Long-Range Intervalence Electron Tunneling through Fully Saturated Systems

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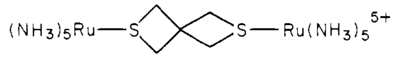
Abstract: The compounds (μ-2,8-dithiadispiro[3.1.3.1]decane)-decaamminediruthenium(II,II) hexafluorophosphate, $[(NH_3)_5RuS_2C_8H_{12}Ru(NH_3)_5](PF_6)_4$, and ($\mu$-2,10-dithiatrispiro[3.1.1.3.1.1]tridecane)-decaamminediruthenium(II,II) hexafluorophosphate, $[(NH_3)_5RuS_2C_{11}H_{16}Ru(NH_3)_5](PF_6)_4$, were prepared, and upon oxidation, their intervalence properties were measured. The spiro binuclear with three rings had an IT band at 808 nm (ϵ 9 ± 1 M^{-1} cm^{-1}) and that with four rings had an IT band at 690 nm (ϵ 2.3 ± 0.7 M^{-1} cm^{-1}). This compares with a band at 910 nm (ϵ 43 ± 2) measured earlier for the two-ring spiro binuclear. The through-bond distances between ruthenium centers range from 11.3 to 17.5 Å. The values of the electron tunneling matrix elements were calculated from Hopfield's theory and were found to be 1.7×10^{-2}, 6.8×10^{-3}, and 3.1×10^{-3} eV for the two-ring, three-ring, and four-ring binuclears, respectively. These correspond to rate constants of 8.0×10^7, 4.9×10^6, and 3.5×10^4 s^{-1}, respectively, for the three binuclears. The results are discussed in terms of long-range tunneling and are compared to results obtained in solid matrices and biological systems.

One of the great mysteries of electron transport involves the mechanism by which electrons are transferred between the biological redox proteins, particularly the cytochromes where the donor and acceptor atoms are often separated by distances of 25 Å or more.[1] It is generally accepted that the electron must tunnel over these vast distances, but the role of the intervening matter, if any, has not yet been elucidated. It is of particular interest to determine if certain groups, such as the aromatic side chains of amino acids in the protein, might play some role in mediating the passage of the electron between the redox centers.[2]

As a first step in determining the role that the "intervening" matter may play in such a process, we decided to look at electron transfer through completely saturated systems where tunneling, if it occurs, would be mediated only by a σ-bonded framework. We used the ideas developed by Taube[3] in that the donor and acceptor atoms are rutheniums, which are substitution inert in both the +2 and +3 oxidation states. Furthermore, the spiro compounds we selected are rigid molecules so that the electrons would have to travel through the bridge and could not simply pass from ruthenium to ruthenium directly, as might be possible if the bridge were free to flop around. Thus, the integrity of the system remains intact throughout the experiment, and the pathway available to the electron is well-defined.

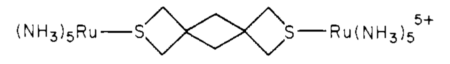
The first compound of this series, I, was prepared some years ago by Stein and Taube. The presence of an intervalence band at 910 nm with an extinction coefficient of 43 M^{-1} cm^{-1} was considered rather remarkable, but no explanation for this curious observation was suggested.[4]



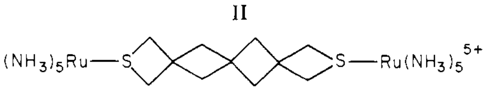
I

Since this system is fully saturated, either a very unusual mechanism was operating or a tunneling route is implicated. The low extinction coefficient is consistent with this latter interpretation, and the reaction is almost certainly nonadiabatic. In order to determine just how far an electron could tunnel with only a σ-bonded framework, we have prepared the corresponding three- and four-ring compounds, II and III, respectively.

Intervalence electron transfer was observed in these molecules, and the results of these investigations enable us to calculate some limits to the distances that electrons may tunnel at a reasonable rate with only a σ-bonded framework.



II



III

Experimental Section

Chemicals and Reagents. All chemicals were reagent grade and were used as supplied. Solvents were purchased from Baker Chemicals and $[Ru(NH_3)_6]Cl_3$ from Strem Chemicals. The oxidant, $(NH_4)_4Ce(SO)_4 \cdot 2H_2O$, was purchased from G. Frederick Smith Chemical Co. The organic ligands were prepared by Seitz following literature procedures.[5,6]

Synthesis of (μ-2,8-Dithiadispiro[3.1.3.1]decane)-decaamminediruthenium(II,II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_8H_{12}Ru(NH_3)_5](PF_6)_4$, and ($\mu$-2,10-Dithiatrispiro[3.1.1.3.1.1]tridecane)-decaamminediruthenium(II,II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_{11}H_{16}Ru(NH_3)_5](PF_6)_4$. To a solution of 100 mg of $[Ru(NH_3)_5(OH_2)](PF_6)_2$[7] in 3.0 mL of argon-deaerated acetone was added 1.9 equiv of the ligand. The reaction was allowed to proceed for 3 h under a steady argon stream. At the end of this time, the solution was pale yellow. Addition of deaerated diethyl ether resulted in the precipitation of a yellow solid. This solid was redissolved in a minimum of deaerated 0.1 M HCl and this solution was filtered. To the filtrate was added solid NH_4PF_6 until a yellow precipitate formed. This was filtered and washed with deaerated diethyl ether or ethanol; yield 40%. Anal. Calcd for $C_8H_{42}N_{10}F_{24}P_4Ru_2S_2$: C, 8.54; H, 3.76; N, 12.45; S, 5.70. Found: C, 9.23; H, 3.91; N, 12.03; S, 5.15. Calcd for $C_{11}H_{46}N_{10}F_{24}P_4Ru_2S_2 \cdot 2C_2H_6O$: C, 14.33; H, 4.65; N, 11.15; S, 5.10. Found: C, 14.32; H, 4.30; N, 11.25; S, 5.58.

Spectral Measurements. Natural abundance ^{13}C NMR spectra of the ligands were measured in $CDCl_3$ solution at 25 °C on a JEOL Model JNM-PS-100 NMR spectrometer with broad-band proton decoupling. The ligand having three rings gave a satisfactory spectrum after 64 scans, and the ligand with four rings produced a good spectrum after 560 scans. The visible and near-infrared spectra were recorded on a Cary 17 spectrophotometer.

The near-IR spectrum for the half-oxidized two-ring spiro binuclear gave the same value for the extinction coefficient over a threefold con-

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(1) "Tunneling in Biological Systems"; Chance, B.; DeVault, D. C.; Frauenfelder, H.; Marcus, R. A.; Schrieffer, J. R.; Sutin, N., Eds.; Academic Press: New York, 1979, p 506.

(2) We are currently constructing models to test these effects.

(3) Taube, H. *Pure Appl. Chem.* **1975**, *44*, 25.

(4) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.

(5) Seitz, G.; Mikulla, W.-D. *Tetrahedron Lett.* **1970**, *9*, 615.

(6) Seitz, G.; Mikulla, W.-D. *Liebigs Ann. Chem.* **1974**, 1328.

(7) Kuehn, G. C.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

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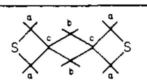
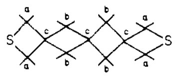
Table I. Nuclear Magnetic Resonance Spectral Data (^{13}C) of the Spiro Ligands[a]

ligand	a	b	c
	38.9	50.9	43.0
	39.2	49.2	44.4

[a] ppm relative to Me_4Si at 0.00 ppm.

centration range. The value for the corresponding three-ring spiro binuclear was the same over a twofold dilution. It was impossible to check the concentration dependence of the intervalence band for the four-ring spiro complex because of the very weak absorption of this species. We did look for an intravalence band between an equimolar mixture of Ru(II) and Ru(III) four-ring spiro monomers, but none was found even in very concentrated solutions.

Electrochemical Measurements. The electrochemical cell was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) and a platinum wire as the auxiliary electrode. The working electrode was a platinum button. All $E_{1/2}$ values are uncorrected for junction potentials. A PAR Model 173 potentiostat/galvanostat was used for potential control and a PAR Model 175 universal programmer was used as a sweep generator for the cyclic voltammetric experiments. The PAR Model 176 was used as a current follower. Voltammograms were recorded on a Hewlett-Packard Model 7000A X-Y recorder.

Analyses. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Results

^{13}C NMR Spectroscopy. The spiro ligands gave clean ^{13}C NMR spectra, indicating that they were free of organic impurities. Table I gives the positions of the observed peaks. The quaternary carbons all were characterized by long relaxation times, and it is assumed that the peaks corresponding to the two types of quaternary carbons in the 4-ring complex were degenerate since only one peak is ever observed for this species, in the appropriate region. The ^1H NMR spectra of these ligands have been reported previously.[5,6]

Electrochemistry. Cyclic voltammograms were run on the binuclear ruthenium complexes in 0.1 M HCl. Only a single broad reversible anodic wave was observed in each case (complex II, +550 mV; complex III, +530 mV, vs. SHE). These data are completely analogous to that obtained earlier for the two-ring complex (single broad peak at +600 mV vs. SHE). The two stages of oxidation are poorly resolved, as might be expected given the lack of direct sulfur–sulfur interaction and the large Ru–Ru distances.

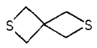
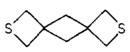
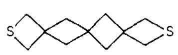
By use of the abbreviations [2,2] for the 4^+ ion, [2,3] for the 5^+ ion, and [3,3] for the 6+ ion, the equation describing the comproportionation equilibrium becomes

$$[2,2] + [3,3] \overset{K_{\mathrm{COM}}}{\rightleftharpoons} 2[2,3] \qquad (1)$$

The value of K_{COM} may be estimated from the separation of $E_{1/2}$ values for the two oxidations. Since no separation was observed in the spiro molecules, the value of K_{COM} must lie close to the statistical value of 4.

Visible Near-IR Spectra. The visible–near-infrared spectra of the [2,2], [2,3], and [3,3] ions were recorded in 0.2 M DCl with matched Suprasil cells. The mixed valence ions ([2,3]) and the fully oxidized binuclears ([3,3]) were generated by oxidation of the completely reduced species by Ce(IV). For both these complexes, addition of the second oxidizing equivalent causes absorption in the near-IR to vanish entirely, but a small non-Gaussian band appears slowly at ~700 nm. Formation of decomposition products with similar absorption properties has been observed for other ruthenium–sulfur-bonded products, e.g., $(NH_3)_5Ru(thiocyclobutane)^{3+}$ and $(NH_3)_5Ru(1,3\text{-dithiatane})^{3+}$.[8] The spectral parameters for the intervalence transition bands are listed in Table II.

Table II. Intervalence Transition Bands for Ruthenium Spiro Binuclears, $(NH_3)_5Ru\text{-bridge-}Ru(NH_3)_5{}^{5+}$

bridge	distance,[a] Å	λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)[b]
	11.3	910 (43 ± 2)
	14.4	808 (9 ± 1)
	17.6	690 (2.3 ± 0.7)

[a] Distances are calculated as "through-bond distances" from Ru to Ru by using the values S–C, 1.80 Å; C–C (sulfur-containing ring), 1.54 Å; C–C (carbon-only containing ring), 1.57 Å; Ru^{II}–S, 2.19; Ru^{III}–S, 2.40 Å. [b] Extinction coefficients are for the half-oxidized binuclears and are uncorrected for K_{COM}.

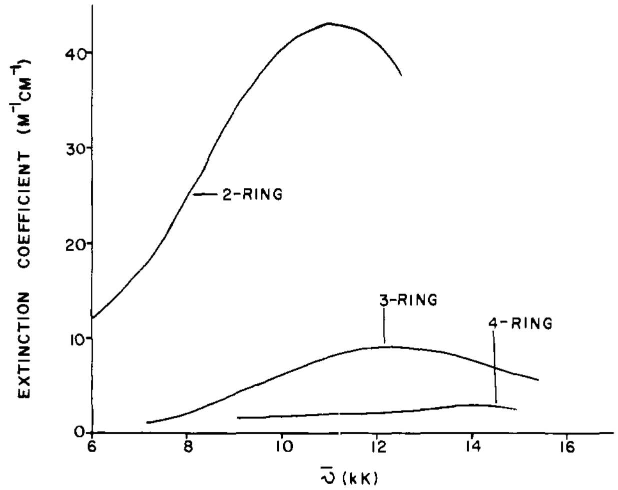


Figure 1. Intervalence bands for the mixed-valence two-ring, three-ring, and four-ring ruthenium spiro binuclears.

Discussion

Hush[9] has developed a theoretical treatment that satisfactorily describes the properties of intervalence transition bands in mixed-valence compounds in which the valencies are localized and interactions between metal sites are weak. A remarkable number of intervalence systems have been rationalized by this theory. However, when the coupling becomes too weak, the Hush model cannot be used because, in calculating the rates of thermal electron transfer rates from optical properties, the assumption is made that the transfer is adiabatic. Intervalence bands of very weakly coupled metal centers are characterized by very small extinction coefficients and bands that are broader than those predicted by Hush's theory.

For the spiro complexes of ruthenium, weak intervalence bands were observed (Table II). By use of Hush's theory for intervalence electron transfer and the assumption of a Gaussian band shape, a lower limit for the bandwidth at room temperature may be calculated from eq 2 where $\bar{\nu}_{max}$ is the IT band maximum and $\bar{\nu}_{1/2}$ is the bandwidth at half-height, in $cm^{-1} \times 10^3$.

$$\bar{\nu}_{max} = (\bar{\nu}_{1/2})^2/2.31 \qquad (2)$$

The shape of the IT bands was obscured by a shoulder at the high energy side (Figure 1). To get the bandwidth, we measured the half-width at half-height on the low energy side and this number was doubled, assuming a Gaussian band shape. For the three-ring complex it was calculated that the bandwidth at half-height was $5.3 \times 10^3\ cm^{-1}$, and for the four-ring complex it was $5.8 \times 10^3\ cm^{-1}$ (see Figure 2). The observed values were somewhat larger: 6.4 and $7.0 \times 10^3\ cm^{-1}$, respectively. Also, the oscillator strengths were extremely small. These results are not unexpected since the coupling in our systems is very weak, and

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(8) Stein, C. A. Ph.D. Thesis, Stanford University, 1978, p 196.

(9) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

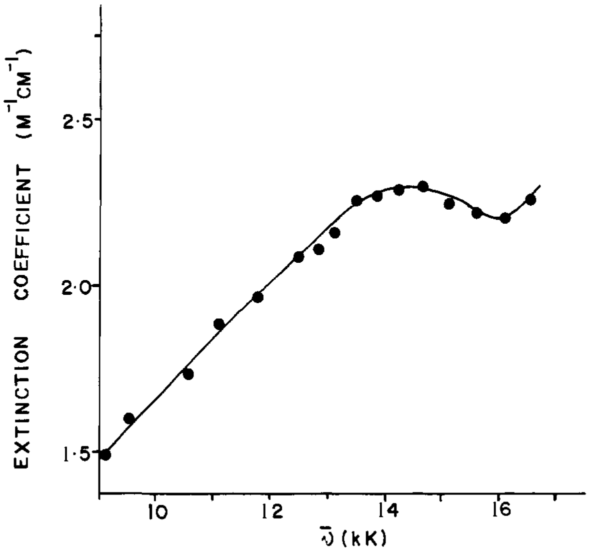

Figure 2. Intervalence band for the four-ring ruthenium spiro binuclear mixed-valence compound on an expanded scale.

the Hush theory should not be used in such cases.

Hopfield[10] has developed a nonadiabatic, multiphonon electron tunneling theory, which has been used with considerable success in correlating and interpreting electron-transfer reactions between large biomolecules such as the cytochromes,[11] *Chromatium*,[12] and the bacteriochlorophylls.[11,13] In this approach, the electron is regarded as being initially localized at site a. In the final state, the electron resides in the region of site b. The rate of electron transfer from a to b is then given by the expression

$$k_{\mathrm{ab}} = (2\pi/\hbar)|\mathbf{T}_{\mathrm{ab}}|^2\int_{-\infty}^{+\infty} D_{\mathrm{a}}(E)D'_{\mathrm{b}}(E)\,\mathrm{d}E \tag{3}$$

where $\hbar$ is Planck's constant/2π, $|\mathbf{T}_{\mathrm{ab}}|$ is the tunneling matrix element which is a function of the distance separating a and b, $D_{\mathrm{a}}(E)$ is the electron removal spectral distribution, and $D_{\mathrm{b}}(E)$ is the electron insertion spectrum. Both $D_{\mathrm{a}}(E)$ and $D_{\mathrm{b}}(E)$ are assumed to be Gaussian line shape functions. This reduces to

$$k_{\mathrm{ab}} = (2\pi/\hbar)|\mathbf{T}_{\mathrm{ab}}|^2(2\pi\sigma^2)^{-1/2}e^{-(E_{\mathrm{a}}-E_{\mathrm{b}}-\Delta)^2/2\sigma^2} \tag{4}$$

where E_{a} and E_{b} are the redox energies, σ is the full bandwidth at 0.61 height of the optical band, and Δ is the vibronic coupling parameter. For a symmetrical binuclear, $E_{\mathrm{a}} = E_{\mathrm{b}}$, and Δ is the energy of the optical transition. Hopfield[10] has further developed an expression that directly relates the oscillator strength of the intervalence transition band to the tunneling matrix element.

$$\epsilon(E_{\mathrm{op}}) = \left(\frac{2n}{n^2+1}\right)\left(\frac{2\pi^2}{3}\right) \times \left(\frac{N_0}{2300}\right)\left(|\mathbf{T}_{\mathrm{ab}}|^2a^2e^2/E_{\mathrm{o}}\hbar c\right)\int_{-\infty}^{+\infty} D_{\mathrm{d}}(E)D'_{\mathrm{a}}(E+E_{\mathrm{o}})\,\mathrm{d}E \tag{5}$$

The convolution of eq 5 is

$$\epsilon(E_{\mathrm{op}}) = \left(\frac{2n}{n^2+1}\right)\left(\frac{2\pi^2}{3}\right)\left(\frac{N}{2300}\right) \times |\mathbf{T}_{\mathrm{ab}}|^2a^2e^2/E_{\mathrm{op}}\hbar c\left(\frac{1}{2\pi\sigma^2}\right)^{1/2} e^{-(E_{\mathrm{op}}+E_{\mathrm{d}}-E_{\mathrm{a}}-\Delta)^2/2\sigma^2}$$

Again, $E_{\mathrm{d}} = E_{\mathrm{a}}$, and at the peak maximum $E_{\mathrm{op}} = \Delta$. All variables in this equation are directly measurable in our systems, and we may calculate the value of the tunneling matrix element $|\mathbf{T}_{\mathrm{ab}}|$.

Table III. Values of the Tunneling Matrix Elements and Rates for Intervalence Electron Transfer in Ruthenium Spiro Binuclears, $(NH_3)_5$Ru-bridge-Ru$(NH_3)_5{}^{5+}$[a]

bridge	$\lvert T_{\mathrm{ab}}\rvert$,[b] eV	k_{AB}, s^{-1}
2-ring	1.7×10^{-2}	8.0×10^{7}
3-ring	6.8×10^{-3}	4.9×10^{6}
4-ring	3.1×10^{-3}	3.5×10^{4}

[a] Calculated from Hopfield's theory; see text. [b] The value of n was assumed to be 1.53 in all cases.

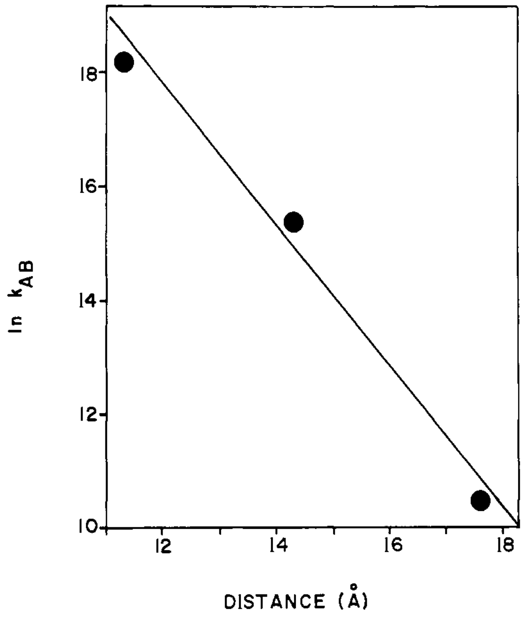

Figure 3. Plot of ln k_{AB} for electron transfer vs. distance for the ruthenium spiro binuclears.

From this, we may then estimate the rate constants for these transfers using eq 3.[14] The values obtained are presented in Table III.

It is not known how far apart the donor and acceptor of an electron transfer reaction can be and what special requirements may be necessary to facilitate this transfer. Using crude, first-approximation estimates of tunneling probabilities, one may calculate distances of tens of angstroms. Experimentally, various values have been found. In 1963, Miller[15] reported that trapped electrons may scavenge electrons in cold, organic glass by tunneling over distances of 30–50 Å. Frozen anions and cations of pentane can neutralize each other at distances up to 50 Å.[16] Electrons may tunnel up to 100 Å through planar sandwiches of metal–insulator–metal materials.[17] Evidence that electron transfer in glassy solids occurs via tunneling is abundant. For 2-methyltetrahydrofuran at 77 K, for example, the rate for benzonitrile as acceptor is 5 × 10^5 s^{-1}.[18] In all these studies, it is assumed that the trapped electron to acceptor distance distribution is random and that a given trapped electron tunnels to its nearest acceptor molecule. The exact geometry of the intervening matter, the extent of bonding, and the type of orbitals available are largely unknown. Contrary to earlier and higher estimates for tunneling distances in biological systems, Hopfield calculates that the tunneling distance in *Chromatium*,[12] for example, where again the exact geometry of the donor and acceptor molecules and the

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(10) Hopfield, J. J. *Biophys. J.* **1977**, *18*, 311.

(11) Hopfield, J. J. "Electrical Phenomena at the Biological Membrane Level"; Roux, E., Ed.; Elsevier: Amsterdam, 1977, p 471.

(12) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640.

(13) Reference 1, p 730 ff.

(14) A more complex theory has been developed by Redi and Hopfield (Redi, M.; Hopfield, J. J. *J. Chem. Phys.* **1980**, *72*, 6651), which may have appreciable effects on our calculations. We are unable to use the equations in this more complex approach because χ was not defined in a way in which we could dimensionally understand it.

(15) Miller, J. R. *Chem. Phys. Lett.* **1973**, *22*, 180.

(16) Brocklehurst, B. *Chem. Phys.* **1973**, *2*, 6.

(17) Kurtin, S. L.; McGill, T. C.; Mead, C. A. *Phys. Rev B* **1971**, *B3*, 3368.

(18) Reference 1, p 272.

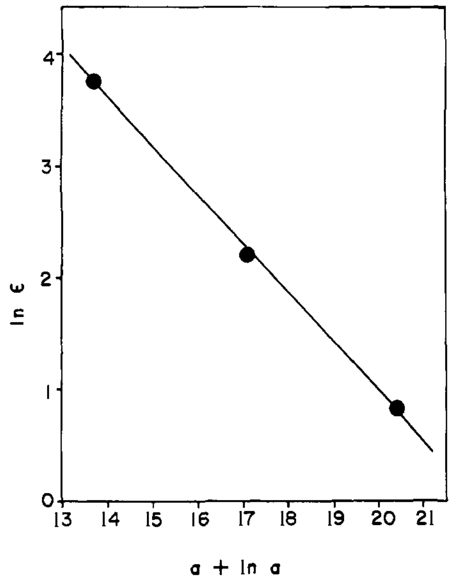

Figure 4. Plot of log ϵ vs. (a + ln a) where a is the "through-bond" distance in Å between the metal atoms in the ruthenium spiro binuclears.

intervening matter is unknown, must be less than 10 Å.

In our approach to the problem, we have a fairly accurate estimate of the distance separating the donor and acceptor metals as well as the geometry of the intervening matter, i.e., the organic bridge. It is interesting to note that the electron transfer is calculated to be still quite rapid (3.5×10^4 s^{-1}) over a distance of 17.6 Å where the mediating material (neglecting any possible assistance from the solvent)[19] possesses only σ bonds. A plot of log k_{AB} vs. distance (Å) between the donor and acceptor metal gives a straight line (Figure 3), which can be extrapolated to predict rate constants at even longer distances, assuming that this linear relationship is obeyed. At a distance of 26 Å, for example, we calculate that the rate of transfer is still about one electron per second, using only a σ-bonded framework to assist in electron mediation. The extinction coefficient would be too weak for this band to be measured by current methods (ϵ 0.036 M^{-1} cm^{-1} by extrapolation of the line in Figure 4). In fact, we are approaching the limit of measurement of weak intervalence bands with the 4-ring spiro binuclear.

This study poses some intriguing questions concerning electron transfer in vivo. Obviously a series of electron-rich mediator groups is not an absolute requirement for long-distance electron transfer, although these groups may be useful for directing the electron to its proper place and in providing a more rapid redox reaction. Conversely, there must be some rather elaborate controls in biologically important systems, designed to keep the electron from getting into the wrong place where it could conceivably do a good deal of harm.

These results also suggest that geometry may not be of overwhelming importance, since the spiro rings are oriented perpendicular to each other yet electron transfer is calculated to be relatively rapid. An investigation of the angular dependence of the cytochrome EPR absorption in oriented membrane multilayers has shown that the c_{553} and c_{555} heme planes are approximately perpendicular to each other, suggesting that the heme orientation is not of great importance in this transfer either.[20] In this latter reaction, there is a possibility that the electrons may not be passed from heme to heme directly but may use some other route through the proteins.

Conclusions

We have established that electrons may tunnel rather effectively over long distances of at least 17 Å with only a σ-bonded framework. It does not appear to be a serious drawback that the rings intervening between the donor and acceptor metals are located at right angles to one another. Whether this in fact assists, retards, or is irrelevant to the electronic motion cannot be determined from our experiments. We are currently constructing bridges of other geometries involving only σ bonds, in an attempt to address these questions and gain a greater appreciation of the fundamental nature of the electron tunneling mechanism between two metal sites in solution.

Acknowledgment. We are deeply indebted to Dr. J. Peisach of Albert Einstein College of Medicine for providing facilities which allowed us to make these compounds (Heart and Lung Institute Grant HC 15399). We are further grateful to Dr. C. Creutz and Dr. N. Sutin of Brookhaven National Laboratories for allowing us to use their UV–vis–near-IR and electrochemistry instruments. This part of the work was performed under the auspices of the U.S. Department of Energy and was supported by its Division of Basic Energy Sciences. Finally we wish to thank Dr. F. Brewer of Albert Einstein College of Medicine for running the ^{13}C NMR spectra and one of the referees for helpful comments. Financial support of this research was provided by the Research Corporation in the form of a Cottrell Grant to N.A.L., and for this we are very grateful.

Registry No. I, 76723-23-4; II, 81205-53-0; III, 81205-54-1; $[(NH_3)_5RuS_2C_8H_{12}Ru(NH_3)_2](PF_6)_4$, 81120-97-0; $[(NH_3)_5RuS_2C_{11}H_{16}Ru(NH_3)_5](PF_3)_4$, 81120-99-2; 2,8-dithiadispiro[3.1.3.1]decane, 27211-80-9; 2,10-dithiatrispiro[3.1.1.3.1.1]tridecane, 54368-40-0; $[Ru(NH_3)_5(OH_2)](PF_6)_2$, 34843-18-0.

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(19) We are presently making more of this material to allow us to look at the effect of solvent on the electron transfer process.

(20) Reference 1, p 347.