erally more positive than the parent species.[26] Indeed binding of the $[Fe(CN)_5]^{3-}$ group to pyrazine (pz) in either [Ru-$(NH_3)_5(pz)]^{2+}$[9,26] or *trans*-$[Ru(NH_3)_4(pz)_2]^{14}$ results in a substantial red shift of the Ru → pz CT band (1940 and 2600 cm^{-1}, respectively).

It is suggested that the strong π-accepting ability of the cyanide groups induces the $[Fe(CN)_5]^{3-}$ group to behave as a σ Lewis acid, leaving the Ru(II) atom to bind the pyrazine in a π sense.[9] However, the appearance of the Fe → bpz(π^*) transition energetically below that seen in the methylpyrazinium [(pzMe$^+$)-$(CN)_5Fe]^{2-}$ and $[(bpz)(CN)_5Fe]^{3-}$ species indicates that the $[Ru(bpz)_3]^{2+}$ group acts as an excellent π-acceptor especially as the $E[Fe(III)/Fe(II)]$ potential is not significantly different from that observed previously in $[Fe(CN)_5L]^{3-}$ complexes.[9,26] The pK_a value for monoprotonation is -2.2,[4] and this value is probably appropriate for binding of all the pentacyanoferrate(II) groups. Thus the peripheral nitrogen atoms are very weak bases. In this case back-bonding from Fe(II) to bipyrazine probably plays a significant role, but the synergistic effects associated with the σ-bonding must conspire to cause no change in energy of either the bpz(π^*) or Ru(d) level.

The presence of two charge-transfer transitions allows one to extract further information where electrochemical data are also available.[25] Thus one may write[25,27]

$$E_{op}(Ru \rightarrow bpz(\pi^*)) =$$
$$E[Ru(III)/Ru(II)] - E[Ru^{III}(bpz)Fe^{II}/Ru^{III}(bpz^-)Fe^{II}] +$$
$$\chi_i(Ru \rightarrow bpz) + \chi_o(Ru \rightarrow bpz) \quad (12)$$

where the first potential is the Ru(III)/Ru(II) redox potential for this species bound to $([Fe^{II}(CN)_5]^{3-})_n$ and the second corresponds with reduction of bipyrazine bound to Ru(III) (and Fe(II)) and is not available by direct electrochemical experiment. The last two terms are the inner and outer reorganization energies for this transition.[23,25,28] Further we may write

$$E_{op}(Fe \rightarrow bpz(\pi^*)) =$$
$$E[Fe(III)/Fe(II)] - E[Ru^{II}(bpz)Fe^{III}/Ru^{II}(bpz^-)Fe^{III}] +$$
$$\chi_i(Fe \rightarrow bpz) + \chi_o(Fe \rightarrow bpz) \quad (13)$$

where the first potential is the observed Fe(III)/Fe(II) redox potential for this species and the second corresponds with reduction of bipyrazine bound to Ru(II) and Fe(III) and is not available by direct electrochemical experiment.

Suppose we assume that the reorganization energies for these two transitions are essentially identical. We may then write, for the differences in energy between the two transitions, the statement

$$E_{op}(Ru \rightarrow bpz(\pi^*)) - E_{op}(Fe \rightarrow bpz(\pi^*)) = 8200 \text{ cm}^{-1}$$

$$= E[Ru(III)/Ru(II)] - E[Ru^{III}(bpz)Fe^{II}/Ru^{III}(bpz^-)Fe^{II}]$$
$$- E[Fe^{III}/Fe^{II}] + E[Ru^{II}(bpz)Fe^{III}/Ru^{II}(bpz^-)Fe^{III}] \quad (14)$$

The value of $E[Ru(III)/Ru(II)]$ is 2.10 V (vs. NHE) for the parent species[3,29] and, given that the Ru(d) level is unaffected by coordination of the $[Fe(CN)_5]^{3-}$ groups, will also be the appropriate value for the heteropolynuclear species. The Fe(III)/Fe(II) reduction potential is measured to be +0.70 V, leading to the conclusion (1 eV = 8065 cm^{-1})

$$E_{op}(Ru \rightarrow bpz(\pi^*)) - E_{op}(Fe \rightarrow bpz(\pi^*)) = 8200 \text{ cm}^{-1}$$

$$1.02 = 2.10 - 0.70 - E[Ru^{III}(bpz)Fe^{II}/Ru^{III}(bpz^-)Fe^{II}] +$$
$$E[Ru^{II}(bpz)Fe^{III}/Ru^{II}(bpz^-)Fe^{III}]$$

and hence

$$E[Ru^{II}(bpz)Fe^{III}/Ru^{II}(bpz^-)Fe^{III}] -$$
$$E[Ru^{III}(bpz)Fe^{II}/Ru^{III}(bpz^-)Fe^{II}] = -0.38 \text{ V} \quad (15)$$

providing information about energy differences between mixed-valence isomers and being the energy for the electron-transfer process
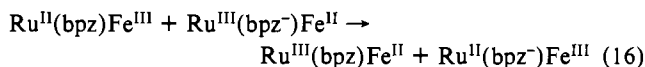
$$Ru^{II}(bpz)Fe^{III} + Ru^{III}(bpz^-)Fe^{II} \rightarrow$$
$$Ru^{III}(bpz)Fe^{II} + Ru^{II}(bpz^-)Fe^{III} \quad (16)$$

Registry No. [Ru(bpz)$_3$](PF$_6$)$_2$, 80907-56-8; Na$_3$[Fe(CN)$_5$NH$_3$], 14099-05-9; Na[Ru(bpz)$_3$(Fe(CN)$_5$)], 99631-50-2; [Fe(CN)$_5$(H$_2$O)]$^{3-}$, 18497-51-3; [Ru(bpz)$_3$(Fe(CN)$_5$)$_2$]$^{4-}$, 99617-64-8; [Ru(bpz)$_3$(Fe-(CN)$_5$)$_3$]$^{7-}$, 99631-51-3; [Ru(bpz)$_3$(Fe(CN)$_5$)$_4$]$^{10-}$, 99617-65-9; [Ru-(bpz)$_3$(Fe(CN)$_5$)$_5$]$^{13-}$, 99617-66-0; [Ru(bpz)$_3$(Fe(CN)$_5$)$_6$]$^{16-}$, 99617-67-1.

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Trends of Magnetic Interactions in Related Transition-Metal Dimers

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Exchange parameters determine the magnetic properties of transition-metal dimers. They can be related to MO energy differences obtained by extended Hückel calculations. Good agreement with experiment is obtained in the series Cr$_2$X$_9^{3-}$ (X = Cl, Br, I). The observed trends in the series Ti$_2$Cl$_9^{3-}$, V$_2$Cl$_9^{3-}$, Cr$_2$Cl$_9^{3-}$ are reproduced semiquantitatively by the model. The extended Hückel technique is not able to account for the observed large increase of the exchange coupling between Cr$_2$Cl$_9^{3-}$ and V$_2$Cl$_9^{5-}$. The experimental ratio of the orbital exchange parameters in V$_2$Cl$_9^{5-}$, J_a/J_e = 36, is exactly reproduced by the calculation. In [(en)$_2$Cr(OH)$_2$Cr(en)$_2$]$^{4+}$ the relative contributions to the total J of the various orbital parameters are reasonably accounted for by the model.

Introduction

Dimers of transition-metal ions are well suited to the study of the nature of magnetic interactions, i.e. exchange coupling. Many compounds have been studied in which the transition-metal ions occur as pairs either by nature or by doping a diamagnetic host lattice with a small amount of a transition metal.[1] In most cases the ground-state exchange parameter J was determined, and for

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some compounds it was possible to obtain information about orbital exchange parameters by the use of optical spectroscopy of excited states.[2]

Of special interest is the study of a series of related compounds for which a correlation between structural and electronic properties and the *J* values may be obtained. A model that is able to rationalize such correlations can lead to predictions of the magnetic properties of unknown compounds. Several methods have been used to rationalize empirical magnetostructural correlations, variations of bridging geometries M–X–M in particular.[3–6] The results are often quite encouraging.

It is the aim of this paper to explore the applicability and the limits of one of those models by applying it to three different situations that are experimentally more or less established: (i) the series $Cr_2X_9^{3-}$ (X = Cl, Br, I); (ii) the series of $M_2Cl_9^{3-}$ (M = Ti, V, Cr); (iii) the isoelectronic dimers $Cr_2Cl_9^{3-}$ and $V_2Cl_9^{5-}$. In addition, we try to obtain some information about the individual orbital exchange parameters in $V_2Cl_9^{5-}$ and $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$. These orbital parameters provide detailed information about exchange pathways.

Theoretical Model

For a dimer consisting of ions in orbital singlet ground states, the following Heisenberg Hamiltonian is appropriate:

$$\mathcal{H} = -2J\mathbf{S}_A \cdot \mathbf{S}_B \tag{1}$$

The exchange parameter can be decomposed into orbital parameters as follows:[7,8]

$$J = -\frac{1}{n^2}\sum_{\alpha\beta}\left(\frac{2}{U}A_{\alpha\beta}^2 - B_{\alpha\beta\beta\alpha}\right) \tag{2}$$

with $A_{\alpha\beta} = (\alpha|\bar{\mathcal{H}}|\beta)$ and $B_{\alpha\beta\beta\alpha} = (\alpha\beta|\bar{\mathcal{H}}|\beta\alpha)$. α and β label the orthonormal magnetic orbitals of the monomer fragments A and B, respectively.[8] $\bar{\mathcal{H}}$ is the appropriate Hamiltonian for the magnetic orbitals of the system. n is the number of unpaired electrons per monomer, and $B_{\alpha\beta\beta\alpha}$ is the exchange integral. $A_{\alpha\beta}$ is a transfer integral and U the electron-transfer energy.[8] The so-called potential exchange, $B_{\alpha\beta\beta\alpha}$, which is ferromagnetic, is difficult to calculate. It is usually small and will be neglected in this work. As a consequence our model will not be able to account for ferromagnetic interactions in detail. The first term of eq 2, the kinetic exchange, leads to an antiferromagnetic contribution. It is expected to be the dominant term in all the examples treated here.

We want to emphasize that the Hamiltonian in eq 1 is appropriate only for ions in orbital singlet states. More complex Hamiltonians are to be used for the coupling of ions in orbitally degenerate states.[7] These Hamiltonians contain orbital parameters that cannot be collected in an overall *J*.

Estimates of the electron-transfer energies, *U*, are difficult. For the free gaseous ions, *U* could be obtained from the known ionization energies. In complexes these values are likely to be reduced, however, by screening effects.[8,9] In this study we use the following approach: We consider *U* as constant within the series $Cr_2X_9^{3-}$. As a consequence the variations in *J* result from variations of the transfer integrals $A_{\alpha\beta}$. In the series $Ti_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Cr_2Cl_9^{3-}$, we use the uncorrected *U* values obtained from atomic ionization potentials. In this series it is the difference in the formula for *J* according to eq 2 that mainly accounts for the different *J* values.
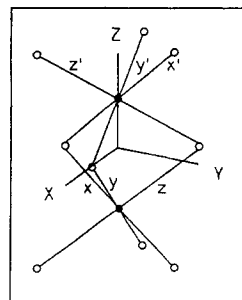
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Figure 1. Schematic structure of the dimer $M_2X_9^{3-}$. The D_{3h} coordinate system (*X, Y, Z*) as well as the local octahedral frames (*x, y, z*) are included.

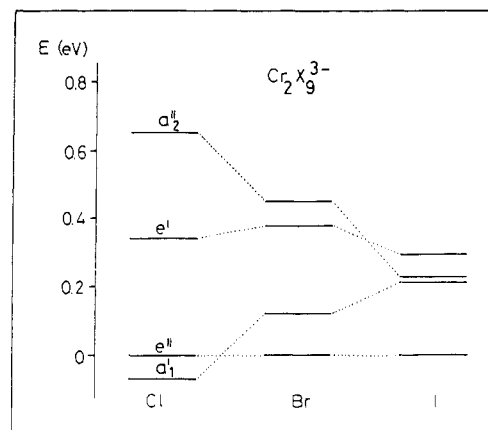**Figure 2.** MO diagram of $Cr_2X_9^{3-}$ (X = Cl, Br, I). Only the relevant d-electron part of the extended Hückel calculation is shown.

In the comparison of $Cr_2Cl_9^{3-}$ and $V_2Cl_9^{5-}$, uncorrected *U* values were used by assuming that screening effects are similar.

Two dimer MO's are built from the monomer magnetic orbitals α and β:

$$\nu_+ = (1/2^{1/2})(\alpha + \beta) \qquad \nu_- = (1/2^{1/2})(\alpha - \beta) \tag{3}$$

The MO energies are easily obtained as

$$e_+ = (\nu_+|\bar{\mathcal{H}}|\nu_+) = \frac{1}{2}(e_\alpha + e_\beta + 2A_{\alpha\beta})$$
$$e_- = (\nu_-|\bar{\mathcal{H}}|\nu_-) = \frac{1}{2}(e_\alpha + e_\beta - 2A_{\alpha\beta}) \tag{4}$$

with $e_\alpha = (\alpha|\bar{\mathcal{H}}|\alpha)$. With use of eq 4, the transfer integral can now be related to energy differences of the corresponding dimer MO's:

$$A_{\alpha\beta} = \frac{1}{2}(e_+ - e_-) \tag{5}$$

A simple method for obtaining the MO's of a dimer is an extended Hückel calculation. The program and the parameters that were used for the extended Hückel calculations are those described in ref 10. The self-consistent charge iteration procedure was used, and the Madelung corrections were applied, when possible.

$Cr_2Cl_9^{3-}$, $Cr_2Br_9^{3-}$, $Cr_2I_9^{3-}$

Compounds of the composition $Cs_3Cr_2X_9$ contain dimeric $Cr_2X_9^{3-}$ units.[11] The crystal structure of $Cs_3Cr_2I_9$ has not been determined. We assume the $Cs_3Cr_2Cl_9$ structure. The point group symmetry of the dimer is D_{3h}, and the site symmetry of Cr^{3+} is C_{3v}. The dimer is shown in Figure 1 with the D_{3h} coordinate system. All the calculations were done in this symmetry-adapted coordinate system.

Cr^{3+} has a $^4A_2$ ground state deriving from the $(t_2)^3$ electron configuration (O_h notation). In C_{3v} symmetry the orbitals

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transform as a_1 and e. Forming the D_{3h} dimer, we obtain a_1'/a_2'' MO's from a combination of the a_1 orbitals and e'/e'' MO's from the e orbitals. Of the nine possible transfer integrals in eq 2, only $A_{a_1 a_1}$ and A_{ee} are nonzero on symmetry grounds. Using eq 2, we obtain:

$$J = -\frac{1}{18}\frac{1}{U}[(e_{a_1'} - e_{a_2''})^2 + 2(e_{e'} - e_{e''})^2] \tag{6}$$

The corresponding MO diagrams, obtained from an extended Hückel treatment, are shown in Figure 2. According to eq 6 we obtain a value of 1.9 for the ratio J^{Cl}/J^{Br}. This is in perfect agreement with the experimental value of 1.8.[12] For the iodide, J is calculated to be half the value of the bromide. Susceptibility and neutron diffraction measurements on $Cs_3Cr_2I_9$ indicate that it is no longer a typical dimer compound. As a result of interdimer exchange, it orders magnetically below 10 K.[13] The intradimer J^I is smaller than J^{Br}. The extended Hückel method thus provides an almost quantitative reproduction of the trend within the $Cr_2X_9^{3-}$ series.

$Ti_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Cr_2Cl_9^{3-}$

In this series we explore the changes of ground-state exchange parameters upon changing the metal ion in analogous complexes. The MO diagram obtained for $V_2Cl_9^{3-}$ is similar to that of $Cr_2Cl_9^{3-}$. For $Ti_2Cl_9^{3-}$ the pattern remains the same, but the energy differences are enlarged by 40–60%. In order to compare the exchange parameters of these compounds, we have to use the appropriate expressions for J. For $Cr_2Cl_9^{3-}$ J is given by eq 6. For $V_2Cl_9^{3-}$, if V^{3+} is assumed to have a $^3A_2$ ground state with no orbital angular momentum, eq 1 is still valid with the following equation for J:

$$J = -\frac{1}{4}\frac{1}{U}(e_{e'} - e_{e''})^2 \tag{7}$$

For $Ti_2Cl_9^{3-}$ eq 1 is no longer applicable due to the orbital degeneracy of the ground state. As a consequence, two independent orbital exchange parameters determine the exchange splitting within the ground state:[7]

$$J_a = -\frac{1}{2}\frac{1}{U}(e_{a_1'} - e_{a_2''})^2 \qquad J_e = -\frac{1}{2}\frac{1}{U}(e_{e'} - e_{e''})^2 \tag{8}$$

For the ratios $J^{Cr}/J^V/J_a^{Ti}/J_e^{Ti}$ we obtain the values 1.0/0.2/ 21.0/2.0 from our calculations. Experimentally, there is evidence from magnetic measurements that J^V is ferromagnetic and small.[13] In ref 7 it was shown that J_a^{Ti} is larger than J^{Cr} by a factor of about 10 and that J_e^{Ti} is likely to be smaller than J_a^{Ti} by at least one order of magnitude. The observed trend is thus semiquantitatively reproduced by the calculations. It should be noted that the trend results mainly from the different expressions for the exchange parameters rather than from the MO energies.

An additional result of our calculation is the ratio of the two orbital exchange parameters J_a/J_e, as defined by eq 8. For M = Ti^{3+}, V^{3+}, and Cr^{3+} we obtain the values 18, 17, and 12, respectively. There is evidence from magnetic and optical spectroscopic experiments for this predominance of the "direct exchange" J_a in $Ti_2Cl_9^{3-}$ and $Cr_2Cl_9^{3-}$.[7,14]

$Cr_2Cl_9^{3-}$, $V_2Cl_9^{5-}$

The main variation between the two dimers is the charge, while the d-electron configuration is retained. The ground-state J is therefore calculated in both cases with the same expression, namely eq 6. The properties of $V_2Cl_9^{5-}$ have recently been studied by doping $CsMgCl_3$ with V^{2+}.[15] Extended Hückel calculations lead to a ratio of 1.3 for J^V/J^{Cr}. The experimental result is approximately 13. This discrepancy by one order of magnitude clearly
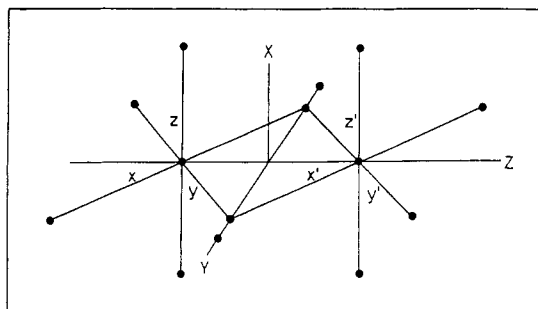
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Figure 3. Schematic structure of the dimer (coordinate system X, Y, Z) in $[(en)_2Cr(OH)_2Cr(en)_2]Cl_4\cdot2H_2O$. The local octahedral coordinate systems are designated as x, y, z.

illustrates the shortcomings of the extended Hückel calculation. Even an error of 50% in our estimate of relative U values would not substantially affect this result. Variation of the transition-metal charge appears to be very critical. This is not surprising on the basis of simple electrostatic considerations. The extended Hückel technique, on the other hand, appears to be unable to properly account for it. The origin of this failure probably lies in a rather poor description of the transition metal by the extended Hückel basis functions.

If we calculate the ratio of the two orbital parameters J_a/J_e, as defined by eq 8, we obtain a value of 36 for $V_2Cl_9^{5-}$. In ref 15, orbital parameters for this complex have been obtained from optical spectroscopic studies of the excited $^4A_2{}^2E$ state. They were determined in the local octahedral coordinate system and then transformed to the symmetry-adapted C_{3v} system (Figure 1). This transformation in ref 15 is not consistent with the present model. For the transformation of the transfer integrals, we have

$$A_{aa} = A_{11} + 2A_{12} \qquad A_{ee} = A_{11} - A_{12} \tag{9}$$

where 1, 2, and 3 number the magnetic orbitals yz, zx, and xy in the local octahedral coordinate system. In this coordinate system we have $A_{11} = A_{22} = A_{33}$ and $A_{12} = A_{13} = A_{23} = A_{21} = A_{31} = A_{32}$ for C_{3v} symmetry. A correlation of the two parameter sets is then obtained by using

$$J_{\alpha\beta} = -\frac{2}{U}A_{\alpha\beta}^2 \tag{10}$$

and thus

$$J_a = J_{aa} = J_{11} + 4J_{12} - 4(J_{11}J_{12})^{1/2}$$
$$J_e = J_{ee} = J_{11} + J_{12} + 2(J_{11}J_{12})^{1/2} \tag{11}$$

This transformation is not unique and depends on the relative sign of the two transfer integrals. A physically meaningful result is obtained by assuming equal signs for A_{aa} and A_{ee} (or A_{11} and A_{12}). From the experimental values $J_{11} = -160$ cm^{-1} and $J_{12} = -62.5$ cm^{-1},[15] we thus obtain the two orbital parameters $J_a = -810$ cm^{-1} and $J_e = -22.5$ cm^{-1}, corresponding to a J_a/J_e ratio of 36. This is in remarkable agreement with the extended Hückel calculation and shows that the "direct exchange" (J_a) significantly dominates the "superexchange" (J_e). Assuming opposite signs for the two transfer integrals would lead to a J_a/J_e ratio of 1/42, a value that seems rather unphysical and that was therefore rejected.

Orbital Parameters in $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$

The schematic structure of this dimer is shown in Figure 3. Its symmetry is approximately D_{2h} and the Cr^{3+} site symmetry C_{2v}. The ground-state J for this dimer was found to depend strongly on the position of hydrogen atoms in the hydroxo bridges. In the chloride salt they lie almost in the plane of the Cr and O atoms. We used this geometry for our calculations. Orbital exchange parameters for this dimer have been deduced from a spectroscopic analysis of the singly excited $^4A_2{}^2E$ state in ref 16, and it is the purpose of this section to compare them with the results of extended Hückel calculations.

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The following nonzero orbital parameters exist for this symmetry:

$$J_{a_1} = -\frac{1}{2}\frac{1}{U}(e_{b_{1u}} - e_{a_g})^2 \qquad J_{a_2} = -\frac{1}{2}\frac{1}{U}(e_{a_u} - e_{b_{1g}})^2$$

$$J_{b_1} = -\frac{1}{2}\frac{1}{U}(e_{b_{3u}} - e_{b_{2g}})^2 \tag{12}$$

The ground-state J is related to the orbital parameters by

$$J = \frac{1}{9}(J_{a_1} + J_{a_2} + J_{b_1}) \tag{13}$$

For simplicity en was substituted by two NH_3 molecules for the extended Hückel calculations. The numerical result for $J_{b_1}/J_{a_1}/J_{a_2}$ was 1.0/3.5/6.2. It is interesting to note that the same order was found by a similar technique for the dimers $Cr_2O_{10}^{14-}$, which have dioxo instead of dihydroxo bridges.[3] The orbital parameters in ref 16 are given in the local octahedral coordinate system. They are related to the parameters in the symmetry-adapted C_{2v} system by

$$\frac{1}{2}(J_{a_2} + J_{b_1}) = J_{yzyz} + J_{yzxz}$$
$$-(J_{a_2}J_{b_1})^{1/2} = J_{yzyz} - J_{yzxz}$$
$$J_{a_1} = J_{xyxy} \tag{14}$$

The following experimental values were determined in ref 16: $J_{yzxz} = -145$ cm^{-1}, $J_{xyxy} = -5$ cm^{-1}, $J_{yzyz} = 33$ cm^{-1}, and $J_{yzxy} = 22$ cm^{-1}. The latter two parameters are ferromagnetic. They cannot be properly accounted for by the present model. The neglect of ferromagnetic contributions restricts the number of parameters to 3 in our present treatment. The additional parameter J_{yzxy}, which does not occur in the transformation (14), should have no antiferromagnetic contribution according to our model, in good agreement with the small ferromagnetic value found experimentally. J_{yzyz} is also ferromagnetic, and it is therefore not meaningful to use eq 14 to derive numerical values for J_{a_2} and J_{b_1}. The main experimental result is the dominant antiferromagnetic contribution of J_{yzxz}. This is in good correspondence with the calculated dominance of J_{a_2}. J_{a_1} is experimentally found to be very small, a result that the calculation does not predict. This may, at least partly, be due to our neglect of a ferromagnetic contribution. This is expected to be largest for J_{a_1}[3] and would

lead to a partial compensation of the kinetic part of J_{a_1}. The overall agreement between experiment and extended Hückel calculation is semiquantitative. The experimental data indicate the presence of relatively large ferromagnetic contributions that the present model does not take into account.

Conclusions

Extended Hückel calculations are quite a useful tool for rationalizing and predicting "kinetic exchange" in a series of related dimeric complexes. Considerable care is necessary, however, because very small energy differences are involved. Furthermore, ferromagnetic exchange contributions are neglected. As a means for obtaining absolute values of exchange parameters, the procedure presented in this paper is not adequate. However, when one considers a trend in a series of related complexes, these problems may be relatively unimportant. By changing the anion in the series $Cr_2X_9^{3-}$, we obtained particularly pleasing agreement between experimental and calculated J ratios. The semiquantitative reproduction of the trend in the series $Ti_2Cl_9^{3-}$, $V_2Cl_9^{3-}$, $Cr_2Cl_9^{3-}$ results from, and therefore confirms, our method of relating exchange parameters to energy differences between MO's. The weaknesses of the extended Hückel technique become apparent in the comparison between the isoelectronic species $V_2Cl_9^{5-}$ and $Cr_2Cl_9^{3-}$. The calculated ratio of the exchange parameters is one order of magnitude too small. One of the major weaknesses of the extended Hückel treatment is the poor description of the transition-metal ion due to the very small number of basis functions centered at M. This deficiency of the technique is much more apparent in a situation where we exchange a trivalent against a divalent metal ion than within a series of complexes with the same metal ion and different ligands. In the same sense we can rationalize the good results obtained in our calculations of relative orbital contributions to the total J in a given complex.

The inability of this model to account for ferromagnetic contributions to the net exchange is probably its most severe weakness. In order to account for experimental orbital exchange parameters with a ferromagnetic sign as well as complexes with rather large ferromagnetic exchange parameters, a different approach is needed.

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Reduction of Peroxotitanium(IV) by Sulfur(IV), Iron(II), and Titanium(III) in Acidic Solution

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The net reduction of peroxotitanium(IV) by sulfur(IV) in acidic solution proceeds by a rate-determining dissociation of peroxide from TiO_2^{2+} followed by the rapid reaction of H_2O_2 and HSO_3^-. The absence of a detectable direct reaction between TiO_2^{2+} and either SO_2 or HSO_3^- is consistent with the previously proposed electrophilic nature of the peroxide moiety when coordinated to a d^0 transition-metal ion. The reduction of TiO_2^{2+} with excess iron(II) or titanium(III) was shown to proceed by both a direct reaction and reduction of H_2O_2 formed by dissociation of the peroxo complex. The rate expressions for the direct reactions are respectively $-d[TiO_2^{2+}]/dt = (k_a + k_b/[H^+])[TiO_2^{2+}][Fe(II)]$ and $(k_c/[H^+])[TiO_2^{2+}][Ti(III)]$. Values of $k_a = 1.1 \pm 0.1$ M^{-1} s^{-1} and $k_b = 0.16 \pm 0.01$ s^{-1} at 17 °C and $k_c = 11.1 \pm 0.4$ s^{-1} at 25 °C were determined at $I = 1.0$ M (LiClO$_4$). These rate constants are smaller than those reported previously for the corresponding reductions of H_2O_2. The results do not allow an assignment of an inner- or outer-sphere mechanism for the direct reactions. The reduced reactivity of the peroxide moiety in TiO_2^{2+} relative to H_2O_2 in our systems is contrasted with its enhanced reactivity observed in other studies.

Introduction

The reduction of hydrogen peroxide in acidic solution has been studied extensively. A one-electron transfer with concomitant formation of the hydroxyl radical is usually inferred for transi-

tion-metal ions.[1] On the other hand, a nonradical mechanism involving nucleophilic displacement on peroxide has been proposed

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(1) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.