Coordination Chemistry Reviews, 60 (1984) 107–129
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MIXED-VALENCE MOLECULES: ELECTRONIC DELOCALIZATION AND STABILIZATION

DAVID E. RICHARDSON * and HENRY TAUBE
Department of Chemistry, Stanford University, Stanford, CA 94305 (U.S.A.)

(Received 16 November 1983)

CONTENTS

A. INTRODUCTION

A reawakening of interest in mixed-valence compounds is traceable to two general papers dealing with them which were published in 1967 [1,2] and to reports only a short time later of the first deliberate syntheses of substitution-inert (robust) mixed-valence molecules [3,4]. The combined properties of molecularity and substitution inertia make possible studies which are difficult or impossible for mixed-valence lattice compounds on the one hand, and labile molecular species on the other. The robust molecular mixed-valence compounds offer some unique investigative advantages, and the advances which have been made by exploiting these are stressed in this article.

Molecularity implies that the species can be studied in solution as well as in the solid state. Thus the effect on the properties of the species brought about by changing the environment can be traced. Moreover, the oxidation–reduction potentials can be measured, and though until now few have taken advantage of the possibilities for the systematic study of other chemical reactions, this is an inviting and important subject. Substitution

---

* Current address: Department of Chemistry, University of Florida, Gainesville, FL 32611, U.S.A.

0010-8545/84/$06.90

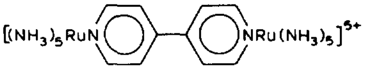
inertia implies that the species retain their integrity in solution, so that the observations made on the solutions can be much more readily interpreted than is the case for labile molecular species. An important advantage which molecular species have over the non-molecular is that composition can be varied almost continuously over a wide range. This is particularly true of the substitution-inert or robust species where compositions obtained by kinetic control become available for study.

In the field of traditional coordination compounds, few redox couples simultaneously meet the criteria that states differing by one oxidation unit are stable and that they each form robust complexes. Among classical complexes, the III/II couples of the iron group offer the most abundant opportunities. Ruthenium has the advantage over iron that the complexes are always low-spin, (Ru(III), πd^5; Ru(II), πd^6) while many complexes of iron, especially with saturated ligands, are high spin and thus tend to be labile; it has an advantage over osmium in that the desired species are much easier to prepare. As a result, much more research has been done on mixed-valence molecules of ruthenium than of its congeners, and the results obtained with binuclear ruthenium molecules are the main focus of this article.

Much of the effort, experimental and theoretical, which has been expended in the study of mixed-valence molecules has been devoted to the extent of electron delocalization between the metal centers. The issue as it arises for mixed-valence molecules is of interest in its own right because this class of molecules makes it possible to extend the idea of a bond from a mixed-valence molecule such as H_2^+, where a large stabilization attends delocalization at the equilibrium separation of the atoms, to systems in which the centers are only weakly coupled. Two important elaborations (complications) must be mentioned which distinguish the systems we shall be dealing with from H_2^+, which is the simplest mixed-valence molecule known. Firstly, in H_2^+, delocalization is by direct orbital overlap while in most of the systems we shall consider, the interacting centers are distant enough so that delocalization by direct orbital overlap can be neglected. Instead, we need to be concerned with the role of the medium in which the centers are immersed in providing for electron delocalization. Secondly, we need to be concerned with charge trapping by the medium. This is not a factor for H_2^+ in the gas phase but would be a serious one were H_2^+ immersed in water, in which case it is likely that most of the stabilization by delocalization would be lost as a result of the interaction of the molecule with the solvent. (The state $H_3O^+ + H$ is in all likelihood more stable than $H_2^+(aq)$.)

The extent of electron delocalization is important in another connection, that is, in trying to understand electron transfer in oxidation–reduction reactions, where the issue of whether and how non-adiabaticity affects the rate invariably arises. To assess its influence, the extent of electronic coupling in the activated complex must be known. In effect, a mixed-valence molecule is a model for the precursor complex of an intermolecular electron transfer reaction, and the information from the study of the mixed-valence molecules is directly applicable to understanding electron transfer processes.

Two aspects of electron delocalization will be emphasized in this article, and an effort will be made to deal with them quantitatively. For the kind of molecule we are concerned with, of which **I** is representative, the mixed-valence state, (III, II) [5], is invariably stable with respect to the isovalent state, (III, III) + (II, II), and it is of interest to learn how much of this stabilization is ascribable to electron delocalization. The stability of the mixed-valence state relative to the isovalent is reflected in the equilibrium quotient, K_c, for the comproportionation reaction



(I)

$$(\text{III, III}) + (\text{II, II}) = 2(\text{III, II})$$

where the stability per mole of (III, II) relative to the isovalent state expressed as a free energy is given by $-(RT/2)\ln(K_c/4)$. (In discussing the stabilization of (III, II) ascribable to electronic and related effects, the statistical factor of 4 needs to be factored out.) An important experimental task is that of determining the values of K_c. This is readily done electrochemically when the values of E_f governing the two stages of reduction

$$(\text{III, III}) \xrightarrow{E_1^0} (\text{III, II}) \xrightarrow{E_2^0} (\text{II, II})$$

are well separated ($\log K_c = 16.9\ (E_1^0 - E_2^0)$ at 25°, the values of E being given in volts) and is much more difficult when K_c approaches the statistical value of 4. Accurate values of K_c in this regime are needed also if accurate values of the molecular properties of the mixed valence molecule are desired: thus when $K_c = 4$, and the overall composition of the solute corresponds to the (III, II) state, the mixed-valence molecules comprise only one-half of the total. For the reasons given, a section of the article is devoted to the determination of values of K_c.

The second aspect of electronic delocalization which will be dealt with is to try to relate the extent of electron delocalization as it is determined from the spectroscopic properties of the mixed-valence molecules to the molecular and electronic structure of the bridging groups. The methods first introduced to this subject by Mayoh and Day [6] are applied here in somewhat modified form to a body of data obtained for systems which were designed to test the validity of the approach.

B. DETERMINATION OF THE COMPROPORTIONATION CONSTANT

The approach outlined by Sokol et al. [7] can be used to relate the microscopic potentials of a binuclear system and K_c. For two oxidized redox sites where each site can be reduced by one electron, four species are possible. These are abbreviated O_1O_2 (fully oxidized), R_1O_2, R_2O_1, and R_1R_2 (fully reduced). These species can be related by the scheme

$$\begin{tikzcd}
 & R_1O_2 & \\
O_1O_2 \arrow[ur, "\omega_1"] & & R_1R_2 \arrow[ul, "\omega_{12}"'] \\
 & O_1R_2 \arrow[ul, "\omega_2"] \arrow[ur, "\omega_{21}"'] &
\end{tikzcd}$$

The constants ω_1, ω_2, ω_{21} and ω_{12} are related to the microscopic Nernst potentials e_1^0, e_2^0, e_{12}^0 and e_{21}^0 for the sites by

$$\omega_1 = \frac{[R_1O_2]}{[O_1O_2]} = \exp\left[F/RT\left(e_1^0 - E\right)\right]$$

$$\omega_{12} = \frac{[R_1R_2]}{[R_1O_2]} = \exp\left[F/RT\left(e_{12}^0 - E\right)\right]$$

and so on. Because R_1O_2 and O_1R_2 are assumed to be in rapid equilibrium, only the macroscopic concentrations $C_0(=[O_1O_2])$, $C_1(=[R_1O_2]+[O_1R_2])$, and $C_2(=[R_1R_2])$ are observed. Thus, the macroscopic constants Ω_1 and Ω_2 are defined by

$$\Omega_1 = \frac{C_1}{C_0} = \exp\left[F/RT\left(E_1^0 - E\right)\right]$$

$$\Omega_2 = \frac{C_2}{C_1} = \exp\left[F/RT\left(E_2^0 - E\right)\right]$$

where E_1^0 and E_2^0 are the macroscopic standard potentials. It is seen that $\Omega_1 = \omega_1 + \omega_2$ and $\Omega_2 = (1/\omega_{12} + 1/\omega_{21})^{-1}$. In general, the difference of the two standard reduction potentials is

$$\Delta E^0 = E_1^0 - E_2^0 = (RT/F)\ \ln\frac{\Omega_1}{\Omega_2} \tag{1}$$

For equivalent sites, the symmetry requires $\omega_1 = \omega_2 = \omega$, $\omega_{12} = \omega_{21} = \omega'$

$$\Delta E^0 = \frac{RT}{F}\ \ln\left(\frac{4\omega}{\omega'}\right) \tag{2}$$

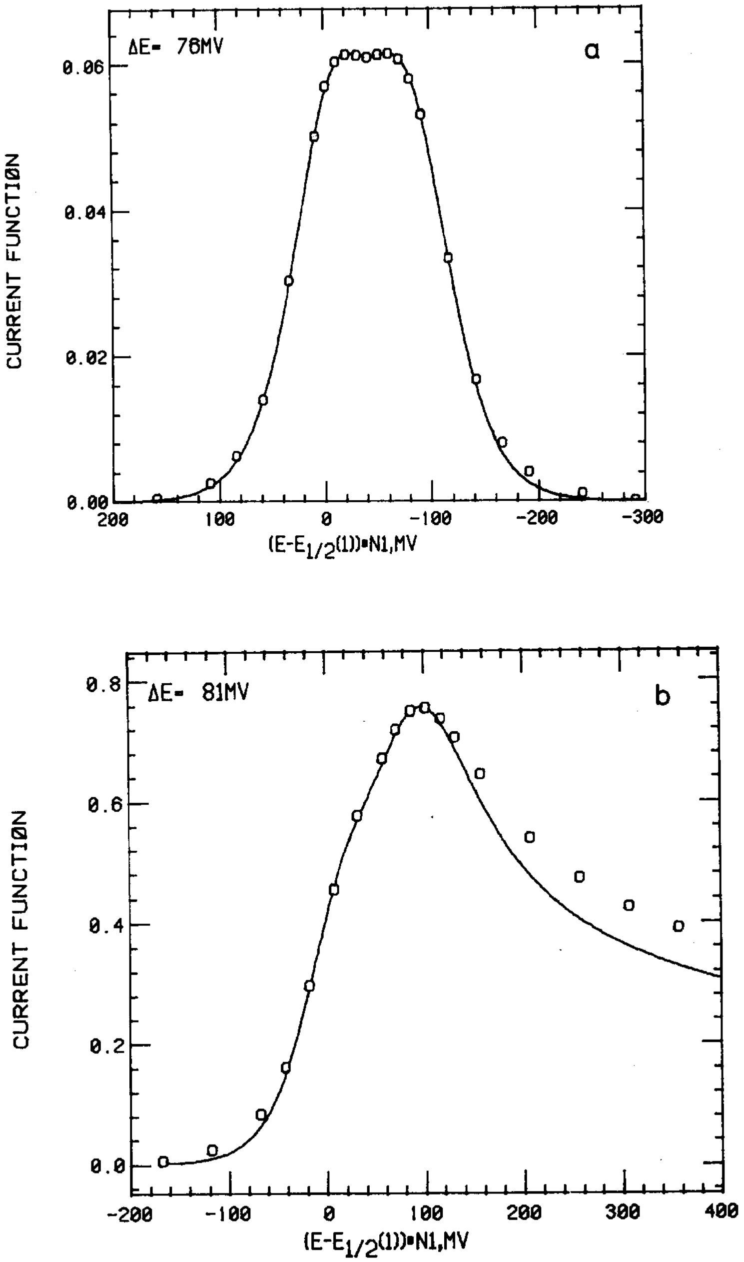


Fig. 1. Comparison of experiment (O) to theory (–) for $[((NH_3)_5Ru)_2(1,4\text{-dicyanobenzene})]^{4+/5+/6+}$ in 1 M HCl: (a) differential pulse voltammetry ($E_{pul} = 10$ mV); (b) linear-sweep (single-scan) voltammetry. The potential scale is $(E - E^1_{1/2})$. Values of ΔE^0 from the fits are shown in upper left of figures.

The statistical factor of 4 is found in eqn. (2), and the difference between ω and ω' reflects interaction between the sites. If the sites are quite different such that, say, $\omega_2 \ll \omega_1$, then

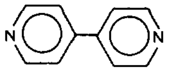
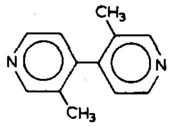
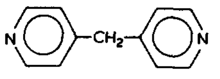
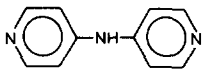
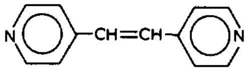
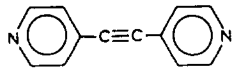
$$\Delta E^0 = \frac{RT}{F} \ln \frac{\omega_1}{\omega_{12}} = e_1^0 - e_{12}^0 \tag{3}$$

and the microscopic potentials define the electrochemical response (no statistical factor).

Historically, electrochemical analysis has been used to estimate ΔE^0 (from the formal potentials, ΔE_f) and thus K_c. In a recent article we described [8] two stationary electrode techniques for measuring ΔE_f in the region where the current potential responses for the two steps are inseparable ($\Delta E_f \lesssim 200$ mV). As an illustration of the techniques, Fig. 1 shows the experimental cyclic and differential pulse-voltammograms obtained for $[(Ru(NH_3)_5)_2$1,4-dicyanobenzene$]^{4/5/6+}$. The theoretical curves have been superimposed on

TABLE 1

Energetics of mixed-valence molecules

Bridge	ν_{max}^{IT} (10^3 cm^{-1})	$10^2 f$	ΔG^0_{tot} [a]	ΔG^0_{el} [b]	ΔG^0_{del} [c]	J (kcal mol^{-1}) [d]	K_c
	9.7	2.2	4.7	1.4	0.45	1.1	20
	11.2	0.43	2.6	1.4	0.9	0.6	10
	12.4	0.10	1.5	1.5	0.2	0.3	73
	10.9	3.03	5.5	1.4	0.25	1.5	~26
	10.4	~1.92	3.7	0.9	0.26	0.9	~14
	10.9	1.63	3.6	0.9	0.391	0.8	14

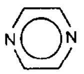
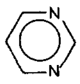
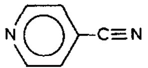
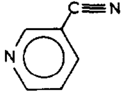
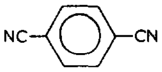
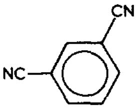
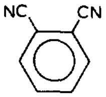
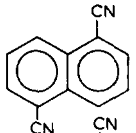
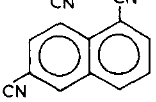
[a] Stabilization of mixed valence form relative to isovalent as calculated from K_c ($\times 10^{-2}$ cal mol^{-1}). [b] Electrostatic contribution to mixed valence state ($\times 10^{-2}$ cal mol^{-1}). [c] Stabilization by delocalization as calculated from oscillator strength ($\times 10^{-2}$ cal mol^{-1}). [d] Estimated from equations given in text: see ref. 15.

the experimental data, and ΔE_f is found to be $\simeq 79$ mV ($K_c \simeq 32$). Rather than simulating experimental curves, working curves and tables can be used to obtain ΔE_f values. It has been estimated that K_c values so obtained are accurate within 10% in the region where $0 < \Delta E \lesssim 200$ mV. At $\Delta E_f > 200$ mV, more accurate determinations are possible by direct methods.

A second method has been described [9] for determining K_c. In this

TABLE 2

Effect of bridging ligand structure on M and K_c [a]

Bridge	ν_{max}^{IT} (10^3 cm^{-1})	M_{IT} (obs.) [b]	M_{IT} (calc.) [c]	K_c [d]
$N\equiv N$	9.8	0.41		$\sim 10^8$
NC—CN	7.0	0.2		10^{13}
	6.4	0.66	0.67	10^6
	7.1	0.12	0.13	325
	10.7	0.47	0.25	5×10^4
	11.8	0.065	0.014	6400
	11.6	0.32	0.14	21
	13.3	0.04	0.02	11
	9.5	0.15	0.07	32
	12.8	0.16	0.034	7
	?	< 0.02	0.0002	9

[a] From ref. 24. [b] Transition moment of intervalence band calculated from experimental band shape and intensity, where $f = 1.085 \times 10^{-5}(\nu_{max})M^2$. [c] Calculated using eqn. (6). [d] From electrochemistry.

method, the absorbance is followed at a wavelength where only the mixed-valence species absorbs while titrating with reductant or oxidant. The intervalence band region often provides such an isolated absorbance. If there are no complications, the profile A_{IT} vs. equivalent reductant or oxidant can be fitted to a unique value of K_c. The ratio of A at n equivalents to $A_{\max}$ (measured at 1 equivalent) is given by

$$\frac{A_n}{A_{\max}} = \frac{K_c - \left[K_c^2 - (2n - n^2)(K_c^2 - 4K_c)\right]^{1/2}}{K_c - 2(K_c)^{1/2}} \tag{4}$$

where n is equivalents titrant added ($0 \leqslant n \leqslant 2$). The limits of the technique are $4 \lesssim K_c \lesssim 200$. The titration method can give accurate values of K_c in certain systems, but it is somewhat more limited in its range of applicability than the electrochemical approach.

Values of K_c determined for various bridging ligands are given in Tables 1 and 2. The cases chosen cover the range $4 \lesssim K_c \lesssim 10^{13}$. The variation in bridging group clearly has a profound effect on the magnitude of the total site–site interaction, and this is discussed in the next section.

C. FACTORS AFFECTING THE STABILITY OF MIXED-VALENCE SPECIES

In all cases studied thus far, the mixed-valence form of binuclear ruthenium complexes is more stable than, or at least in statistical equilibrium with, the isovalent forms (i.e., $K_c \geqslant 4$). The value of K_c governing the comproportionation reaction for species **I** is entered in Table 1 as 20. On correcting for the statistical factor, the stabilization of **I** relative to the isovalent states is $\Delta G^0_{\mathrm{tot}} = (\frac{1}{2})RT \ln(20/4)$ or 4.8×10^2 cal mol^{-1} at 25°C (0.02 eV mol^{-1}). Small though this is, we believe that it places an upper limit on the stabilization of **I** ascribable to electronic delocalization. This conclusion is valid if the following analysis of the factors affecting the energy difference is even qualitatively correct, that is, if the various contributions are correct only in the matter of sign.

We begin by considering a binuclear complex containing some typical π-acid bridging ligands L (for example, any of those in Table 1). In assessing the stability of 2(III, II) (state A) relative to (III, III) + (II, II) (state B), we will refer both to the reference state (Ru(III)–L, Ru(II)–L, Ru(III), Ru(II)) and analyze the factors that contribute to the energy difference when the reference state is assembled in the two different ways. We consider first the energy differences that can rise when electron delocalization is not operative. A purely electrostatic factor will favor state A over state B; this arises from the greater repulsion of the charges in state B (proportional to $3^2 + 2^2$) compared to state A (proportional to 2×6). In systems which are coordinatively symmetrical, the electrostatic factor always stabilizes the mixed-valence state, but this is not necessarily the case for arbitrary choices of the charges residing on the metal complexes [10]. On introducing delocalization, the reference state is stabilized by back-bonding in Ru(II)–L; there is no evidence that back-bonding contributes significantly to stabilization of Ru(III)–L. In proceeding to compare the stability of state A to state B, we first compare the energy difference attending the addition of Ru(III) to Ru(II)–L to that of Ru(III) to Ru(III)–L. Magnetic studies [11] done on a solid containing $[(NH_3)_5Ru)_2pyz]^{6+}$ show that interactions between the metal centers in the (III, III) state are very small, and they are certain to be even less in the fully oxidized state for the bridging ligands we shall be considering for present purposes. However, when Ru(III) is added to Ru(II)–L, even apart from stabilization arising from electron delocalization between metal centers, there is benefit from the negative charge which has been transferred from Ru(II) to the ligand, a benefit which is vividly illustrated by the greater pK_a of Ru(II)(pyzH) (2.5) compared to ($pyzH^+$) (0.6) [12]. To complete the cycle, Ru(II) is added to Ru(III)–L on the one hand, and to Ru(II)–L on the other. It is expected that in the former case there will be more stabilization owing to the effect of Ru(III) as compared to Ru(II) in lowering the energy of the π^* orbital, thus increasing the back-bonding interaction.

In using the data on the comproportionation equilibrium to calculate the stabilization arising from delocalization, it would be necessary to estimate the contributions arising from the other interactions, all of which favor the mixed-valence state. Even on the semi-quantitative level, this is at all straightforward only for the electrostatic factor ΔG^0_{el} where the Kirkwood–Westheimer [13] theory as modified by Ehrenson [14] has been applied [15]. For species **I**, the stabilization ascribable to the electrostatic effect is calculated as 1.4×10^2 cal mol^{-1}. The upper limit on stabilization by electron delocalization for molecule **I** then is $4.8 \times 10^2 - 1.4 \times 10^2 = 3.4 \times 10^2$ cal. The following analysis suggests that this quantity is still far in excess of that attributable to delocalization.

In Fig. 2a, the energy parameters for a case such as **I**, which according to all the evidence is valence-trapped, are defined. The potential wells are assumed to be simple harmonic. When the electronic coupling energy is defined as J, the stabilization of the ground state ascribable to electronic delocalization is $J^2/4W_0$ [16,17] where W_0 is defined in Fig. 2. $J^2/4W_0$ then is the contribution to the stability of the mixed-valence state ascribable to electronic delocalization (ΔG^0_{del}), and it is the quantity which we shall try to extract from the experimental data. The difference in energy between the system at a minimum and the higher energy state at the same value of X remains equal to $4W_0$, as long as J does not become so large that the energy

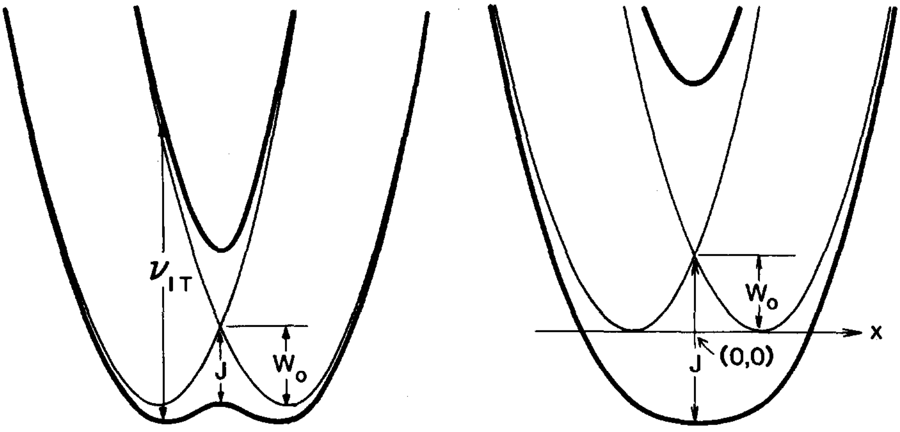


Fig. 2. Potential energy curves for cases of zero (light line in both figures), intermediate (a), and strong (b) electronic interaction. The parameters are defined as follows: J, electronic delocalization energy; W_0, zero order barrier to thermal electron transfer; ν_{IT}, intervalence transition energy. Typical values of W_0 are 2000–3000 cm^{-1} for MV ruthenium ammines.

barrier at $X = 0$ disappears [16]. Thus, $4W_0$ is given by the energy of the intervalence transition (this crude model is quite approximate since it assumes that the optical transition originates at the minimum of the lower surface, but essentially the same result is found using the more sophisticated vibronic coupling model of Schatz and co-workers [18]). Following Hush [1] J is estimated from the properties of the intervalence absorption band using the equations

$$f(\text{oscillator strength}) = 4.6 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2}$$

$$M(\text{dipole strength of the intervalence transition}) = \left(f/1.085 \times 10^{-5} \nu\right)^{1/2}$$

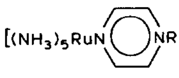
$$J = h\nu_{IT} M R^{-1}$$

where R is the separation of the metal centers (energy in cm^{-1}; distance in Å).

In Table 1 are summarized the results of the above analysis as applied to systems featuring variants of the bipyridine unit as the bridging group. In appraising the data, it should be noted that the exact agreement between the values of ΔG^0_{tot} and ΔG^0_{el} for dipyridylmethane as bridging group cannot be taken as establishing the validity of the approach. To fix the parameters required for calculating the electrostatic contribution, it was assumed that electronic effects of any kind for the dipyridylmethane bridged system are insignificant compared to the electrostatic contribution. In view of the small oscillator strength of the intervalence band, this assumption seems justified.

It is difficult to set limits of reliability on the entries for ΔG^0_{del} but it does seem certain, as already claimed, that the values of ΔG^0_{tot} less those of ΔG^0_{el} set upper limits on stability ascribable to electron delocalization. The inductive effect of Ru(III) replacing one Ru(II) in forming the mixed-valence molecule from the reduced form, is likely to be substantial, and it may well be that the values of ΔG^0_{del} are in error by no more than a factor of 2 or 3. In any event, for these systems, it seems certain that even when ϵ for the intervalence band approaches 1×10^3 M^{-1} cm^{-1}, the stability of the mixed-valence state is not significantly enhanced by electron delocalization between the metal centers.

A strategy which has been suggested [19] for assessing the contribution to stabilization of a mixed-valence molecule by delocalization is to replace Ru(III) in the mixed-valence molecule by Rh(III). The latter is like Ru(III) in all major respects, but lacking as it does the electron hole in the πd level (Rh(III) is a πd^6 system) electron delocalization from Ru(II) to the oxidized center is virtually eliminated. The argument is then made, and it does seem intuitively reasonable, that if the work of extracting an electron from the mixed-valence molecule is compared to that for the Ru(II)–Rh(III) analog, and after allowance is made for the statistical factor, the extra work required for the mixed-valence molecule measures the stabilization ascribable to delocalization. This argument is in fact rather sound as applied to deeply trapped systems such as have been dealt with in the preceding section. Unfortunately, the energy differences in these cases are so small that electrochemical measurements much more refined than those which have thus far been made would be needed to yield meaningful differences. The approach, though valid in principle, is impotent.



(II)

It might be supposed that the above strategy would be useful in the case of **II**, where there is agreement that there is considerable delocalization but a division of opinion on the presence of a barrier in the ground state potential energy profile. Schatz and co-workers [18] have argued for a small barrier (Fig. 2a) while Hush [20] interprets the properties of **II** in terms of complete delocalization (Fig. 2b). The way that J is reflected in the spectroscopic results is quite different for the two possibilities, there being an abrupt change when the minimum just disappears. When there are two minima, the energy of the intervalence band is predicted to be independent of J and equal to $4W_0$. When $J \geqslant 2W_0$, the residual barrier disappears and the energy of the intervalence band measures $2J$ (Fig. 2b), at least for this simple one-electron model. Despite the apparent sensitivity of the intervalence band energy to the shape of the ground state profile, it appears that the additional observations made in applying the Rh(III) substitution strategy does not settle the basic issue of whether or not the ground state potential has only one minimum.

If **II** is assumed to be localized, the net stabilization of the ground state attending delocalization is given by the difference in E_f for the (III, II) species (0.772 V) compared to the Rh(III) analog (0.709 V), after correction is made for the statistical factor. This stabilization is given by $J^2/4W_0$ and on setting $4W_0$ equal to the energy of the intervalence band, J is calculated as 4.4 kcal. The reorganization energy W_0 is $\frac{1}{4}$ the energy of the intervalence band or 4.6 kcal. This is some 2 kcal less than that estimated from the rate of some related pseudo self-exchange processes [21], but because of the inherent uncertainties in both estimates, the difference cannot be used to invalidate the conclusion that there is a residual barrier in the ground state potential energy profile for the mixed valence ion.

The analysis of the problem if **II** is assumed to be delocalized (in the sense that the ground state barrier has disappeared) is fraught with serious difficulty. In the deeply trapped case, the electronic systems of the two metal centers are assumed to be independent, so that the energy levels of the centers are not perturbed by delocalization. When delocalization becomes great, this condition is no longer met, and the stability of the mixed-valence state no longer simply reflects a value of J as defined by a one-electron model, but is the net result of deep seated perturbations in both the mixed-valence and isovalent states. The role of the bridging ligand is probably not adequately represented by the J parameter, and the two-site approximation is no longer sufficient. It is not at all clear that any transition can necessarily be identified as fixing the value of J as it is defined in the simple model [22,23]. If the concerns expressed are disregarded, and the simple one-electron model is taken to apply, J and W_0 can be calculated [16] from the energy of the intervalence band taken together with the difference in E_f for species **II** and the Rh(III) analog. When this is done, $J(h\nu_{IT} = 2J)$ is calculated as 9.2 kcal and W_0 as 7.7 kcal. The condition that there be a single minimum, namely is that $J \geqslant 2W_0$ is not met, but for the reasons given earlier in the paragraph, we feel that the analysis which has been applied is invalid for a strongly delocalized system. Nevertheless, we need not abandon the goal of estimating just how much electronic stabilization is ascribable to the presence of a πd vacancy in a pair of metal centers. Though, as we believe, this quantity does not follow simply and directly from the spectrum, we still are left with an approach based on an energy cycle, making use of the differences introduced by replacing Ru^{3+} by Rh^{3+}, and the stability of the mixed valence state relative to the isovalent. To complete the analysis, the instability of the (II, II) state, and the increase in stabilization by back-bonding which attends placing a tripositive ion such as Rh^{3+} on

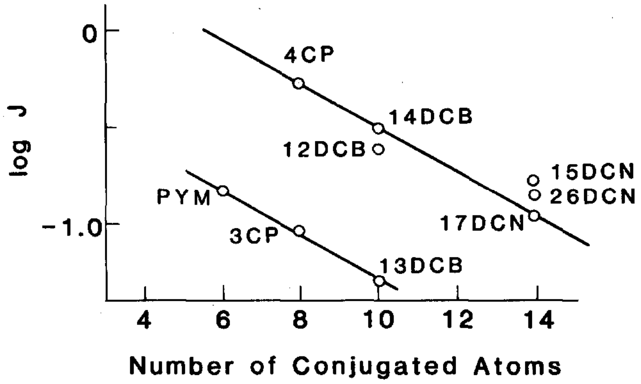


Fig. 3. Illustration of exponential dependence of estimated values of J on the number of conjugated atoms in the bridging ligands. All cases shown are strongly valence-trapped (localized) MV ions. Abbreviations: 3CP: 3-cyanopyridine; 4CP: 4-cyanopyridine; *ij*DCB: *i*, *j*-dicyanobenzene; pym: pyrimidine; *ij*DCN: *i*, *j*-dicyanonaphthalene.

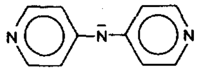
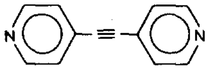
pentaammineruthenium(II) needs to be assessed. It is of course of interest to apply the strategy outlined to other strong interaction cases. The systems with NCCN and NN as bridging ligands are obvious candidates, but only the former is amenable to the substitution approach.

D. ELECTRONIC INTERACTIONS MEDIATED BY BRIDGING LIGANDS [24]

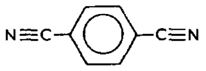
Electronic interactions between redox centers are of fundamental importance in determining the intramolecular electron transfer rate. For example, very weak interaction will lead to non-adiabatic behavior, and the square of the interaction energy J will be directly proportional to the rate of electron exchange [25]. A goal has been to understand how bridging ligand (BL) structure controls the magnitude of the interaction. The most direct probe of the purely electronic interaction is the characteristic intervalence band. The energy, intensity, and shape of this band have much to say about the degree to which the metal centers communicate via the BL.

The rather large variety of bridging ligands studied gave us an opportunity to observe significant variations in metal–metal interaction with changes in the BL structure. Several trends were noticed for the Ru^{II}/Ru^{III} ammines, among them:

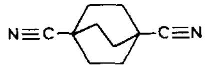
(a) In general, there is a strong correlation between the number of atoms in the BL and the degree of interaction, with the interaction decreasing exponentially as the BL size increases (Fig. 3).

(b) Strong interaction (characterized by relatively intense, often narrow and asymmetric near-IR bands) occurs only with smaller ligands that feature strong π-donor or π-acceptor tendencies. To illustrate the former case, one can cite the oxo group (O^{2-}) [26] and the deprotonated malononitriles $[NCCRCN]^-$ [27] (where the central carbon lone pair has delocalized over the 5 atom framework). The latter case is illustrated by the potent π-acids N_2, NCCN and pyrazine. For larger ligands such as  and  [15], the presence of an interacting lone pair or extensive conjugation is insufficient to couple the *d* orbitals of the metal sites strongly.

(c) A saturated bond system separating the donor groups of organic BLs will lead to weak coupling, typically weaker than found for conjugated bridges of comparable size. Consider the cases of BL = 1,4-dicyanobenzene(**III**) and 1,4-dicyanobicyclooctane(**IV**), where the metal–metal distances are quite similar.



(III)



(IV)

The observed interaction for BL = **IV** is much less than for BL = **III** (the intervalence band is 10 times more intense for the latter case) [28]. In the bipyridine series, a methylene bridge between the pyridyl groups strongly attenuates the interaction [15].

(d) For aromatic bridging groups with two or more substitutional isomers (e.g., dicyanobenzenes, diazabenzenes), the stronger electronic interactions occur with the *ortho* and *para* isomers. Figure 3 and entries in Table 2 clearly illustrate this trend.

Qualitative explanations for the above results have been offered, and we recently sought to examine the problem on a more quantitative level by using a perturbational approach similar to one that first appeared to explain magnetic coupling between atoms in solids [29]. In this "superexchange" method, the interaction between the metal site is attributed to the bridging ligand, and direct interaction is neglected. The description of the metal–BL–metal interaction is then described by perturbations of the idealized single ion ground states by mixing with higher-lying states involving charge transfer to and from the bridge. Note that in the case of magnetic superexchange (e.g., $Mn^{2+} \leftrightarrow Mn^{2+}$), charge transfer states involving the metals are also considered (e.g., $Mn^{+} \leftrightarrow Mn^{3+}$). In MV systems, the analogous state involves intervalence transfer, where the oxidation states of the metals interchange.

The application of superexchange to BL-mediated redox reactions was discussed by George and Griffith [30] and later by Halpern and Orgel [31]. However, the theory was not used to estimate interactions for real redox systems until Mayoh and Day [6] calculated intervalence band intensities for a few MV systems. As described earlier, MV systems are relevant to the general field of intramolecular electron transfer.

The ground state $\psi_g(\mathrm{Ru^{II}}\text{–}\mathrm{Ru^{*III}})$ and the intervalence state ψ_{IT}-$(\mathrm{Ru^{III}}\text{–}\mathrm{Ru^{*II}})$ are assumed to interact via higher lying charge transfer states ψ_i, and the improved ground state wavefunction to second order is

$$\Psi_g \cong \psi_g + \left(\sum_i \frac{\langle \psi_g | H | \psi_i \rangle \langle \psi_i | H | \psi_{IT} \rangle}{(E_{IT} - E_g)(E_i - E_g)} \right) \psi_{IT}$$

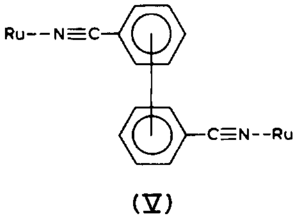
$$\simeq \psi_g + \alpha \psi_{IT} \qquad (5)$$

when $\langle \psi_g | H | \psi_{IT} \rangle$ is assumed to be negligible. To relate the mixing to experimental observables, the IT band intensity is calculated by an approximate dipole length expression

$$M_{IT} = \langle \Psi_g | er | \Psi_{IT} \rangle \cong \alpha R \Lambda \qquad (6)$$

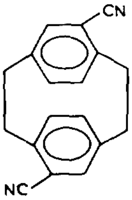
where R is the metal–metal distance and Λ is a constant to account for distribution of the electron hole in d^5 $\mathrm{Ru^{III}}$ among the three πd orbitals. Evaluation of the integrals and energies in eqn. (5) is done semi-empirically by combining an energy-corrected molecular orbital description of the BL with information from the charge transfer bands that involve the BL. Agreement between theory and experiment is surprisingly good, and points (a), (b) and (d) above are accounted for by the theoretical approach (Table 2). The effect of saturation (point (c)) is more difficult to incorporate, since the reduced symmetry leads to breakdown of σ/π separability. However, the effect of saturation can be rationalized easily by considering the factors that influence the magnitude of integrals and energies in eqn. (5).

Although there are relatively few experimental data available on metal–metal interactions mediated by stacked aromatic rings, the theoretical approach outlined above does provide insight into that problem. Our calculations for the hypothetical case of two $[\mathrm{Ru(NH_3)_5}$benzonitrile$]$ moities arranged with rings overlapping (V) show the expected correlation between interaction and overlap integrals.



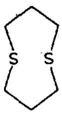
(V)

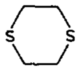
In the region $R \simeq 3.3$ Å to 5 Å, the interaction is found to decrease exponentially. This point has some application to proposed "pathways" in biological redox reactions, where ring-to-ring hopping is often invoked. For the bridging ligand *pseudo para*-dicyano[2.2]paracyclophane, **VI**, the inter-ring distance is ~ 3.25 Å, and an intervalence band is found at 12,500 cm^{-1} ($\epsilon \sim 10\ \text{M}^{-1}\ \text{cm}^{-1}$).



(VI)

In addition to the through-bond interactions described above, some bridging ligands apparently couple the orbitals of the metals by through-space interaction. This has been demonstrated by Stein [32] in his studies of dithiane BLs, where an interesting comparison is found for BL = **VII** and **VIII**.





(VII) (VIII)

The IT band in the MV case where BL = **VII** is actually the more intense despite the presence of an additional methylene linkage. Examination of models shows that the metal centers can approach more closely in **VII** than **VIII**, and a through-space interaction is suggested. Photoelectron studies of the free ligand **VII** show splitting of the S lone pair orbitals due to S–S interaction, indicating that the communication is probably via the sulfur atoms.

E. FUTURE DIRECTIONS

In this section, we will consider two general areas for future development in mixed-valence chemistry. The first of these is a refinement of theoretical and experimental approaches to elucidate the fundamental electronic and dynamic aspects of mixed-valence materials. The second represents a relatively unexplored area, where coupling between the metal centers is used to modify chemical reactivity in redox and ligand exchange processes.

In some respects, the current state of theoretical work on MV compounds is similar to that of magnetic coupling theories some 25 years ago. At that time, the fundamental quantum mechanical theories treating magnetic interactions between isovalent ions through diamagnetic bridging ligands had been proposed, and crude calculations gave predictions that for the most part were confirmed experimentally [29]. The current understanding of electronic interaction in MV materials is at much the same point, but there is a substantial difference in the two problems. In MV molecules, the dynamic aspects of the systems (where the opportunity for localized vs. delocalized behavior exists) must also be considered. In the limiting case of strongly localized MV ions, the straightforward "superexchange" approach is no doubt justified, but in cases of strong interaction and delocalization, one must proceed with great caution in applying theories based on idealized models.

There is ample scope for the development of theory competent to describe the strong interaction cases. For example, how can the bridging ligand be included to provide for its contribution to delocalization? The parameter J is a useful phenomenological device, but it does obscure the complexity of the interactions in strongly coupled cases. In addition to the appearance of intervalence bands and new transitions, what effect does extended electronic interaction have on other optical transitions? Magnetic coupling between metal centers is known to have a profound influence on the intensities of ligand field transitions, and, in some cases, new transitions are identified (simultaneous pair excitation) [33]. New experimental results will complement theoretical developments, especially when structurally characterized single-crystal materials are used [34].

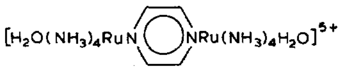
Although the weak-interaction cases of mixed valency seem more straightforward, many mysteries remain unsolved. Consider for example the IT band energy of the weakly coupled MV ion $[(Ru(NH_3)_5)_2pyrimidine]^{5+}$ [24]. The IT band at ca. 7000 cm^{-1} is almost solvent-independent, so that application of the usual equations [35] for separating the inner-shell (E_{in}) and solvent (E_{out}) contributions to the IT band energies put the E_{in} contribution at more than 6000 cm^{-1}. However, if reasonable estimates for the bond lengths and metal–ligand frequencies are used, the calculated E_{in} will put the IT energy in the infrared region (1000–2000 cm^{-1}). What is the source of this discrepancy [36]?

Weak electronic interactions between redox pairs in biological systems should also be addressed in more detail in the future. In the context of non-adiabatic theories, the extent of metal–metal interaction will play a dominant role in determining the electron-transfer rates. The type of theoretical approach we have used to describe interactions in simple binuclear complexes can be extended in principle to biological bridging materials. Recent advances in experimental aspects of this area show promise of providing well-defined, biologically relevant redox systems [37,38] and the observations may well reveal that there are configurations even for "saturated" systems which greatly facilitate electron transfer over large distances.

From time to time reference has been made to chemical properties of mixed-valence molecules in the context of trying to understand their electronic structure, and thus it is recognized that electron delocalization will affect the chemical behavior. Despite this realization, little has been done in a systematic way to demonstrate how the properties change as a function of the extent of delocalization.

The estimates described above for the stabilization of the ground state by delocalization in the valence-trapped systems is germane to the present concern. In view of the small energy changes attributable to delocalization for such molecules, it is not at all clear that anything new and interesting in the way of chemical properties for them is in prospect. The strongly delocalized systems likely are quite another matter. In fact, some observations made in the course of preparing and characterizing μ-dinitrogen mixed-valence (III, II) osmium species may well have their explanation in the stabilization of the mixed-valence state by delocalization. The mixed-valence molecules of this type are certainly delocalized. It appears that aquation of chloride in $[(NH_3)_5OsN_2Os(NH_3)_4Cl]^{4+}$ is much slower than is expected for either Os(III) or Os(II) as mononuclear species [39]. In view of comproportionation constants of $> 10^{17}$ (for a closely related substitutionally symmetrical species) it is reasonable to assume that there is considerable stabilization of the mixed-valence state by delocalization. Now whether substitution takes place by an S_N1 or S_N2 process, the coordination sphere for the center undergoing substitution is greatly altered, and because of the asymmetry introduced when one end of the molecule undergoes substitution, the stabilization by delocalization is largely sacrificed in the activated complex. Thus, the substitution rates will not be the average of those expected for a 2 + center on the one hand or a 3 + center on the other, and in a strongly delocalized system, the rates may be slower than for either.

It is appropriate here to return to the comparison of the rate of substitution in



(IX)

and in the molecule in which Ru(III) is replaced by $Rh(NH_3)_5^{3+}$(X). Although delocalization between the metal centers is virtually excluded for species **IX**, the rates of substitution by isonicotinamide for the two cases are almost the same for **IX** and **X** respectively. This has been cited [19] as evidence that little Ru(II) character has been lost in **IX** as a result of electron delocalization. The argument, however, was made without taking into account the fact that the rate of substitution in Ru(II), as it appears in **IX**, is so greatly reduced by the π-acid hetero ligand that it may be little different from that in Ru(III), and the experiment, though valid in principle, may simply be insensitive.

Stabilization attending delocalization is reflected even more directly in the kinetic behavior of $[((NH_3)_5Os)_2N_2]^{5+}$ relative to $[(NH_3)_5OsN_2]^{3+}$. The dinitrogen ligand in aqueous solution at room temperature is lost from the latter ion on the timescale of seconds; the former is indefinitely stable to $Os-N_2$ bond rupture by aquation. This kinetic stabilization cannot be attributed simply to extra electron density being deposited on the *exo* nitrogen atom by back-bonding from Os(II) to the π^* orbital of the ligand. Effects of this kind have been documented for pyrazine on Os(II) but have not been directly observed for N_2, and they are not great enough for H^+_{aq}, which is by many orders of magnitude a stronger Lewis acid than $(NH_3)_5Os^{3+}$, to show a measurable affinity for $(NH_3)_5OsN_2^{3+}$. The kinetic stability of the osmium–N_2 bonds in the mixed-valence molecules is attributable to the fact that the system is delocalized, and this delocalization energy is lost when the binuclear structure is disrupted. It is important to realize that the result says nothing about the mechanism of delocalization; in the μ-N_2 species it may involve direct orbital overlap between the osmium center, as well as bridge mediated effects.

The effects of delocalization will be manifested also in equilibrium behavior, for example in the acidity of **IX** compared to analogous mononuclear species. These equilibrium effects, now under investigation for the example cited, will not be easy to predict. While most of the delocalization energy will be lost in forming the activated complex for substitution, in the present example this may not be the case, because OH^- in replacing water is not as drastic a reorganization of the first coordination sphere as is a change in coordination number.

It is not clear that the valence trapped binuclear molecules of the type considered here will be particularly interesting or unusual as redox reagents, except that they make possible two successive $1e^-$ changes, each requiring little in the way of reorganization energy, in contrast to a $2e^-$ change at a single center, where, except in special cases, large distortions accompany the change of oxidation state. There may in fact be cases in which it is an advantage in having a second $1e^-$ center at hand for rapid reaction with the product of the reaction of the first center. No such applications come to mind, and we turn to consider the question of the transition from the successive $1e^-$ steps, to a genuine $2e^-$ transfer. Consider the molecule

$(NH_3)_5Ru^{III}(LL)^{III}Ru(NH_3)_5$

XI

where LL is a group providing electronic coupling between the metal atoms. In acting on a substrate that can be oxidized by a net 2e$^-$ change, there may be a kinetic advantage if the oxidant acts by a 2e$^-$ change, thus avoiding the necessity of generating an unstable species as an intermediate and leading to a lower activation energy. The basic question that arises is this: how much electronic coupling is required so that the postulated lower activation energy for the 2e$^-$ path can be realized? It seems reasonable that the successive acts must follow one another so closely that the short lifetime of the intermediate mixed valence oxidation state gives rise to significant uncertainty broadening. Again in concrete terms, when 4,4′-bipyridine is the bridging group, the metal centers are so weakly coupled (e$^-$ transfer in the mixed-valence state of the order of $10^8 s^{-1}$ [15]) that the two centers will act independently. To lead to significant "lifetime" broadening, the electron transfer rates within the mixed-valence intermediate would need to be of the order 10^{15} s^{-1}.

Invariably in the cases we have been considering, the mixed-valence state is stable relative to the isovalent, so that $E_1^0 \gg E_2^0$, while E^0 governing the 2e$^-$ change is given by $(E_1^0 + E_2^0)/2$, so that strong coupling increases the driving force for a 1e$^-$ change compared to the 2e$^-$ change. Still, there may be instances in which the 2e$^-$ change is so favored and the 1e$^-$ path is strongly disfavored energetically that the 2e$^-$ change becomes a possibility. For this possibility to be realized, an additional factor must be taken into account.

The virtue of a molecule such as **XI** as a potential 2e$^-$ redox reagent arises because, comprised as it is of two centers, each of which undergoes only a 1e$^-$ change, the inner-sphere reorganization for the 2e$^-$ change is small. This is in marked contrast to the situation when the 2e$^-$ change takes place on a single center where, except in special cases, as may arise when the ligands can undergo a redox change, the inner-sphere reorganization barrier is very high. In the interest of concrete discussion, we consider the oxidation of a typical 2e$^-$ reducing agent, SO_3^{2-}. The oxidation of SO_3^{2-} by simple electron extraction to produce SO_3 is undoubtedly even less favored energetically than the oxidation to SO_3^-. For the 2e$^-$ oxidation to compete with 1e$^-$, SO_3 as product must be stabilized by the addition to it of some nucleophile such as OH^-, and this addition must take place in the act of oxidizing SO_3^{2-}. Thus for 2e$^-$ oxidation to compete with the 1e$^-$ path, species **XI** must be suitably modified to accommodate the additional demand. A suitable modification might be to replace an ammonia on each center by OH^- or Cl^- so that, in effect, SO_3^{2-} is oxidized by transferring OH^+ or Cl^+ to it from oxidant **XI**.

The condition $E_1^0 < E_2^0$ would favor a concerted 2e$^-$ reduction of **XI** over a $1e^-$ reduction, but it is doubtful if this condition will be met for any molecules of the type we have considered, where we have tried to avoid steric interactions between the centers. But such situations can arise when substantial changes in geometry accompany the changes in oxidation state, and the coordination spheres of the two centers are interlocked so that a geometrical readjustment at one center can influence the ease at which the second stage of the redox change occurs. At least two such systems have been reported in the literature [40]. If the geometries at the two centers are quite different, it is unlikely that the electronic coupling will be great enough to make possible a concerted $2e^-$ change. The only advantage that such systems have over the mononuclear analog is that the second oxidation stage can follow rapidly on the first: note that the second stage is more strongly oxidizing than the first. This can of course be an important advantage when the second act follows so rapidly on the first that the radical product does not escape the vicinity of binuclear oxidant. The time requirement, $t_{1/2} < 10^{-10}\ \mathrm{s}^{-1}$, is not severe, and in just meeting this requirement no benefit in terms of a lowered activation energy from a coupling of the two stages can be expected. There can be an advantage if the time interval between the first and second stages is not too short, because this provides an opportunity for the environment around the intermediate oxidation states to adjust, so as to facilitate the oxidation to the final product.

ACKNOWLEDGMENTS

Support of this work by National Institutes of Health Grant No. GM13638-17 and National Science Foundation Grant No. CHE81-10545-A1 are gratefully acknowledged.

REFERENCES

1 N.S. Hush, Prog. Inorg. Chem., 8 (1967) 391.

2 M.B. Robin and P. Day, Adv. Inorg. Radiochem., 10 (1967) 247.

3 C. Creutz and H. Taube, J. Am. Chem. Soc., 91 (1969) 3988; 95 (1973) 1086.

4 D.O. Cowan and F. Kaufmann, J. Am. Chem. Soc., 92 (1970) 219.

5 A designation such as (III, II) is intended only to define the total oxidation state and does not address the issue of whether the molecule is valence-trapped or delocalized.

6 (a) B. Mayoh and P. Day, J. Chem. Soc., Dalton Trans., (1974) 846.
(b) B. Mayoh and P. Day, Inorg. Chem., 13 (1974) 2273.

7 W.F. Sokol, D.H. Evans, K. Niki, T. Yagi, J. Electroanal. Chem., 108 (1980) 107.

8 D.E. Richardson and H. Taube, Inorg. Chem., 20 (1981) 1278.

9 J.E. Sutton, P.M. Sutton and H. Taube, Inorg. Chem., 18 (1979) 1017.

10 When the oxidized end of the molecule carries a net charge of x and the reduced end y, the electrostatic term for the comproportionation reaction is proportional to $(x - y)$.

11 B.C. Bunker, R.S. Drago, D.N. Hendrickson, R.M. Richman and S.L. Kessell, J. Am. Chem. Soc., 100 (1978) 3805.

12 P.C. Ford, R.G. Gaunder, DeF.P. Rudd and H. Taube, J. Am. Chem. Soc., 90 (1968) 1787.

13 J.G. Kirkwood and F.H. Westheimer, J. Chem. Phys., 6 (1938) 506, 513.

14 S. Ehrenson, J. Am. Chem. Soc., 98 (1976) 7510.

15 J.E. Sutton and H. Taube, Inorg. Chem., 20 (1981) 3125.

16 J. Wishart, H. Taube, in preparation.

17 This result is slightly different from that given by Sutton et al. [9,15]. The difference is small as a practical matter but it is important as a matter of principle. In the treatment by Sutton et al. the nuclear coordinates were constrained to remain fixed even when the electronic interaction developed. In a real system, the nuclei will readjust to find the point of minimum energy on the potential energy vs. normal coordinate surface (Fig. 2). For the weakly interacting systems they dealt with, $J^2/4W_0 \ll h\nu_{\mathrm{IT}}$, and thus the results reported in refs. 9 and 15 are not materially in error.

18 (a) K.Y. Wong and P.N. Schatz, Prog. Inorg. Chem., 28 (1981) 369.
(b) K.Y. Wong, P.N. Schatz and S.B. Piepho, J. Am. Chem. Soc., 10 (1979) 2793.
(c) S.B. Piepho, E.R. Krausz and P.N. Schatz, J. Am. Chem. Soc., 100 (1978) 2996.

19 H. Taube, Ann. N.Y. Acad. Sci., 313 (1978) 481; Pure Appl. Chem., 44 (1975) 25.

20 N.S. Hush, in D.B. Brown (Ed.), Mixed-Valence Compounds, Reidel, Dordrecht, 1980, p. 151.

21 G.M. Brown and N. Sutin, J. Am. Chem. Soc., 101 (1979) 883.

22 In referring to the molecule orbital descriptions by Lauher [23], the splittings that give use to the low energy electronic transitions in delocalized mixed-valence ions of the kind we are discussing, are seen to depend on interaction of πd orbitals with π and πd orbitals of the ligand.

23 J. Lauher, Inorg. Chim. Acta, 39 (1980) 119.

24 D.E. Richardson and H. Taube, J. Am. Chem. Soc., 105 (1983) 40.

25 (a) V.G. Levich, Adv. Electrochem. Electrochem. Eng., 4 (1966) 249.
(b) J. Jortner, J. Chem. Phys., 64 (1976) 4860.
(c) N.R. Kestner, J. Logan, J. Jortner, J. Phys. Chem., 78 (1974) 2148.
(d) B.S. Brunschwig, J. Logan, M.D. Newton and N. Sutin, J. Am. Chem. Soc., 102 (1980) 5798.

26 J.A. Baumann, T.J. Meyer, Inorg. Chem., 19 (1980) 345.

27 H. Krentzien and H. Taube, J. Am. Chem. Soc., 98 (1976) 6379; Inorg. Chem., 21 (1982) 4001.

28 A. Hammershoi, unpublished results, 1981.

29 (a) P.W. Anderson, in G.T. Rado and H. Suhl (Eds.), Magnetism, Vol. 1, Academic Press, NY, 1963, p. 25.
(b) J.B. Goodenough, Magnetism and the Chemical Bond, Interscience, NY, 1963.
(c) R.L. Martin, in E.A.V. Ebsworth, A.G. Maddock and A.G. Sharpe (Eds.), New Pathways in Inorganic Chemistry, Cambridge University Press, London, 1968.
(d) A.P. Ginsberg, Inorg. Chim. Acta Rev., 5 (1971) 45.
(e) G. van Kalkeren, W.W. Schmidt and R. Block, Physica B + C (Amsterdam), 97B (1979) 315.

30 P. George and J. Griffith, 2nd Edn., Enzymes, Vol. 1, 1959, p. 347.

31 J. Halpern and L.E. Orgel, Discuss. Faraday Soc., 29 (1960) 32.

32 C.A. Stein and H. Taube, J. Am. Chem. Soc., 100 (1978) 1635.

33 (a) D.L. Dexter, Phys. Rev., 126 (1962) 1962.
(b) J. Ferguson, H.J. Guggenheim and Y. Tanabe, J. Phys. Soc., Jpn., 21 (1966) 692.
(c) H.N. Gudel and L. Dubicki, Chem. Phys., 6 (1974) 272.

(d) H.N. Gudel, Chem. Phys. Lett., 36 (1975) 328.
(e) J. Ferguson, H.N. Gudel, E.R. Krausz and H.J. Guggenheim, Mol. Phys., 28 (1974) 893.

34 A. Furholz, H. Burgi, F.E. Wagner, A. Stebler, J.H. Ammeter, E.R. Krausz, R.J.H. Clark, M.J. Stead and A. Ludi, J. Am. Chem. Soc., 106 (1984) 121.

35 T.J. Meyer, in D.B. Brown (Ed.), Mixed-Valence Compounds, Reidel, Dordrecht, 1980, p. 75.

36 In the complexes of second and third row transition metals, spin-orbit coupling becomes increasingly important in determining transition energies, but this point has been disregarded for the most part (however, see J.C. Curtis and T.J. Meyer, Inorg. Chem., 21 (1982) 1562).

37 J.R. Winkler, D.G. Nocera, K.M. Yocum, E. Bordignon and H.B. Gray, J. Am. Chem. Soc., 104 (1982) 5798.

38 S.S. Isied, G. Worosila and S.J. Atherton, J. Am. Chem. Soc., 104 (1982) 7659; 106 (1984) 1722.

39 R. Magnuson, Ph.D. Thesis, Stanford University, 1973.

40 (a) L.S. Hollis and S.J. Lippard, J. Am. Chem. Soc., 103 (1981) 6761.
(b) D.E. Fenton, R.R. Schroeder and R.L. Lintvedt, J. Am. Chem. Soc., 100 (1978) 1932.