Electron Transfer in Chemical and Biological Systems. Orbital Rules for Nonadiabatic Transfer

Sven Larsson

Contribution from Physical Chemistry 2, Department of Chemistry, University of Lund, Lund, Sweden. *Received July 29, 1980*

Abstract: The relative ability of molecules to act as bridges for nonadiabatic transfer of electrons between metal centers is studied by theoretical means. Orbital rules are established, which show that occupied as well as unoccupied orbitals contribute to the transfer rate. Rules for parallel bridges and bridges in series are derived. Molecules like cyanogen, pyrazine, and dipyridine are used as examples. It is found that π-electron systems often have high σ as well as π transfer rates. Aliphatic bridges with amine groups as end groups have a low π transfer ability but the σ transfer ability is comparable to that of π systems. The nonadiabatic transfer rate through molecular bridges which are not bonded to the transition metal ions is also examined.

I. Introduction

The transfer of electrons between metal ions in biological systems is an interesting phenomenon which has not yet been explained in any detail on the electronic level. A good example is provided by the cytochromes of the respiratory chain in which the transition metal ions Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} act as redox centers capable of accepting an electron for an extensive period of time. In a recent review article,[1] Moore and Williams noted a number of factors which seem to facilitate electron transfer and which depend on the electron structure of the intervening atoms and molecules. It remains to be shown exactly how electron-transfer rates depend on electron structure parameters. Actually the most basic question is perhaps in what sense the electron can be said to follow certain "pathways", and in that case why certain molecular groups are more apt than others to provide such pathways.

The electron-transfer proteins belong to a larger group of mixed valence systems which are able to exchange electrons between the transition-metal ions. Electron-transfer reactions are further very commonly studied in reaction kinetics. Of particular interest is the extensive work of Taube and his collaborators.[2,3] Common to most experimental studies is the difficulty involved in separating the influence of nuclear and electronic factors.[4] Theoretical studies have been made by Libby,[5] Marcus,[6] Hush,[7] and the Soviet school[8] and more recently by Hopfield,[9] Jortner, et al.,[10,11] and Schmidt.[12] Some studies are of a quantum-chemical nature, i.e., involving electron-structure calculations.[13-18] In spite of the latter work there are not yet any well-established criteria for electron-transfer properties. It is often contended that large overlap is necessary. Conjugated systems are believed to have good transfer properties via the π system, although the π orbitals overlap less than the σ orbitals. It is hoped that such somewhat contradictory issues will be resolved in the present study, which broadly speaking deals with the quantum chemistry of electron transfer.

In thermal electron transfer the nuclear motions have to take the system to a geometry where the energies of the two states corresponding to D–A and D^{+}–A^{-} are very close (P_3 in Figure 1).[5-7] This is referred to as the Franck-Condon condition. In the intersection region of the two potential surfaces one may apply the Landau–Zener theory.[19] In an adabatic case most of the "encounters" lead to electron transfer, i.e., the lowest surface is followed. The transfer rate depends only on the accessibility of the intersection region. The most favorable nuclear conditions occur when the equilibrium points P_1 and P_2 are close and their ground state energy difference small. Said in other terms the equilibrium nuclear configurations for the two oxidation states should not be very different. As pointed out by Marcus,[4,6] the transfer reaction should not be very exotermic, i.e., the difference between the metal centers in redox potential is small. These conditions seem to hold for the electron-transfer proteins.[1] Actually the transfer rate becomes temperature independent for very low temperatures for some systems,[20] which suggests that the intersection region is accessible from the lowest vibrational states.[11]

Due to the usually large distance between the metal centers in electron-transfer proteins the interaction element H_{12} (Figure 1) is very small. The system then tends to follow the surface denoted H_{11} and electron transfer takes place very rarely. This is the nonadabatic case. Electron-transfer proteins seem to be characterized by unfavorable electronic factors but, as discussed in the previous paragraph, favorable nuclear factors. The magnitude of the matrix element H_{12} is crucial for the transfer rate. In the Landau–Zener as well as in theories more pertinent to the biological problem,[9,10] the transfer rate is proportional to H_{12}^2.

In this paper we will make rough calculations of H_{12} and study how H_{12} depends on the properties of the molecular groups between the metal centers. A formula will be derived which expresses H_{12}

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[2] H. Taube "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, 1970.

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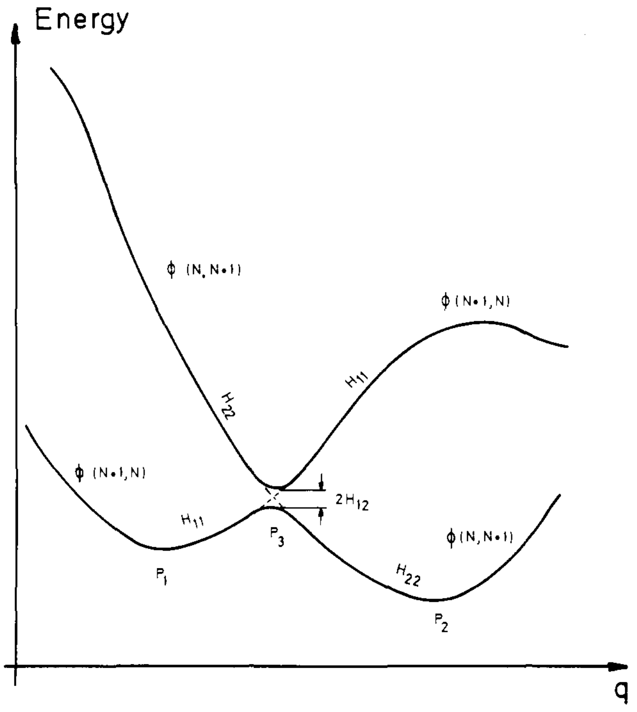

Figure 1. Energy surfaces for an electron transfer system. In P_1 the nuclear coordinates (q) are such that the additional electron is at M_1 in the ground state and vice versa in P_2. P_3 denotes an intersection region where the system may jump between the upper and lower surfaces.

in terms of orbital energies and coefficients at the bridge atom adjacent to the metal ions. From this formula simple rules will be derived, similar to the rules used to study reactivity.[21,22] Since the molecular groups between the metal ions in a biological system may be connected in very complicated ways, we will also derive formulas to calculate a total H_{12} from the values of the component groups.

II. Basic Theory

We may assume that the two electronic states in Figure 1 have been calculated in the Born–Oppenheimer approximation along an appropriate collective nuclear coordinate q. P_1 represents a point where the ligands around the center M_1 have the most favorable geometry along q for an additional electron at M_1. The excited state at P_1 is $\phi(N,N+1)$. The notation indicates that in $\phi(N,N+1)$ one electron has been transferred to M_2 relative to the ground state $\phi(N+1,N)$. The excitation energy $E(N,N+1) - E(N+1,N)$ is often in the visible region and may give rise to strong colors in mixed valence crystals. At P_2 the nuclear coordinates of the ligands around M_2 are the most favorable for an additional electron at M_2.

At P_3 the system may or may not jump the gap. The probability for jump is given by[19]

$$P = \exp[-8\pi H_{12}^2/v|S_1 - S_2|] \tag{1}$$

For small absolute values of the exponent the probability for electron transfer, i.e., for staying on the lowest energy curve, is

$$P' = 8\pi H_{12}^2/v|S_1 - S_2| \tag{2}$$

$2H_{12}$ is the gap at P_3 between the energy surfaces, v the velocity of the nuclei, and $S_1 - S_2$ the difference in slope at the crossing point between the surfaces without interaction. Atomic units are used. Energy (au) = $E_h = 4.360 \times 10^{-18}$ J; time (au) = $\hbar E_h^{-1} = 2.419 \times 10^{-17}$ s; length (au) = 1 bohr = 0.529 Å.

Equation 1 may be derived from the two-configuration eigenvalue problem[19]

$$\begin{vmatrix} H_{11} - \epsilon & H_{12} \\ H_{12} & H_{22} - \epsilon \end{vmatrix} = 0 \tag{3}$$

where H_{11} and H_{22} are the time-dependent unperturbed energies (Figure 1). The solutions represented by the full-drawn curves in Figure 1 are given by

$$\epsilon_{1,2} = \frac{H_{11} + H_{22}}{2} \pm \left[\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12}^2\right]^{1/2} \tag{4}$$

with the energy difference

$$\Delta\epsilon = \epsilon_1 - \epsilon_2 \geq 2H_{12} \tag{5}$$

where the equal sign holds for $H_{11} = H_{22}$.

The simplest possible treatment including the molecules of the medium between the redox centers is the "extended Hückel" (EH) method,[21] using the atomic functions 2s, $2p_x$, ..., etc. as basis functions and an empirical estimate of the matrix elements. Although the EH method is insufficient for an accurate treatment of the electronic problem we may use it here, since we are primarily interested in qualitative results. The two-configuration problem [eq 3] is now automatically transferred to an orbital problem represented by a Hamiltonian matrix where we let u_1 and u_2 be the 3d functions centered on M_1 and M_2, respectively. These 3d functions interact with the bridge atomic orbitals via the matrices η_1 and η_2. The EH matrix of the bridge is denoted **B** and corresponds to the atomic functions u_3, ..., u_{n+2}. By partitioning[23] the eigenvalue problem may be reduced to a two-configuration problem for the two 3d orbitals of interest:

$$\det\left|\begin{array}{cc|c} a_1 - \epsilon_1 & \delta_{12} & \eta_1 \\ \delta_{12} & a_2 - \epsilon_1 & \eta_2 \\ \hline \eta_1^+ & \eta_2^+ & \mathrm{B} - \epsilon \end{array}\right| = 0 \rightarrow$$

$$\det\left|\begin{pmatrix} a_1 - \epsilon_1 & \delta_{12} \\ \delta_{12} & a_2 - \epsilon_1 \end{pmatrix} - \begin{pmatrix} \eta_1(\mathrm{B} - \epsilon)^{-1}\eta_1^+ & \eta_1(\mathrm{B} - \epsilon)^{-1}\eta_2^+ \\ \eta_2(\mathrm{B} - \epsilon)^{-1}\eta_1^+ & \eta_2(\mathrm{B} - \epsilon)^{-1}\eta_2^+ \end{pmatrix}\right| = 0 \tag{6}$$

Equation 6 defines a two-valued function $\epsilon_1 = \epsilon_1(\epsilon)$ (Figure 2). The solutions of the eigenvalue problem are obtained by imposing the condition

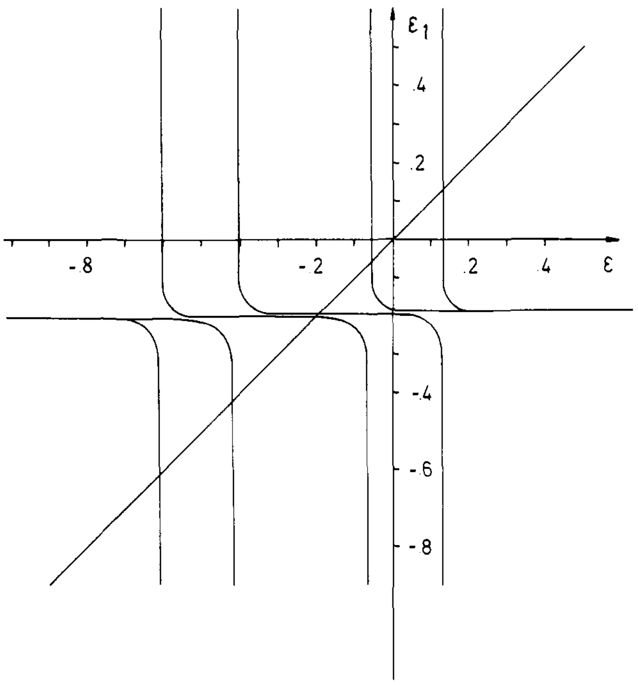

Figure 2. The ϵ_1 roots of eq 12 as a function of ϵ for the case of a cyanogen bridge. The solutions of the secular problem are in the intersection points with $\epsilon_1 = \epsilon$. Only π orbitals are included.

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(21) R. Hoffman, *J. Chem. Phys.*, **45**, 397 (1966).

(22) (a) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968); (b) L. Salem, *ibid.*, **90**, 543 (1968).

(23) P. O. Löwdin, *J. Mol. Spectrosc.*, **10**, 12 (1963); *J. Math. Phys.*, **3**, 969 (1962).

$$\epsilon_1 = \epsilon \qquad (7)$$

The vertical asymptotes are at the eigenvalues of the matrix **B**. The horizontal asymptotes are $\epsilon_1 = a_1$ and $\epsilon_1 = a_2$ since the direct interaction between the metal centers, δ_{12}, is small enough to be neglected in our case. The functions $\epsilon_1(\epsilon)$ of Figure 2 are quite typical for our case of weak interactions between the metal centers. The eigenvalues of **B** are very close to the eigenvalues of the full matrix. The two new eigenvalues correspond to the orbitals of importance for electron transfer. They are close to the energies of the metal ion orbitals, a_1 and a_2, but are modified slightly by the bridge part of the 2 × 2 secular matrix. Close to a_1 and a_2, but away from the vertical asymptotes, we may replace ϵ by $a = a_1 = a_2$ or an average of a_1 and a_2 if they are different. This corresponds to one step in the iterative process of the partitioning technique.[23] The effective interaction matrix element between M_1 and M_2 is thus represented by

$$\delta = \eta_1(\mathbf{B} - a)^{-1}\eta_2^{+} = H_{12} \qquad (8)$$

In section IV we will derive equations based on eq 8 which will make it possible to estimate δ for an almost arbitrary shape of the bridge, provided the δ values for simple bridges are known.

For simplicity the overlap matrix is assumed to be a unit matrix. This is normally done in the more advanced CNDO and INDO methods. In the numerical applications to be discussed later, it was found that this simplification did not affect the conclusions in any significant manner.

III. Orbital Structure

Before proceeding further it is necessary to examine the general orbital structure of the bridge and metal ions. In the EH theory[21] the metal ion 3d orbitals fall in the gap between the HOMO and LUMO of the bridge. In the case of a stronger bond to the bridge than to the other ligands, the 3d orbital between the metal ion and the bridge is the most antibonding one of the 3d-type MO and therefore has the highest energy of the 3d orbitals. If the bond to other ligands is stronger, the 3d orbitals directed along these bonds have the highest energies. In the case of Cu^{+}/Cu^{2+}, where only one electron is missing from two complete $3d^{10}$ shells, the hole may thus be σ or π (or both) with respect to the bridge depending on where the binding forces are the strongest.

In the case of Fe^{3+}/Fe^{2+} only 11 electrons occupy the 3d shells. The highest occupied orbital will then be a π orbital. Depending on the circumstances we may have configurations like

$$\begin{gathered} \text{a, } (xz - xz)^2(xz + xz); \qquad \text{b, } (xz - xz); \\ \text{c, } (xz - xz)^2; \qquad \text{d, } (xz - xz)^2(yz - yz); \\ \text{e, } (xz - xz)^2(yz - yz)^2 \end{gathered} \qquad (9)$$

In cases d and e the transfer may take place either via the xz or yz orbitals, since both $(xz - xz)$ and $(yz - yz)$ are occupied but $(xz + xz)$ and $(yz + yz)$ are unoccupied.

IV. Orbital Rules for Transfer through One Molecular Bridge

Without too much loss of generality we may assume that the bridge is connected to the metal ion only via two atomic orbitals which are numbered 1 and n, respectively. The system is then characterized by the hamiltonian matrix

$$\mathcal{H} = \left(\begin{array}{cc|cccc} a_1 & 0 & \eta_1 & 0\cdots 0 & & 0 \\ 0 & a_2 & 0 & 0\cdots 0 & & \eta_2 \\ \hline \eta_1 & 0 & & & & \\ \cdot & \cdot & & & & \\ \cdot & \cdot & & \mathbf{B} & & \\ \cdot & \cdot & & & & \\ 0 & \eta_2 & & & & \end{array}\right) \qquad (10)$$

Diagonalization of **B** yields the eigenvalues $b_1, b_2, ..., b_3$ and the eigenvector matrix **C**. The hamiltonian matrix $\mathcal{H}$ may now be transformed into

$$\mathcal{H}' = \mathbf{U}^{+}\mathcal{H}\mathbf{U} = \left(\begin{array}{cc|ccc} a_1 & 0 & \eta_1 c_{11} & \eta_1 c_{12}\cdots & \eta_1 c_{1n} \\ 0 & a_2 & \eta_2 c_{n1} & \eta_2 c_{n2}\cdots & \eta_2 c_{nn} \\ \hline \eta_1 c_{11} & \eta_2 c_{n1} & b_1 & 0\cdots & 0 \\ \eta_1 c_{12} & \eta_2 c_{n2} & 0 & b_2 & 0 \\ \cdot & \cdot & \cdot & \ddots & \\ \cdot & \cdot & \cdot & & \\ \cdot & \cdot & \cdot & & \\ \eta_1 c_{1n} & \eta_2 c_{nn} & 0 & 0 & b_n \end{array}\right) \qquad (11)$$

where

$$\mathbf{U} = \left(\begin{array}{cc|cc} 1 & 0 & 0\cdots & 0 \\ 0 & 1 & 0\cdots & 0 \\ \hline 0 & 0 & & \\ \cdot & \cdot & & \\ \cdot & \cdot & \mathbf{C} & \\ \cdot & \cdot & & \\ 0 & 0 & & \end{array}\right) \qquad (12)$$

The partitioned secular matrix is then equal to

$$\begin{pmatrix} a_1 - \epsilon_1 & 0 \\ 0 & a_2 - \epsilon_1 \end{pmatrix} - \begin{pmatrix} \eta_1 c_{11}\cdots\eta_1 c_{1n} \\ \eta_2 c_{n1}\cdots\eta_2 c_{nn} \end{pmatrix}\begin{pmatrix} (b_1 - \epsilon)^{-1} & 0 \\ 0 & \ddots (b_n - \epsilon)^{-1} \end{pmatrix}\begin{pmatrix} \eta_1 c_{11} & \eta_2 c_{n1} \\ \cdot & \cdot \\ \cdot & \cdot \\ \cdot & \cdot \\ \eta_1 c_{1n} & \eta_2 c_{nn} \end{pmatrix} =$$

$$\begin{pmatrix} a_1 - \sum\limits_{\nu}\dfrac{\eta_1{}^2 c_{1\nu}{}^2}{b_\nu - \epsilon} - \epsilon_1 & \sum\limits_{\nu}\dfrac{\eta_1\eta_2 c_{1\nu}c_{n\nu}}{b_\nu - \epsilon} \\ \sum\limits_{\nu}\dfrac{\eta_1\eta_2 c_{1\nu}c_{n\nu}}{b_\nu - \epsilon} & a_2 - \sum\limits_{\nu}\dfrac{\eta_2{}^2 c_{n\nu}{}^2}{b_\nu - \epsilon} - \epsilon_1 \end{pmatrix} \qquad (13)$$

According to the discussion above we may replace ϵ by

$$a = a_1 - \sum_{\nu}\frac{\eta_1{}^2 c_{1\nu}{}^2}{b_\nu - a_1} = a_2 - \sum_{\nu}\frac{\eta_2{}^2 c_{n\nu}{}^2}{b_\nu - a_2} \qquad (14)$$

or an average if the two right-member quantities are different. The effective interaction matrix element δ, cf. eq 7, will be

$$\delta = \eta_1\eta_2\sum_{\nu}\frac{c_{1\nu}c_{n\nu}}{b_\nu - a} \qquad (15)$$

where the summation extends over all the bridge orbitals.

Equation 15 shows the importance of a large interaction between the metal ion and the atomic orbitals of the bridge (large η_1 and η_2). In the EH approximation[21] this means large overlap according to the Wolfsberg–Helmholtz formula[24]

$$\eta_1 = K{\cdot}S_{12}(a_1{}^2 + b_1{}^2)/2 \qquad (16)$$

An orbital which contributes to conduction should have large coefficients on the atoms adjacent to the metal ions (large $c_{1\nu}{\cdot}c_{n\nu}$) and an orbital energy b_ν close to the energy of the metal 3d orbital. Somewhat surprisingly it makes no difference if the orbital is occupied or not. The reason is that after interaction between the metal ion and the bridge the 3d orbitals mix into the occupied bridge orbitals which permits a corresponding mix of the bridge orbitals into the 3d orbitals.

Equation 15 allows us to establish orbital rules for electron transfer. Figure 3a shows the interaction between the 3d orbitals and an occupied bridge orbital with $c_{1\nu}c_{n\nu} > 0$. The orbital energy of the 3d(+−) MO is raised. Figure 3b shows the interaction between 3d(+−) and an unoccupied bridge orbital with $c_{1\nu}c_{n\nu} > 0$. In this case the energy of the transferring orbital is lowered. $b_\nu - a$ is positive contrary to the case for an occupied orbital.

3d(++) combines with bridge orbitals with negative $c_{1\nu}c_{n\nu}$. The orbital energy is again lowered by interaction with an unoccupied orbital. The contributions to δ have opposite signs compared to the contributions for 3d(+−). An occupied bridge orbital with $c_{1\nu}c_{n\nu} > 0$ and an unoccupied bridge orbital with $c_{1\nu}c_{n\nu} < 0$ both give contributions with the same sign to δ—the first one by raising the energy of 3d(+−) and the latter by lowering the energy of 3d(++).

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(24) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

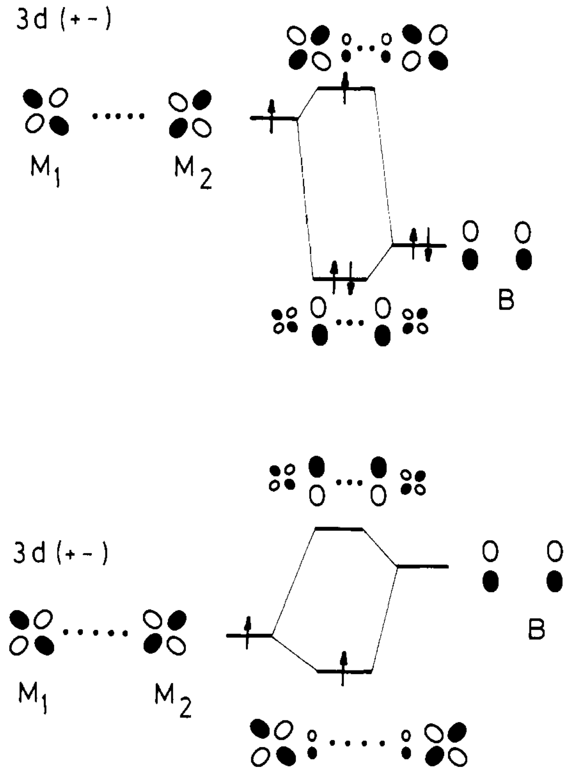
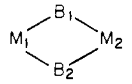


Figure 3. Interaction between the metal center 3d orbitals and the occupied (a, top) and unoccupied (b, bottom) bridge orbital.

V. Double Bridge

The case of a double bridge (I)



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leads to the hamiltonian matrix

$$\mathcal{H} = \left(\begin{array}{cc|cc} a_1 & 0 & \eta_1 & \eta_2 \\ 0 & a_2 & & \\ \hline \eta_1^+ & & \mathbf{B}_1 & 0 \\ \eta_2^+ & & 0 & \mathbf{B}_2 \end{array}\right) \quad (17)$$

assuming no interaction between the atomic orbitals on different bridge molecules. By partitioning the eigenvalue problem of $\mathcal{H}$ is reduced to

$$\left| \begin{pmatrix} a_1 - \epsilon & 0 \\ 0 & a_2 - \epsilon \end{pmatrix} - \eta_1(\mathbf{B}_1 - \epsilon)^{-1}\eta_1 - \eta_2(\mathbf{B}_2 - \epsilon)^{-1}\eta_2 \right| = 0 \quad (18)$$

From this equation it follows that the effective interaction matrix element is obtained as a sum of matrix elements of the individual bridges.

VI. Molecular Groups in a Chain

We will now derive a general formula for a bridge consisting of two molecular or atomic groups $\mathbf{B}_1$ and $\mathbf{B}_2$ in a chain between the redox centers M_1 and M_2 (II).

$$\underset{\text{II}}{M_1\text{—}B_1\text{—}B_2\text{—}M_2}$$

The hamiltonian matrix is:

$$\mathcal{H} = \left(\begin{array}{cc|cc} a_1 & 0 & \eta_1 & 0 \\ 0 & a_2 & 0 & \eta_2 \\ \hline \eta_1^+ & 0 & \mathbf{B}_1 & \beta \\ 0 & \eta_2^+ & \beta & \mathbf{B}_2 \end{array}\right) \quad (19)$$

$\mathbf{B}_1$ is interacting with M_1 through the matrix η_1 and $\mathbf{B}_2$ with M_2 through η_2. $\mathbf{B}_1$ and $\mathbf{B}_2$ are interacting via β. To calculate the inverse of the bridge secular matrix we make use of the following formula[23]

$$(\mathbf{D} + \beta)^{-1} = \mathbf{D}^{-1} - \mathbf{D}^{-1}\beta\mathbf{D}^{-1} + \mathbf{D}^{-1}\beta\mathbf{D}^{-1}\beta\mathbf{D}^{-1} + \ldots \quad (20)$$

We assume that the norm of $\mathbf{D}^{-1}\beta$ is small enough for this series to converge and obtain

$$\begin{pmatrix} \mathbf{B}_1 - \epsilon & \beta \\ \beta^+ & \mathbf{B}_2 - \epsilon \end{pmatrix}^{-1} = \begin{pmatrix} (\mathbf{B}_1 - \epsilon)^{-1} & 0 \\ 0 & (\mathbf{B}_2 - \epsilon)^{-1} \end{pmatrix} - \begin{pmatrix} (\mathbf{B}_1 - \epsilon)^{-1} & 0 \\ 0 & (\mathbf{B}_2 - \epsilon)^{-1} \end{pmatrix} \begin{pmatrix} 0 & \beta \\ \beta^+ & 0 \end{pmatrix} \begin{pmatrix} (\mathbf{B}_1 - \epsilon)^{-1} & 0 \\ 0 & (\mathbf{B}_2 - \epsilon)^{-1} \end{pmatrix} + \ldots \quad (21)$$

The third term in the series gives a contribution only in the diagonal and therefore has no interest in the calculation of an effective δ. We assume that the convergence of eq 20 is sufficiently rapid to neglect all higher order terms. The second term in eq 21 is equal to

$$\begin{pmatrix} 0 & (\mathbf{B}_1 - \epsilon)^{-1}\beta(\mathbf{B}_2 - \epsilon)^{-1} \\ (\mathbf{B}_2 - \epsilon)^{-1}\beta^+(\mathbf{B}_1 - \epsilon)^{-1} & 0 \end{pmatrix} \quad (22)$$

Multiplying by the matrix η we obtain the following off-diagonal matrix

$$\eta_1(\mathbf{B}_1 - \epsilon)^{-1}\beta(\mathbf{B}_2 - \epsilon)^{-1}\eta_2^+ \quad (23)$$

Comparison with eq 6 gives a rule for adding a molecular or atom to the bridge as in (II).

If $\mathbf{B}_1$ and $\mathbf{B}_2$ are prediagonalized the following substitutions have to be made [cf. eq 11]:

$$\eta_1 \rightarrow \eta_1\mathbf{C}_1;\ \eta_2 \rightarrow \eta_2\mathbf{C}_2; \qquad \beta \rightarrow \mathbf{C}_1^+\beta\mathbf{C}_2 = \beta' \quad (24)$$

We then obtain

$$\delta = \eta_1\eta_2 \sum_{\nu,\mu} \frac{c_{1\nu}}{b_\nu - a} \beta_{\nu\mu}' \frac{c_{n\mu}}{b_\mu - a} \quad (25)$$

It is straightforward to extend eq 23 and 25 to 3, 4, ..., etc. intervening atoms or molecules. The equation then obtained will be more general than the following formula sometimes seen in the literature.

$$\delta = \eta_1\beta_1\beta_2 \ldots \beta_{n-1}\eta_2/(b_1 - a)(b_2 - a)\ldots(b_n - a) \quad (26)$$

This formula refers to n intervening atoms with only one orbital per atom. It should be remembered that eq 26 as well as eq 23 and 25 only apply in the case of weak interactions between the atoms in the chain, i.e.

$$\frac{\beta_k'}{(b_k - a)(b_{k+1} - a)} \ll 1 \text{ for all } k \quad (27)$$

VII. Calculations

Even if the contributions to δ may be estimated from eq 15 by using tables or pictures of molecular orbitals,[25] it is instructive to carry out calculations of the EH type directly. This was done by using standard parameter sets.[26-28] The geometries were obtained from crystallographic data or by using distances and angles for related molecules. The difference in energies of 3d(++) and 3d(+−) was calculated and put equal to 2δ. The results are given in Table I. In some cases it was necessary to solve the eigenvalue problem in double precision to keep enough significant figures for calculation of the small energy difference 2δ.

In test calculations it was found that leaving out the ligands other than the bridge did not affect the value of δ significantly. These ligands were therefore left out in the majority of calculations. In the case of Cu^+/Cu^{2+} the singly occupied orbital will

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(25) See, for example, W. L. Jorgensen and L. Salem "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973.

(26) C. Clack, *Mol. Phys.*, **27**, 1513 (1974).

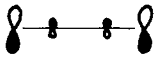
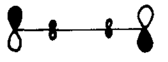
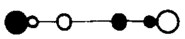
(27) G. Burns, *J. Chem. Phys.*, **42**, 1521 (1964).

(28) The program is an extension of QCPE 261 kindly provided by Mr. Manuel Braga.

Table I. Calculated values of δ

bridge molecule	M_1-M_2 dist, Å	δ Fe^{2+}/Fe^{3+} (π)	Cu^+/Cu^{2+} (σ)
cyanogen	7.7	3.9×10^{-3}	4.6×10^{-4}
pyrazine	6.8	3.5×10^{-3} (xz) 3.8×10^{-4} (yz)	1.1×10^{-2}
pyrazine	7.9	2.2×10^{-4} (xz) 1.6×10^{-5} (yz)	1.7×10^{-3}
p-dipyridine (planar)	10.8	1.4×10^{-3}	1.7×10^{-3}
p-dipyridine (orthogonal planes)	10.8	3.2×10^{-4}	4.2×10^{-3}
m-dipyridine (planar)	7.6	1.9×10^{-4}	1.4×10^{-3}
imidazolate	6.2	2.3×10^{-3}	2.9×10^{-3}
diamine	4.8	4.3×10^{-3}	1.3×10^{-2}
1,2-diaminoethane	7.2	5.1×10^{-4}	4.7×10^{-3}
1,4-diaminobutane	9.7	3.3×10^{-6}	1.6×10^{-3}
1,6-diaminohexane	12.1	1.9×10^{-7}	8.5×10^{-4}
1,2-diaminoethane (orthogonal)	4.8	3.8×10^{-3}	1.8×10^{-3}
1,2-diaminoethane (orthogonal)	4.8	2.7×10^{-3}	0.8×10^{-3}
no bridge	4.8		4.8×10^{-5}

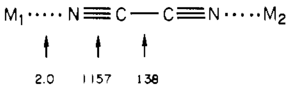
Table II. MO for Cyanogen (σ_4 = HOMO)

Orbital N≡C —— C≡N		Energy (a.u.)
σ_5		0.14
π_3		-0.06
σ_4		-0.38
π_2		-0.41
σ_3		-0.43
π_1		-0.61

then always be the antibonding σ orbital of the bond between metal ion and bridge. As was discussed above in a real case Cu^{2+} may bind more strongly to the other ligands and this leads usually to smaller values of δ since the singly occupied orbital in that case is not directed along the bond and therefore overlaps less strongly with the bridge. The values in Table I always refer to a σ bond between Cu and bridge.

VIII. Results

a. Cyanogen. The π orbitals of cyanogen (III) are given in Table II. The unoccupied orbital π_3 decreases the in-phase

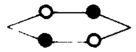
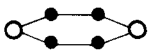
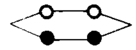
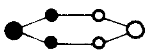
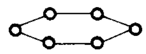


III

3d(+ −) orbital energy, whereas the occupied orbital π_2 increases the orbital energy of the out-of-phase combination. Both orbitals thus contribute to an increase of δ. The contribution from the other two π orbitals is less. This results in good π conduction properties for cyanogen in spite of the rather large distance between the metal centers.

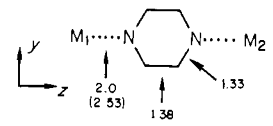
For the σ orbitals the situation is the opposite, since the contributions tend to cancel out. The resulting value is small compared to that of many other systems (Table I).

Table III. π MO for Pyrazine (π_1, π_2, and π_3 Are Occupied)

Orbital		Energy (a.u.)
π_6		0.11
π_5		0.01
π_4		-0.07
π_3		-0.35
π_2		-0.40
π_1		-0.66

The good π-transfer properties of cyanogen are in agreement with experiments. The Ru^{2+}/Ru^{3+} complex (isoelectronic with Fe^{2+}/Fe^{3+}) has been found to have a single C≡N stretching frequency in a region midway between those for the Ru^{2+} and Ru^{3+} complexes,[29] indicating that the odd electron is delocalized on the 10^{-13} time scale. With the use of the calculated value of δ, the frequency (δ/π) will be 5×10^{13} s^{-1} which should be interpreted to mean that the electronic factors are not rate limiting in this case (adiabatic transfer).

b. Pyrazine. Pyrazine (IV) has one unoccupied π orbital of



IV

low energy (π_4, table 3) and one occupied (π_2) which leave large constributions with the same sign to δ. π_3 and π_5 do not contribute due to the zero amplitude at the nitrogens, and the contributions from π_1 and π_6 are unimportant. Again we find good π-transfer properties although less good than those for cyanogen. The σ-transfer properties are also remarkably good for pyrazin (Table I). This is due to the nitrogen lone pair orbitals, which strongly overlap the metal ion 3d orbitals. The lone-pair orbitals which give contributions to the δ with different signs [eq 15] have to be significantly different in energy to give a large total contribution. In the EH calculation the energy difference turned out to be ~0.1 au which is sufficient to explain a rather large contribution to δ. The calculations including the overlap matrix gave values of δ within 15% of those without this matrix.

The experimental results on various Ru^{2+}/Ru^{3+} are somewhat hard to interpret.[30] Mössbauer spectra[31] suggest trapped valencies even on the time scale of $\sim 10^{-9}$. These results were obtained at 4 K and cannot be directly compared to results obtained at room temperature. The major problem with the comparison to experimental results is that the geometries in solution are not known. In a complex like $(NH_3)_5Ru$-pyz-$Ru(NH_3)_5$ it is possible that the orbital ordering is different in the 2+ 2+, 2+ 3+, or 3+ 3+ complexes. $x^2 - y^2$ and z^2 are unoccupied (the x axis is perpendicular to the molecular plane). $xz(+-)$ is stabilized by back-donation and certainly occupied, as is probably $yz(+-)$. The order between $xz(++)$, $yz(++)$, and the two xy orbitals is less clear,

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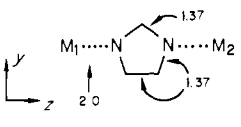
(29) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975).
(30) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(31) C. Creutz, M. Good, and S. Chandra, *Inorg. Nucl. Chem. Lett.*, 1 (1973).

however. If one of the *xy* orbitals is unoccupied in the 3+ 3+ case but *xz* is occupied, the bonding to the NH_3 ligands in the *xy* plane is increased at the expense of the bonding to pyrazine. This may affect the bond lengths considerably. For 2+ 3+ complex the orbital ordering is even more crucial since if the *xz*(+) orbital is filled the electron transfer has to go via the *yz* orbital with a considerably smaller transfer rate. In Table III are given results for two different pyz–Fe distances for *yz* as well as *xz* transfer.

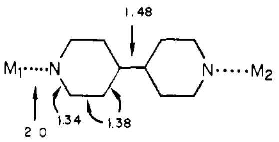
In the case of Cu^+/Cu^{2+} the molecular orbital ordering is also of the greatest importance. If an $x^2 - y^2$ orbital is left unoccupied rather than a z^2 orbital, the distance Cu–pyz is increased and at the same time the σ channel closed. The transfer is then only possible via the $x^2 - y^2$ channel, in which case the transfer rate is very small.

c. Imidazolat (V). Imidazol is one of the axial ligands to Fe–porphyrin in some cytochromes. In the exploratory calculations reported here the metal ions were placed as in the original imidazol pump model[32] which nowadays has historical interest only. We find π transfer almost as good as for pyrazine. The σ transfer is less rapid than for pyrazine but still of the same magnitude as the π transfer. This may be of importance in the blue copper proteins where, at least in the case of plastocyanin, two histidine imidazols are bonded to a copper ion.[33]

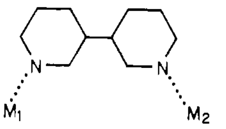


V

Dipyridine. Two cases were compared, with the two nitrogens in the para and meta positions, respectively. Para-dip (VI) turns out to have a δ^2 only a factor of 7 less than pyrazin in spite of the considerably longer distance between M_1 and M_2. δ^2 for meta-dip (VII) is smaller than δ^2 for para-dip by a factor of 50. In the molecular orbital picture this may be explained by the rather large stabilization of the MO with the same phase on the two pyridines, due to the rather strong interaction at the C–C bridge. The in-phase $3d_1 - 3d_2$ will have a larger difference in energy for the occupied orbitals and will therefore be less destabilized than $3d_1 + 3d_2$ due to the antibonding interaction. The interaction with the unoccupied orbitals tends to increase the energy gap between $3d_1 - 3d_2$ and $3d_1 + 3d_2$ because of back-bonding. In the meta position, however, the MO coefficients are smaller for those MO's which interact strongly across the bridge, whereas the orbitals which have large coefficients at the meta positions interact less strongly. The contributions to δ are therefore cancelling each other to a large extent.

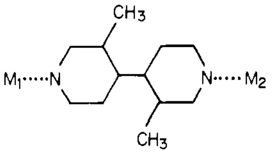


VI



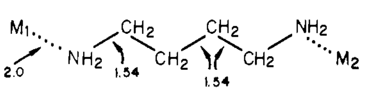
VII

A series of Co^{3+}/Ru^{2+} binuclear complexes with dip and related molecules as bridges have been studied by Taube and co-workers.[34-36] Since the substitutions are in the bridge or close to the bridge the metal ions are in the same environment approximately in the different cases. The differences in transfer rate should then be due to differences in nonadiabatic electronic factors.[35] At first rather similar values were found for the transfer-rate constant. This was surprising since in particular 3,3′-dimethyl-4,4′-dipyridine (VIII) was expected to have a small transfer rate compared to dip since the planes of the two rings are more or less perpendicular due to conformational constraints from the methyl groups. However, our calculations suggest that the difference in rate should not be too large (if the planes are strictly perpendicular a factor 18). Likewise by eq 23 substitutions in the bridge between the two pyridine rings cannot be expected to decrease the transfer rate dramatically. Unfortunately extensive comparison with experiments would be difficult since the geometries of these complexes in solution are not known.



VIII

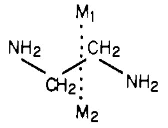
NH_2–$(CH_2)n$–NH_2. The π-transfer rate for these molecules (IX) is extremely small. The σ-transfer rate is surprisingly large, less than for pyrazine and dipyridine but considerably larger than for cyanogen. The former result agrees qualitatively with experiments on the Ru^{2+}/Ru^{3+} compound of $C(CH_2NH_2)_4$.[36]



IX

The σ transfer through the saturated diamines is somewhat slower than that for the conjugated systems for the same distance between the metal ions. This reflects the longer distances between the carbon atoms in the aliphatic chain.

Nonbonded Bridge. One may ask whether electrons can be transferred from one metal ion to another perpendicular through the peptide chain. The results, diamineethane (X) (Table I, entries marked "perp") suggest that the transfer rate is higher than in direct transfer (entry "no bridge"). On the other hand comparing with the bonded diamine complexes at the same M_1–M_2 distance, δ for π transfer is slightly less but δ for σ transfer much less. Some caution is necessary, however, regarding the direct transfer between the metal atoms. The EH method cannot be expected to behave accurately at a long distance between the atoms. Actually Newton[18] suggests on the basis of more accurate calculations that two Fe ions interact directly even at the distance 6.9 Å.



X

IX. Conclusion

In this paper an attempt is made to understand electron transfer between metal redox centers on the basis of the molecular orbital structure of the bridging molecules. A simple rule has been derived [eq 15] which shows the importance of orbital energy as well as symmetry and overlap with metal ions. In reality there are usually more than one possible bridge. Equation 17 shows that the contributions to δ from the various bridges should be added. Finally eq 22 shows how contributions from different molecules along a chain should be added to obtain an effective δ. This equation is only applicable in the case of weak interactions, however.

Some calculations of extended Hückel type were carried out to exemplify the theory. The comparison with experiments is usually not straightforward. The degree of localization for cyanogen–pyrazin–dipyridine is reproduced by the calculations. The calculations also show that σ transfer may be more important

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[32] D. W. Urry and H. Eyring, *J. Theor. Biol.*, **8**, 198, 214 (1965).

[33] P. M. Coleman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature* (*London*), **272**, 319 (1978).

[34] S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).

[35] H. Fischer, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **98**, 5512 (1976).

[36] K. Rieder and H. Taube, *J. Am. Chem. Soc.*, **99**, 7891 (1977).

for the Cu^+/Cu^{2+} pair than previously thought.

We have not attempted any calculation of the rate constant for electron transfer. This would require detailed information of the energy surfaces and is not feasible within the EH model used here. Due to the complicated nature of biological structures it is doubtful whether any quantum chemical method in current use could contribute to the solution of this problem.

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Molecular and Electronic Structures of Two Quadruply Bonded Ditungsten Compounds and a Dimolybdenum Homologue

F. Albert Cotton,*[1a] Michael W. Extine,[1b] Timothy R. Felthouse,[1a] Brian W. S. Kolthammer,[1a] and Dennis G. Lay[1a]

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received January 2, 1981*

Abstract: The structures of the isomorphous compounds $W_2Cl_4(PMe_3)_4$ (**1a**) and $Mo_2Cl_4(PMe_3)_4$ (**1b**) and also that of $W_2Cl_4(Me_2PCH_2CH_2PMe_2)_2$ (**2**) are reported and discussed. Compounds **1a** and **1b** crystallize in space group $C2/c$ with the following unit cell parameters (each given for **1a** and **1b** in that order): a = 18.296 (3) Å, 18.369 (2) Å; b = 9.192 (2) Å, 9.172 (2) Å; c = 17.274 (2) Å, 17.331 (4) Å; β = 115.34 (1)°, 115.33 (1)°; V = 2626 (2) Å^3, 2639 (2) Å^3. With Z = 4 each molecule lies on a special position with the M–M bond coincident with a crystallographic twofold axis. The structures have been refined to R_1 = 0.027, 0.018 and R_2 = 0.038, 0.027 with inclusion of all hydrogen atoms. The sets of chlorine and phosphine ligands are staggered within themselves while the overall ligand arrangement about the dimetal unit defines an eclipsed conformation. The approximate symmetry is D_{2d}. The metal–metal bond lengths are 2.262 (1) and 2.130 (1) Å for **1a** and **1b**, respectively. Crystals of **2** belong to the space group $P2_1/n$ with a cell of dimensions a = 9.150 (2) Å, b = 12.029 (1) Å, c = 14.245 (2) Å, and β = 105.88 (2)°. The structure has been refined to R_1 = 0.029 and R_2 = 0.038. Two tungsten dimers and a toluene molecule reside on crystallographic centers of inversion within the unit cell. One dmpe ligand is chelated to each metal atom, and to satisfy the center of inversion, the entire arrangement of ligands then corresponds approximately to C_{2h} symmetry. The W–W distance is 2.287 (1) Å. The UV–visible spectra of **1a** and **1b** are reported, and the variations in M–Cl and M–P distances as a function of cis and trans stereochemistry as well as the change from Mo to W are discussed.

The preparation [2] and structural characterization[3] of quadruply bonded ditungsten compounds of the type $W_2X_4(PR_3)_4$, where the four PR_3 ligands may also be replaced by two diphosphines, has recently been reported in preliminary form. A series of papers describing this work in detail, of which this is the first, will be appearing in the near future.

In this paper we report the structures of the three compounds $W_2Cl_4(PMe_3)_4$ (**1a**), its molybdenum analogue $Mo_2Cl_4(PMe_3)_4$ (**1b**), and $W_2Cl_4(dmpe)_2$ (**2**), where dmpe is a code for $Me_2PCH_2CH_2PMe_2$. The particular points of interest, upon which the decision to cover these three compounds together in one paper was based, are the following: (1) the comparison of **1a** and **1b** provides new insight into the similarities, and differences, between molybdenum and tungsten in their capacity for the formation of multiple M–M bonds; (2) the comparison of **1a** and **2** affords the first opportunity to evaluate the effect of changing the geometric arrangement of ligands on each metal atom from trans to cis while making, as nearly as possible, no change in the nature of the ligands themselves. Compound **2** is also interesting intrinsically because it is the first example of a chelating, rather than bridging, diphosphine ligand in dinuclear, multiply bonded M–M chemistry.

Experimental Section

All chemicals used were of reagent grade or of comparable purity. All reagents were purchased from commercial suppliers. All manipulations were carried out under anhydrous anaerobic conditions unless otherwise specified. Tungsten(IV) chloride was prepared by the sodium amalgam reduction of WCl_6 in tetrahydrofuran.

Mass spectral measurements were performed at 10 eV on an AEI MS902 mass spectrometer.[4] These spectra were obtained by the direct probe insertion method with an ionization chamber temperature of 190 °C. A Cary 17 spectrophotometer was employed to obtain solution UV–visible spectra of **1a** and **1b**.

Preparation of the $M_2Cl_4(PMe_3)_4$ Complexes. The tungsten compound **1a** was prepared according to the literature method[2] by the alkali metal reduction of WCl_4 in the presence of 2 equiv of trimethylphosphine. The green product was purified by filtering a toluene solution of $W_2Cl_4(PMe_3)_4$ through a 3 × 6 cm column of Florisil. The filtrate was concentrated in vacuo and cooled to −10 °C to induce crystallization of complex **1a**.

The molybdenum analogue was prepared by stirring a suspension of $K_4Mo_2Cl_8$[5] in methanol at room temperature in the presence of a twofold excess of trimethylphosphine. After 70 h, the red starting material had been replaced by a dark blue solid. This precipitate was collected, washed with water, and dried under vacuum. Compound **1b** was further purified by dissolution in a minimum amount of toluene followed by filtration of the resulting solution through a 3 × 10 cm column of Florisil and removal of the solvent under reduced pressure.

X-ray Diffraction Studies. Single crystals of compound **1b** suitable for crystallographic study were obtained by slow cooling of a toluene solution from room temperature to −10 °C. Crystals of complexes **1a** and **2** were obtained from Professor R. R. Schrock. Crystals were examined by using the automatic search routine on an Enraf-Nonius CAD-4 dif-

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(1) (a) Texas A&M University. (b) Molecular Structure Corporation.

(2) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(3) Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1431.

(4) Mass Spectral measurements were performed by Dr. G. Eigendorf of the University of British Columbia.

(5) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7.

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