalent wavefunctions considered so far.

We will explain this effect for the  ${}^3E_g$  state of Ti—O—Ti. In the zeroth-order covalent wave function (17a) the  $e_u^*$  orbital has the occupation  $1/2$ . We can reduce this occupation by allowing the second configuration in (17a),  $b_{1u}e_u^*$ , containing the antibonding  $e_u^*$  orbital, to have a smaller weight than the first one,  $b_{2g}e_g$ , in which the antibonding orbital is not occupied, i.e., by choosing

$$\Psi = \frac{1}{\sqrt{1+C^2}}(b_{2g}e_g - Cb_{1u}e_u^*) \quad (20)$$

with  $C < 1$ . Apparently, in eq 20 the ionic terms are not completely eliminated (that would need  $C = 1$ ). Since eq 20 can also be written as a linear combination of the purely covalent and purely ionic configurations (17a) and (17b)

$$\Psi = A\frac{1}{\sqrt{2}}(b_{2g}e_g - b_{1u}e_u^*) + B\frac{1}{\sqrt{2}}(b_{2g}e_g + b_{1u}e_u^*) \quad (21)$$

where  $A = 1, B = 0$  and  $A = 0, B = 1$  represent the limits of purely covalent and ionic states, we can also say that in eq 20 ionic terms are mixed to the purely covalent wave function (17a).

The gain in energy by the admixture of the ionic configuration is given in second-order perturbation theory by

$$\Delta E^{(2)} = -\frac{(\Psi_{\text{cov}}|\hat{V}|\Psi_{\text{ionic}})^2}{E_{\text{ionic}} - E_{\text{cov}}} \quad (22)$$

where  $E_{\text{cov}}$  and  $E_{\text{ionic}}$  are the energies belonging to the covalent and ionic wave functions, respectively. In the case of the  ${}^3E_g$  state of Ti—O—Ti the matrix element in the numerator is easily evaluated to be

$$(\Psi_{\text{cov}}|\hat{V}|\Psi_{\text{ionic}}) = -b/2 \quad (23)$$

using the wave functions (17a) and (17b) and the form (18a) of the perturbation operator. The energy denominator is approximately given by the following combination of one- and two-center Coulomb integrals

$$\begin{aligned} E_{\text{ionic}} - E_{\text{cov}} &= (d_{xy}(1)d_{xy}(1)|d_{xz}(1)d_{xz}(1)) \\ &\quad - (d_{xy}(1)d_{xy}(1)|d_{xz}(2)d_{xz}(2)) \\ &\quad - (d_{xy}(1)d_{xz}(1)|d_{xy}(1)d_{xz}(1)) \\ &\quad - (d_{xy}(1)d_{xz}(1)|d_{xy}(2)d_{xz}(2)) \end{aligned} \quad (24)$$

The by far largest of these integrals is the first one, a one-center Coulomb integral, which is commonly denoted by  $U$ . The second integral is a two-center Coulomb integral, approximately equal to  $1/R$ , while the remaining two one- and two-center off-

diagonal Coulomb integrals are even smaller. Using the 3d AOs for isolated Cr(III) ions we have calculated the following values for these four parameters: 0.881, 0.145, 0.036, and 0.005 au, respectively. This gives an estimate for the energy denominator of 0.695 au = 19.0 eV. Several other estimates, also for the Ti and V complexes, have yielded energy denominators consistently between 16.0 and 19.0 eV.

If we neglect the smaller integrals in the energy denominator (24)—or, equivalently, combine the four integrals into one empirical parameter  $U$ —we obtain

$$\Delta E^{(2)} = -\frac{1}{4}\frac{b^2}{U} \quad (25)$$

which is similar to Anderson's formula (5). (Of course, the factor in front of  $b^2/U$  depends on the specific form of the covalent and ionic wave functions and will be different for different states.)

In the same way we have applied second-order perturbation theory to the admixture of ionic contributions to the covalent wave functions for all states of the binuclear Ti(III), V(III), and Cr(III) complexes studied in the present paper. The results of the first- and second-order perturbation treatments are also included in the Tables 4 and 5,  $\Delta E^{(1)}$  in units of  $b$ ,  $\Delta E^{(2)}$  in units of  $b^2/U$ . (However, one has to recall that the energy denominators for different states and complexes differ to some extent, mostly in the signs of the two small integrals in eq 24 such that a common energy denominator  $U$  gives only a qualitative estimate for  $\Delta E^{(2)}$ .)

Table 4 shows that for the Ti(III) complex second-order perturbation theory can rationalize the small, but noticeable splitting of  $\sim 1000 \text{ cm}^{-1}$  between the four "g" states belonging to  $e_g^2$  and  $e_u^{*2}$  and the four "u" states belonging to  $e_g e_u^*$ . Using typical values of  $b \approx 1.5 \text{ eV}$  and  $U \approx 17.5 \text{ eV}$ , one obtains indeed  $b^2/U \approx 1050 \text{ cm}^{-1}$  for this splitting. However, as explained in the previous section, the main splitting between the bunches of states at 0, 5000, and 10 000  $\text{cm}^{-1}$  is accounted for in first-order.

In the V(III) complex the analysis is more difficult since the covalent and ionic four-electron MO configurations are already quite complicated. In first-order all 12 low-lying states have the same energy, the splitting in second-order amounts again to about 1500  $\text{cm}^{-1}$ , but is not sufficient to unambiguously predict the correct energetic order of the states. The perturbation estimates as given in Table 5 are roughly parallel to the VCI and CASSCF results; however, since the energy denominators  $U$  are slightly different for different states, the calculations exhibit even more fine structure than the  $\Delta E^{(2)}$  estimates. This holds for instance for the four triplet states, all of them with  $\Delta E^{(2)} = -1/2b^2/U$ , but split by  $\sim 400 \text{ cm}^{-1}$ .

The largest energy gain is found for the  ${}^5A_{1u}$  state ( $\Delta E^{(2)} = -b^2/U$ ) which is also predicted by the VCI and CASSCF calculations to be the ground state (Table 5). The explanation that this state is the true ground state is as follows. The purely covalent and ionic wavefunctions for this state are

$$\Psi_{\text{cov}} = \frac{1}{\sqrt{2}}(|b_{2g}b_{1u}e_{gx}e_{gy}| - |b_{2g}b_{1u}e_{ux}e_{uy}|) \quad (26a)$$

$$\Psi_{\text{ionic}} = \frac{1}{\sqrt{2}}(|b_{2g}b_{1u}e_{gx}e_{gy}| + |b_{2g}b_{1u}e_{ux}e_{uy}|) \quad (26b)$$

Since in the first of the two determinants in eqs 26a,b only the nonbonding  $e_g$  orbitals and in the second one only the antibonding  $e_u^*$  orbitals are occupied, the off-diagonal matrix element in the numerator of eq 22 and therefore  $\Delta E^{(2)}$  is large



$$\langle \Psi_{\text{cov}} | \hat{V} | \Psi_{\text{ionic}} \rangle = 1/2(0b - 2b) = -b \quad (27)$$

For all other states, the determinants in the covalent and ionic wave functions contain both  $e_g$  and  $e_u^*$  orbitals, as for instance in the  ${}^5B_{2g}$  state

$$\Psi_{\text{cov}} = \frac{1}{\sqrt{2}}(|b_{2g}b_{1u}e_{gx}e_{uy}^*| + |b_{2g}b_{1u}e_{gy}e_{ux}^*|) \quad (28a)$$

$$\Psi_{\text{ionic}} = \frac{1}{\sqrt{2}}(|b_{2g}b_{1u}e_{gx}e_{uy}^*| - |b_{2g}b_{1u}e_{gy}e_{ux}^*|) \quad (28b)$$

which leads to small, for  ${}^5B_{2g}$  even to a vanishing, matrix elements of  $\hat{V}$  and therefore to a smaller gain in energy upon admixing of ionic states.

The situation is again slightly simpler for the binuclear Cr(III) complex. Obviously, for the  ${}^7A_{2u}$  state with the purely covalent wave function given in eq 19 no ionic counterpart can be constructed since there is only one possibility of placing six electrons with parallel spins into six valence orbitals. Hence  $\Delta E^{(2)} = 0$  for this state. Each of the other three low-lying states— ${}^5A_{1g}$ ,  ${}^3A_{2u}$ ,  ${}^1A_{1g}$ , compare Table 6—has exactly one ionic counterpart with the same spin and spatial symmetry. The corresponding covalent and ionic wave functions are quite lengthy linear combinations of simple MO configurations; they have been given explicitly by Glerup in terms of AO Slater determinants.<sup>41</sup> If they are used in second-order perturbation theory one obtains  $\Delta E^{(2)} = 0, -6/9, -10/9, -12/9$ , in units of  $b^2/U$  for  ${}^7A_{2u}, {}^5A_{1g}, {}^3A_{2u}, {}^1A_{1g}$ , respectively. This corresponds to an antiferromagnetic coupling with a regular Landé pattern and a superexchange integral given by

$$J = -1/2(E({}^3A_{2u}) - E({}^1A_{1g})) = -\frac{1}{9} \frac{b^2}{U} \quad (29)$$

If we again use the values  $b \approx 1.5$  eV and  $U \approx 17.5$  eV we obtain  $J = -120$  cm<sup>-1</sup> in reasonable agreement with the VCI and CASSCF calculations. The discrepancy to the VCI and CASSCF results ( $\sim 60$  cm<sup>-1</sup> for  $J$ ) is caused by the ambiguity of defining SCF orbital energies for singly occupied or virtual orbitals in the ROHF treatment.

**III.5. Occupation of the  $e_u^*$  Orbitals.** Our explanation for the mechanism of the superexchange coupling in the three complexes is confirmed by Figure 3 where we have plotted the excitation energies of the low-lying states as functions of the occupation  $n_{eu}$  of the antibonding orbitals  $e_u^*$ . The VCI results with basis I have been used for this plot. For all three complexes a nearly linear dependence is found; for the chromium complex the deviation from linearity is negligible.

In the titanium complex the splitting between the 12 lowest states is a first-order effect; according to eq 18b the excitation energies are expected to be proportional to  $n_{eu}$ , the slope is simply given by  $b$ . Exactly this behavior is found in Figure 3a. In the vanadium and chromium complexes, on the other hand, the splitting between the 12 or 4 lowest states, respectively, is a second-order effect, as discussed in sections III.3,4. If we apply second-order perturbation theory to calculate the occupation of the  $e_u^*$  orbitals we obtain

$$n_{eu} = (n_{eu})_{\text{cov}} + \frac{2\Delta E^{(2)}}{b} \quad (30a)$$

or

$$\Delta E^{(2)} = \frac{b}{2}(n_{eu} - (n_{eu})_{\text{cov}}) \quad (30b)$$

where  $(n_{eu})_{\text{cov}}$  is the occupation in the pure covalent zeroth-order wavefunction. (According to section III.3  $(n_{eu})_{\text{cov}}$  is 1 for the 12 low-lying states of the vanadium complex and 2 for the four low-lying states of the chromium complex.) Equation 30b shows that also for these complexes  $\Delta E^{(2)}$  depends linearly on  $n_{eu}$ , the slope is now given by  $b/2$ . Figures 3b and in particular 3c agree with this prediction.

#### IV. Dynamic Correlation Effects

In the previous section we have shown that the VCI or CASSCF calculations are able to correctly predict the ground state spin multiplicities and the energetic order of the low-lying electronic states of the complexes. Furthermore, they furnish a reliable basis for a qualitative analysis of the antiferromagnetic superexchange coupling by means of first and second order perturbation theory. However, the calculated values for the exchange coupling constants  $J$  are considerably too small, at least in those cases like the Cr(III)—O—Cr(III) complexes for which a reasonable comparison with experiment is possible. The same experience has been made for calculations on Ni(II)—O—Ni(II) complexes<sup>42</sup> and on the antiferromagnetic coupling in KNiF<sub>3</sub>.<sup>24</sup>

Though it might be that part of this discrepancy is caused by the use of model ligands instead of real ligands, the largest deficiency of the VCI or CASSCF calculations is the lack of dynamic correlation, i.e., excitations from the occupied orbitals into the full virtual space. The reason for this assumption is that (a) experimentally  $J$  is rather insensitive to the precise nature of the ligands and (b) VCI values for  $J$  are also too small if real ligands such as F<sup>-</sup> or NH<sub>3</sub> are used in the calculation.<sup>37</sup>

Tables 7 and 8 contain the results of our large-scale MC-CEPA calculations on top of the CASSCF reference space—starting from individual CASSCF calculations for each state separately—for the vanadium and chromium complexes. Both tables contain the absolute energy of the respective electronic ground state and the excitation energies for the low-lying states. For the Cr(III)—O—Cr(III) complex we have normalized the energy differences in such a way that the value of  $2J$  is immediately visible. Several basis sets have been used in order to check to what extent the excitation energies depend on the size of the basis.

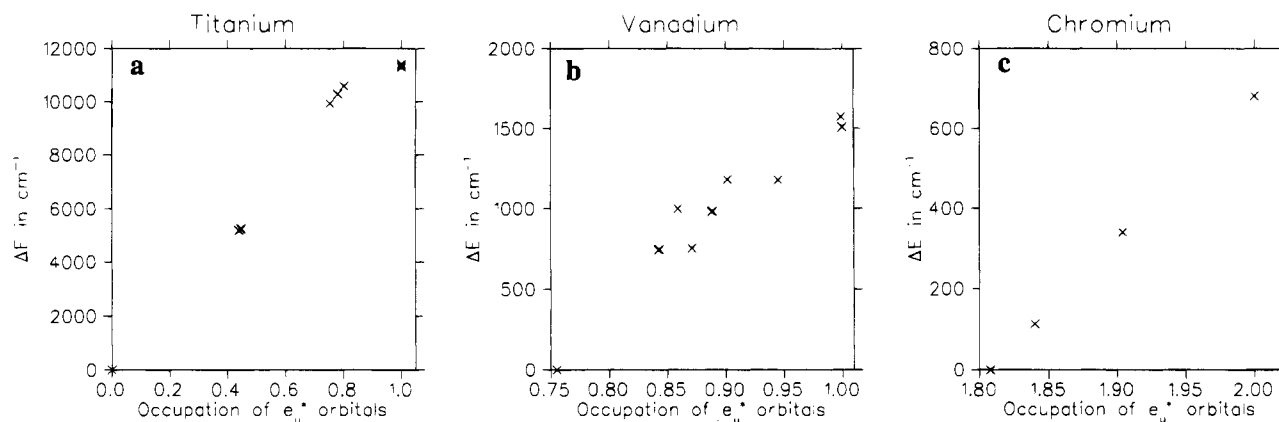
The main results of the MC-CEPA calculations can be summarized as follows:

(i) The energetic order of the states is the same as in the CASSCF and VCI calculations, except for some of the very close states of the V(III) complex. This means that the analysis of the coupling mechanism based on the VCI or CASSCF results is still valid.

(ii) The irregular spacing of the levels in the V(III) complex as well as the regular Landé pattern in the Cr(III) complex is preserved also after the inclusion of dynamic correlation effects. For the Cr(III) complex one observes a small decrease of the value  $J$  for the higher states, but this decrease is so small that it is hardly significant.

(iii) There is a significant, but not very large increase in  $J$  with the improvement of the basis set for the Cr(III) complex in Table 8. (Since basis I is too small to reliably account for correlation effects, its results should not be taken too seriously.) A further improvement of the basis might lead to slightly larger values for  $J$ .

(iv) The ACPF approximation yields consistently higher excitation energies than a CI which is uncorrected for size consistency errors. Since in all applications so far, excitation



**Figure 3.** Correlation of the excitation energies and the occupation number  $n_{eu}$  of the  $e_u^*$  orbitals. (a) Titanium (slope:  $11850 \text{ cm}^{-1}/\text{electron}$ ). (b) Vanadium (slope:  $5600 \text{ cm}^{-1}/\text{electron}$ ). (c) Chromium (slope:  $3550 \text{ cm}^{-1}/\text{electron}$ ).

**Table 7.** Excitation Energies of the Low-Lying Electronic States of  $L_5V-O-VL_5$  ( $\text{cm}^{-1}$ )

	basis I			basis II		
	CASSCF	CI	ACPF	CASSCF	CI	ACPF
$E(^5A_{1u})^a$	-1975.433335	-1975.672093	-1975.701995	-1977.347551	-1977.630572	-1977.665229
$^5A_{1u}$	0	0	0	0	0	0
$^1B_{2g}$	815	1741	2462	754	1560	2260
$^3A_{2g}$	846	1542	2462	793	1422	1836
$^1B_{1g}$	820	1790	2529	761	1606	2325
$^3B_{1u}$	1076	2191	3017	1002	1984	2794
$^3B_{2u}$	1082	2223	3040	1007	2010	2819
$^1A_{1g}$	1075	2301	3278	993	2048	3014
$^1A_{1u}$	1283	2409	3017	1198	2203	2834
$^3A_{2u}$	1278	2623	3641	1186	2360	3371
$^5B_{2g}$	1597	3176	4246	1489	2880	3939
$^5B_{1g}$	1598	3160	4154	1488	2860	3857
$^5A_{1g}$	1659	3281	4330	1548	2970	4030

<sup>a</sup> In au.

**Table 8.** Excitation Energies of the Low-Lying Electronic States of  $L_5Cr-O-CrL_5$  ( $\text{cm}^{-1}$ )

basis	method	$E(^1A_{1g})^a$	$^3A_{2u} - ^1A_{1g}$ $E/\text{cm}^{-1}$	$^5A_{1g} - ^3A_{2u}$ $1/2\Delta E/\text{cm}^{-1}{}^b$	$^7A_{2u} - ^5A_{1g}$ $1/3\Delta E/\text{cm}^{-1}{}^b$
I	CASSCF	-2175.922915	140.8	132.9	119.6
	CI	-2176.100957	286.3	277.2	261.0
	ACPF	-2176.122805	324.1	310.1	297.7
II	VCI	-2178.115193	111.7	111.8	111.8
	CI	-2178.375585	243.3	236.0	231.4
	ACPF	-2178.395703	281.4	267.3	264.0
IV	VCI	-2178.138348	111.7	111.8	111.6
	CI	-2178.422398	265.6	256.7	254.8
	ACPF	-2178.444089	314.7	299.3	302.3

<sup>a</sup> In au. <sup>b</sup> The energy difference is normalized in such a way that the value for  $2J$  is given.

energies at the MC-CEPA or ACPF level are much closer to the corresponding full CI results<sup>28</sup> or experimental data,<sup>43</sup> we assume that also in the present case the ACPF results are more reliable than those at the CI level.

(v) In both complexes, the inclusion of dynamic correlation effects leads to excitation energies which are consistently by a factor of 2–3 larger than those at the VCI or CASSCF level.

In the case of the chromium complex, our best calculation (basis IV, ACPF) yields an average value for  $J$  of  $-151.7 \text{ cm}^{-1}$  (for the excitation  $^1A_{1g} \rightarrow ^7A_{2u}$ ) which is in the correct order, but still smaller than the experimental value of  $-225 \text{ cm}^{-1}$  for the  $(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5$  complex.<sup>8</sup> The use of model ligands, neglect of spin-orbit coupling, still too small basis sets for the dynamic correlation, and the exclusion of the 3s, 3p core orbitals of Cr(III) as well as the ligand orbitals from the correlation treatment are probably the main sources for this

discrepancy. For the V(III) complex no experimental values of the excitation energies, except for the information that the coupling is ferromagnetic,<sup>4</sup> are available.

We have also performed MC-CEPA calculations for the two lowest states of the Ti(III)–O–Ti(III) complex. The results for the  $^1A_{1g} \rightarrow ^3A_{2u}$  excitation energy obtained with basis I are as follows: CASSCF,  $-0.2 \text{ cm}^{-1}$ ; CI,  $-7.3 \text{ cm}^{-1}$ ; ACPF,  $-13.3 \text{ cm}^{-1}$ . If we again regard the ACPF results as most reliable, we conclude that the two Ti(III) ions are antiferromagnetically coupled with a very small exchange integral of  $-6.5 \text{ cm}^{-1}$ . This is in remarkably good agreement with the values of  $J = -7.8$  and  $-5.6 \text{ cm}^{-1}$  measured recently by Jeske et al.<sup>4</sup> for two different linear  $L_5\text{Ti(III)}-\text{O}-\text{Ti(III)}L_5$  compounds. However, it should be noted that our excitation energy has been obtained as the very small difference between the energies of two electronic states treated in two separate calculations. Thus, this agreement is nice, but should not be taken too seriously.

(43) Hegemann, K.; Staemmler, V.; Fink, R. *Z. Phys. D* **1993**, *27*, 211.

The last question is: Why do dynamic correlation effects lead to such a dramatic increase in the excitation energies, preserving the energetic order, the Landé pattern, etc. for states which differ only in the spin-coupling of the orbitals? The analysis of our MC-CEPA wave functions and several additional test calculations which are not documented here explicitly—inclusion of the  $3d_{x^2-y^2}$ ,  $3d_{z^2}$  AOs at the metal ions or the  $2s, 2p$  AOs at  $O^{2-}$  in the active space, correlation of only the 3d electrons, etc.—lead to the conclusion that dynamic correlation causes a lowering of the energy denominator, in particular of the repulsion integral  $U$ , and therefore to an increase of all excitation energies simultaneously. The use of a common set of orbitals for the “neutral” and the “charge-transfer” configurations in the VCI or CASSCF calculations has the consequence that the energies of the charge transfer configurations and therefore also the energy denominators are too high and are lowered by dynamic correlation and relaxation effects which are included in our MC-CEPA calculations. This explanation is in agreement with the observation that our estimate for  $U$  of about 17.5 eV is much higher than the semiempirical values for  $U$  (6.0–10.0 eV) derived by Zaanen and Sawatzky<sup>14</sup> for the superexchange in transition metal oxides or the very low value of only about 4.0 eV derived by Glerup<sup>41</sup> for the Cr(III)–O–Cr(III) complex.

## V. Conclusions

The results of the present ab initio study of the superexchange coupling in linear oxo-bridged Ti(III), V(III), and Cr(III) complexes can be summarized as follows.

(i) The mechanism of the spin coupling in the three complexes is essentially the superexchange interaction as proposed by Kramers and Anderson and depends on the overlap between

the 3d AOs on the transition metal cations and the 2p AOs on the bridging  $O^{2-}$  anion.

(ii) The application of simple MO theory in order to rationalize the differences in the signs and absolute values of the exchange integrals of the three complexes leads to reasonable results only if the balance of covalent and ionic contributions to the wave functions is correctly described. This can be done by means of first-order and second-order perturbation theory based on MO configurations.

(iii) In agreement with all experimental observations, our qualitative VCI and CASSCF and semiquantitative MC-CEPA calculations yield paramagnetic (or weak antiferromagnetic) coupling of the two spins in the Ti(III) complex, strong ferromagnetic and antiferromagnetic coupling in the V(III) and Cr(III) complexes, respectively.

(iv) The “active electron approximation”, i.e., the inclusion of only the 3d and 2p AOs in the active space, leads to the correct energetic order of the states but to too low values of  $J$ .

(v) The inclusion of dynamic correlation and relaxation effects is necessary if reliable values for the exchange integrals  $J$  are to be calculated. The main reason is that one single set of 3d and 2p AOs cannot correctly describe the covalent and ionic configurations simultaneously.

**Acknowledgment.** This work has been supported financially by the Deutsche Forschungsgemeinschaft through the project Modellkat and the graduate college Dynamische Prozesse an Festkörperoberflächen and by the Schweizerische Nationalfonds, Project 20-37624.93. We thank Prof. K. Wieghardt, Bochum, for stimulating discussions on this subject and his experimental results prior to publication.