Fe^{3+}(aq), 15377-81-8; Co^{2+}(aq), 15276-47-8; Ni^{2+}(aq), 15365-79-4; Cu^{2+}(aq), 14946-74-8; Zn^{2+}(aq), 15906-01-1; Ga^{3+}(aq), 19521-89-2; Y^{3+}(aq), 73890-49-0; Ag^{+}(aq), 42566-53-0; Cd^{2+}(aq), 14752-06-8; U^{4+}(aq), 86392-55-4.

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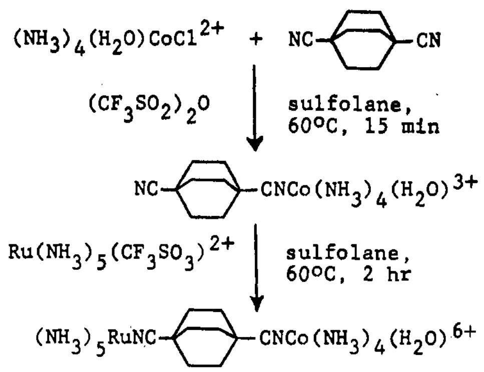
Inhibition of Thermal Electron Transfer by the Saturated Bridging Ligand in (μ-1,4-Dicyanobicyclo[2.2.2]octane)(pentaammineruthenium(II))aquotetraamminecobalt(III)

Sir:

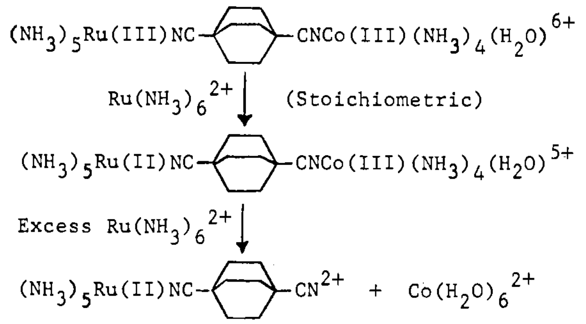
The reduction of oxygen to water in mitochondria involves a series of oxidation–reduction reactions that produce several ATP molecules for each oxygen atom that is reduced. The electron-transfer series involves metal-containing enzymes (cytochromes and ferredoxins) that do not react as they would be expected to react in homogeneous solution. Since many of these species are membrane bound, it has been widely assumed that the reaction specificity derives from the spatial arrangement of enzymes in and across mitochondrial membranes.[1] An important aspect of this arrangement is the distance that separates various components. Determining these distances in intact systems has been an intractable problem, and experimental results for protein complexes have also proven to be conjectural.[2] Some interesting data have recently been obtained in the laboratories of Gray and of Isied for individual proteins that have been chemically modified to include a redox center that can undergo an electron-transfer reaction with the native prosthetic group.[3,4] Comparison of results from structurally well-defined models and these protein complexes should be valuable in determining the types of mechanisms that may allow efficient electron-transfer reactions in natural systems. The aim of our work is to define parameters for rather simple, structurally well-defined complexes that contain reducing and oxidizing centers.

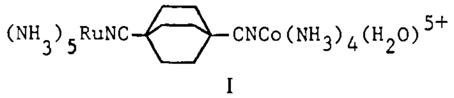
Several groups have been involved in developing systems to model the spatially separated metal-to-metal atom biological electron-transfer reactions. An appropriate system would involve electron transfer from one metal atom to another across a saturated bridge, which would separate the metal atoms by a known, fixed distance. In designing such systems, Taube and co-workers have ingeniously exploited two general patterns of metal ion reactivity: (1) the inertness to ligand exchange of metal atoms that have highly populated bonding and nonbonding orbitals and empty antibonding orbitals (low-spin d^5 and d^6 ions, Ru(III), Co(III) and Ru(II)) and (2) the sluggishness of reactions that involve a high Franck–Condon barrier (i.e. those of Co(III) → Co(II) relative to Ru(III) → Ru(II)).[5] Thus, a bimetallic complex with Co(III) and Ru(III) can remain intact in solution, and the addition of a suitable reducing agent will cause the Ru(III) atom to be reduced before the Co(III) atom even if the potential favors the Co(III) reduction. An additional advantage of this scheme is that subsequent reduction of the Co(III) site by the newly generated Ru(II) site produces Co(H$_2$O)$_6^{2+}$, which is very difficult to oxidize, rendering the reaction irreversible. Thus, even a reaction with an unfavorable free energy difference can be accomplished. In several reported applications of this scheme, a major difficulty has been encountered—saturated ligands are generally flexible and the first-order reactions that have been observed quite likely result from the reaction of the metal atom on one end of the bimetallic complex with the metal atom at the other end when the two metal atoms are in relatively close proximity. In this report, we present results for the first case of an unambiguously rigid, bimetallic complex that is capable of thermal electron transfer, (μ-1,4-dicyanobicyclo[2.2.2]octane)(pentaammineruthenium(II))aquotetraamminecobalt(III) (I).

Scheme I



Scheme II





I

This bimetallic complex is synthesized from Co(NH$_3$)$_4$(H$_2$O)Cl^{2+}, 1,4-dicyanobicyclo[2.2.2]octane, and Ru(NH$_3$)$_5$(CF$_3$SO$_3$)$^{2+}$ (Scheme I).[7] The visible–UV spectrum (498 nm, $\epsilon = 62$; 383 nm, shoulder; 283 nm, $\epsilon = 613$) is characteristic of Co$^{\text{III}}$N$_5$O and Ru$^{\text{III}}$(NH$_3$)$_5$NCR coordination spheres (where R is a bridgehead nitrile),[8] the cyclic voltam-

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(7) The selective dehalogenation of the Co(III) complexes in situ is analogous to the preparation of [(NH$_3$)$_5$CoO$_3$SCF$_3$]$^{2+}$: Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrence, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470. The use of [(NH$_3$)$_5$RuO$_3$SCF$_3$]$^{2+}$ has been described: Anderes, B.; Collins, S. T.; Lavallee, D. K. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Kansas City, MO, 1982; American Chemical Society: Washington, DC, 1982; INOR 15; and submitted for publication.

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mogram ($E_{1/2}$ vs. NHE = 0.467 V) is characteristic of $Ru(NH_3)_5NCR^{3+/2+}$,[9] and the infrared spectrum shows Ru(III) and Co(III) coordination of NCR[8c] (γ(CN) shifts from 2240 cm^{-1} for the ligand to 2310 and 2240 cm^{-1} when only Co(III) is coordinated to a single peak at 2300 cm^{-1} when both Co(III) and Ru(III) are bound). Free ligand is eliminated in the synthesis by extraction, so no diruthenium species should be formed. The elemental analysis is consistent with $CoRuC_{16}H_{43}N_{11}F_{18}O_{19}S_6$. (Anal. Calcd: C, 13.88; H, 2.96; N 11.13. Found: C, 13.71; H, 2.72; N 11.30).[9] When excess $Ru(NH_3)_6^{2+}$ is added, the Ru(III) atom is reduced and the remainder of the $Ru(NH_3)_6^{2+}$ reduces the Co(III) with a rate constant of 0.54 M^{-1} s^{-1}. When $Ru(NH_3)_6^{2+}$ is added as the limiting reagent, the only Ru(II) in solution after mixing is in the bimetallic complex (reduction of $Ru(NH_3)_5NCR^{3+}$ is rapid and essentially quantitative). In this case (at 25 °C, 0.10 M ionic strength with $H_3O^+CF_3SO_3^-$, and [I] = 1.0×10^{-5} M), reduction of the Co(III) is very slow (less than 10% after 10 h) (Scheme II). A cyclic voltammogram of the product shows that the ruthenium atom is still coordinated to the NCR moiety (i.e. $E_{1/2}$ is still 0.470 ± 0.010 V), and the visible absorption spectrum shows that the initial coordination sphere of the Co(III) is still intact (i.e. the 498-nm peak remains while the absorption in the UV region due to both Ru(III) and Co(III) shifts to lower wavelength on reduction as expected[8c]).

Since no reaction is observed, an upper limit of the rate constant is estimated. On the assumption that O_2 is excluded and that a 10% change in absorbance is within experimental uncertainty, the estimated upper limit is 3×10^{-6} s^{-1}. To deduce the effect of the saturated barrier, the rate constant for the same reaction without the bridge must be estimated. The rate constant for the reduction of $Co(NH_3)_4(H_2O)NCR^{3+}$ by $Ru(NH_3)_6^{2+}$ at 25 °C and an ionic strength of 0.10 M is 7.0 M^{-1} s^{-1}, and the $\Delta E_{1/2}$ between $Ru(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_5NCR^{3+/2+}$ is 0.417 V, leading to a rate constant of 2.7×10^{-3} M^{-1} s^{-1} by Marcus' theory.[11] Account must be taken of the advantage of preassembly of the 2+ and 3+ ions, 1.8 kcal/mol[12] and a statistical factor for the effective concentration of an intermolecular reaction (for unit probability of contact of two species the size of the Ru(II) and Co(III) coordination spheres in a close-packed liquid model,[13] this factor is $^1/_6$ M), giving an effective concentration factor of 3.7 M. The predicted rate constant is thus 1.0×10^{-2} s^{-1} for the analogous intramolecular reaction without the bicyclooctane bridge, and the barrier due to the bridge is at least a factor of 3×10^4.

The theories most commonly applied to predictions of rates of tunneling reactions are due to Hopfield and Jortner.[14,15] Marcus and Siders[16] have discussed the importance of distinguishing cases involving matter between the sites (as in Hopfield's estimation of $e^{-1.4\Delta r}$ for cytochromes)[12] and cases involving vacuum (Jortner's estimate of $e^{-2.6\Delta r}$).[13] All approaches have resulted in an exponential dependence of the rate on distance, but the value of the exponential factor is difficult to ascertain theoretically. Our observed value of over 10^4 for 4 Å requires a value of, at most, $e^{-2.3\Delta r}$.[17] It is certainly possible for electron-transfer reactions to occur over large distances, as recently shown by Calcaterra, Closs, and Miller,[18] but it appears from this work that further experiments now under way that involve higher driving forces and/or shorter barriers will be necessary to achieve measurable electron-transfer reactions with bimetallic complexes of Ru(II) and Co(III).

Acknowledgment. We gratefully acknowledge support of the Petroleum Research Fund, administered by the American Chemical Society, the NSF (Grant CHE 8006094), and the NIH (Grants GM 27179 and RR 08176). We are indebted to Dr. J. C. Krause of Du Pont for supplying us with 1,4-dichlorobicyclo[2.2.2]octane for synthesis of the dicyano ligand and to Dr. John Petersen of Clemson University for generously providing 1,4-dicyanobicyclo[2.2.2]octane made by a different method.

Registry No. I^{6+}, 86542-42-9; I^{5+}, 86542-43-0; $Co(NH_3)_4(H_2O)Cl^{2+}$, 39262-43-6; $Ru(NH_3)_5(CF_3SO_3)^{2+}$, 84278-97-7; $Ru(NH_3)_6^{2+}$, 19052-44-9; (1,4-dicyanobicyclo[2,2.2]octane)pentaammineruthenium(II), 86542-44-1.

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(11) The method used to estimate this rate is the cross-relation of Marcus, $k_{12} = (k_{11}k_{22}K_{12}f)^{1/2}$, where $\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)]$: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. To calculate one cross-reaction ($Ru(NH_3)_5NCR^{2+} + Co(NH_3)_4(H_2O)NCR^{3+}$) from the rate of another ($Ru(NH_3)_6^{2+} + Co(NH_3)_4(H_2O)NCR^{3+}$), the most important factor is ΔK_{12}, as long as the self-exchange rates and f are very similar. Since the self-exchange rates for ions of the same charge and size and very similar inner-sphere reorganization energies, as in this case, should be very similar, the relative magnitude of the f values for the two reactions (f'/f) needs to be determined. Due to the difficulties with the measurement of the $Co(NH_3)_6^{2+/3+}$ self-exchange rate (Taube, H., paper presented at the 182nd National Meeting of the American Chemical Society, New York, NY, 1982) the best established self-exchange rate for a cobalt–amine complex is that of $Co(en)_3^{3+/2+}$ (5×10^{-5} M^{-1} s^{-1}): Endicott, J. F.; Schroeder, R. R.; Chidester, D. H.; Ferrier, D. R. *J. Phys. Chem.* **1973**, *77*, 2579. Using the values of the $Ru(NH_3)_6^{3+/2+}$ self-exchange rate constants of Meyer and Taube (Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369) and correcting to $I = 0.01$ M (as in: Lavallee, C.; Lavallee, D.; Deutsch, E. A. *Inorg. Chem.* **1978**, *17*, 2217) give $k = 3 \times 10^3$. Then with use of the cross-relation, $\Delta E°$ for the first reaction above is calculated to be −0.10 V and for the second, 0.32 V, giving $(f'/f)^{1/2} = 1.3$. The absolute values of these potentials are questionable, but relative values for very similar reactants were reliably determined by the cross-relation. The $(f'/f)^{1/2}$ ratio is not very sensitive to the absolute $\Delta E°$ values (i.e. using −0.20 and +0.22 V gives $(f'/f)^{1/2} = 1.2$). The estimate of the rate for the reaction of $Ru(NH_3)_5NCR^{2+}$ with $Co(NH_3)_4(H_2O)NCR^{3+}$ from that with $Ru(NH_3)_6^{3+}$ thus becomes $k' = k(f'/f)^{1/2} \exp[nF(\Delta\Delta E°)/2RT] = (7.0\ \mathrm{M^{-1}\ s^{-1}})(1.3) \exp(-0.417\ \mathrm{V})(23.05\ \mathrm{kcal/(mol\ V)})/(2 \times 1.987\ \mathrm{kcal/(mol\ K)})(298\ \mathrm{K}) = 2.7 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$.

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