Volume 24
Number 12
June 5, 1985

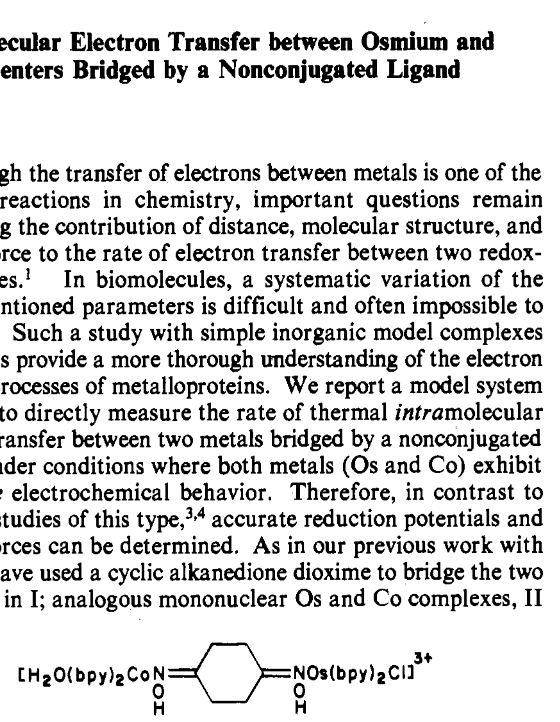
Inorganic Chemistry

Communications

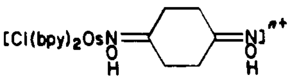
Intramolecular Electron Transfer between Osmium and Cobalt Centers Bridged by a Nonconjugated Ligand

Sir:

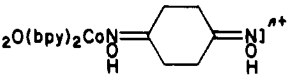
Although the transfer of electrons between metals is one of the simplest reactions in chemistry, important questions remain concerning the contribution of distance, molecular structure, and driving force to the rate of electron transfer between two redox-active sites.[1] In biomolecules, a systematic variation of the above-mentioned parameters is difficult and often impossible to achieve.[2] Such a study with simple inorganic model complexes would thus provide a more thorough understanding of the electron transfer processes of metalloproteins. We report a model system designed to directly measure the rate of thermal *intra*molecular electron transfer between two metals bridged by a nonconjugated ligand, under conditions where both metals (Os and Co) exhibit *reversible* electrochemical behavior. Therefore, in contrast to previous studies of this type,[3,4] accurate reduction potentials and driving forces can be determined. As in our previous work with Ru,[5] we have used a cyclic alkanedione dioxime to bridge the two metals as in I; analogous mononuclear Os and Co complexes, II and III, have also been prepared.[6] The relevant physical properties of these and similar Os– and Co–bipyridyl complexes are presented in Tables I and II. In particular, a cyclic voltammogram of I shows reversible waves at 0.617 and 0.314 V vs. SCE for the Os and Co centers, respectively. The Co(II) monomer (IIIa) and I both exhibit EPR signals characteristic of six-coordinate Co(II) complexes.[11]



I



IIa, $n = 1$
b, $n = 2$



IIIa, $n = 2$
b, $n = 3$

bpy = 2,2'-bipyridine

Table I. Analytical Data for the Os–Co Dimer, Os Monomer, and Co Monomers[a]

complex		% C	% H	% N
I·H_2O	calcd	36.28	3.04	9.20
	found	36.52	3.04	8.77
IIa	calcd	37.84	3.18	10.18
	found	37.68	2.64	9.88
IIIa	calcd	38.01	3.44	10.23
	found	38.13	2.70	9.46
IIIb·H_2O	calcd	31.72	3.07	8.54
	found	31.54	2.68	8.37

[a] PF_6^- salts. C, H, N analyses provided by Robertson Laboratory, Florham Park, NJ.

Although the cobalt is the more easily oxidized metal in the Os(II)–Co(II) dimer, addition of 1 equiv of Ce(IV) leads to rapid oxidation of the Os as evidenced by the disappearance of the characteristic Os(II)–oxime charge-transfer bands.[12] This gen-

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(1) See for example: (a) "Tunneling in Biological Systems"; Chance, B., De Vault, D., Frauenfelder, H., Marcus, R. A., Schreiffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979. (b) *Faraday Discuss. Chem. Soc.* **1982**, *74*.

(2) Elegant experiments by Gray, Isied, and co-workers have measured rates of intramolecular electron transfer with known driving forces in semi-synthetic metalloproteins: (a) Winkler, J. R.; Nocera, D. G.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798. (b) Yocom, K. M.; Winkler, J. R.; Nocera, D. G.; Bordignon, E.; Gray, H. B. *Chem. Scr.* **1983**, *21*, 29. (c) Kostić, N. M.; Margalit, R.; Che, C.-M.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 7765. (d) Yocom, K. M.; Shelton, J. B.; Schroeder, W. A.; Worosila, G.; Isied, S. S.; Bordignon, E.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 7052. (e) Nocera, D. G.; Winkler, J. R.; Yocom, K. M.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5154. (f) Isied, S. S.; Kuehn, C.; Worosila, G. *J. Am. Chem. Soc.* **1984**, *106*, 1722.

(3) Anderes, B.; Lavallee, D. K. *Inorg. Chem.* **1983**, *22*, 2665.

(4) Isied, S. S.; Vassilian, A. *J. Am. Chem. Soc.* **1984**, *106*, 1732.

(5) Geno, M. J. K.; Dawson, J. H. *Inorg. Chem.* **1984**, *23*, 1182.

(6) Complex I was synthesized by refluxing equimolar quantitites of IIIa and $[cis\text{-(bpy)}_2\text{OsCl}(\text{H}_2\text{O})]^+$ in 4:1 ethanol/water (v/v) under nitrogen for 1 h.[7,8] Purification of the dimer was done essentially as reported for the analogous Ru–Ru dimer.[5] Complex IIIa was synthesized from $[cis\text{-(bpy)}_2\text{CoI}_2]\text{I}$[9] and 1,4-cyclohexanedione dioxime[10] in aqueous ethanol at refluxing temperature. Column chromatography (alumina or Bio-Gel P-2) was necessary to separate the desired oxime complex from other products of the reaction. The Os(II) monomer (IIa) was isolated from the reaction of $[cis\text{-(bpy)}_2\text{OsCl}(\text{H}_2\text{O})]^+$ with 1,4-cyclohexanedione dioxime and was purified as for I. The Os(III) monomer (IIb) was generated in situ upon addition of 1 equiv of Ce(IV) to IIa in acidic solution. The Co(III) monomer (IIIb) was synthesized from $[cis\text{-(bpy)}_2\text{CoI}_2]\text{I}$[9] and 1,4-cyclohexanedione dioxime[10] by using the procedure described for the synthesis of other Co(III)–bipyridyl complexes: Maki, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2275.

(7) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

(8) The synthesis of $cis\text{-(bpy)}_2\text{OsCl}_2$ from OsCl_3 was done according to a modification (Geno, M. J. K.; Dawson, J. H. *Inorg. Chim. Acta*, in press) of the procedure reported by: Buckingham, D. A.; Dwyer, F. P.; Goodwin, H. A.; Sargeson, A. M. *Aust. J. Chem.* **1964**, *17*, 325.

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(12) In control experiments, addition of 1 equiv of Ce(IV) to the Co(II) monomer (IIIa) showed no significant changes in absorption over a period of 5 h. It was also found that addition of 1 equiv of Ce(IV) to the Os(II) monomer (IIIa) in acidic solution[13] led to the immediate production of IIb without further reaction over a period of at least 4 h. The rate of oxidation of Co(II)–bipyridyl complexes is slow compared to analogous Os(II)–bipyridyl complexes.[14]

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Table II. Electrochemical and Spectroscopic Characteristics of the Os–Co Dimer and of Os and Co Monomers Containing Bipyridyl Ligands

complex	EPR[a] g value	$E_{1/2}$,[b] V vs. SCE	electronic abs[c] λ_{max}, nm (log ϵ)
I	1.998	0.617 0.314	648 (3.56), 551 (3.63), 481 (4.07), 442 (4.04), 384 (3.99), 363 (4.02), 303 (3.99), 291 (4.98), 252 sh, 243 (4.81)
IIa	silent[d]	0.597	648 (3.50), 551 (3.61), 481 (4.00), 442 (4.01), 384 (4.00), 363 (4.02), 291 (4.73)
IIIa	1.998	0.304	303 (3.99), 291 (4.80), 252 sh, 241 (5.00)
IIIb	silent	0.300	423 (1.26), 319 (4.47), 306 (4.51), 222 (5.00[e])
$Co(bpy)_3^{2+}$	4.35[f]	0.241[f]	300 (4.62)[e–g]
$Co(bpy)_3^{3+}$	silent	0.241[f]	454 (1.82), 345 (3.14), 307 (4.48), 244 (4.80)[e,f]
$Os(bpy)_3^{2+}$		0.81[h]	
2,2′-bipyridine			282 (4.08), 236 (3.95)[e]

[a] EPR spectra were recorded in the solid state at room temperature as well as in frozen dimethyl sulfoxide (−77 K) at 9.018 GHz. 2,2-Diphenyl-1-picrylhydrazyl hydrate was used as a standard. [b] Electrochemical system used: Pt-disk working electrode, Pt-wire auxiliary electrode, and saturated calomel reference electrode. Experiments were performed under nitrogen at 25 °C in acetonitrile in the presence of 0.1 M tetra-*n*-butylammonium perchlorate. [c] Spectra were recorded (Cary 210 spectrophotometer) at 25 °C in 0.10 M HCl unless otherwise noted. [d] "Silent" refers to the observation that no EPR signal was observed in the solid state nor at −77 K in dimethyl sulfoxide. [e] Aqueous solution. [f] Similar properties were observed in this work under the same experimental conditions as noted. EPR: (i) Schrauzer, G. N.; Lee, L.-P. *J. Am. Chem. Soc.* **1968**, *90*, 6541. (ii) Mizuno, K.; Imamura, S.; Lunsford, J. H. *Inorg. Chem.* **1984**, *23*, 5310. Electrochemistry: (i) Tanaka, N.; Sato, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2059. (ii) Margel, S.; Smith, W.; Anson, F. C. *J. Electrochem. Soc.* **1978**, *125*, 241. [g] Simic, M. G.; Hoffman, M. Z.; Cheney, R. P.; Mulazzani, Q. G. *J. Phys. Chem.* **1979**, *83*, 439. [h] Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383.

erates the Os(III)–Co(II) dimer, which, in a slow intramolecular electron transfer step ($k_{intra} = 7.2 \times 10^{-5}\ s^{-1}$), produces the more thermodynamically stable Os(II)–Co(III) dimer.[13] The overall reaction sequence is

$$\mathrm{Os^{II}\text{–}Co^{II}} \xrightarrow{\mathrm{Ce(IV)}} \mathrm{Os^{III}\text{–}Co^{II}} \xrightarrow{k_{intra}} \mathrm{Os^{II}\text{–}Co^{III}}$$

The second reaction in this process is clearly shown to be *intra*molecular on the basis of (a) the lack of concentration dependence of the electron transfer rate[13] and (b) the determination of the rate of *inter*molecular electron transfer between the appropriate mononuclear complexes (IIb, IIIa).[6,15]

The rate reported herein for a system of known electrochemical driving force ($\Delta E_{1/2} = 300$ mV) is within the same order of magnitude as the intramolecular electron transfer rates estimated by Anderes and Lavallee[3] in a dicyanobicyclo[2.2.2]octane-bridged Co(III)–Ru(II) dimer ($k_{intra} < 3 \times 10^{-6}\ s^{-1}$) and measured by Isied and Vassilian[4] in a proline-bridged Co(III)–Ru(II) dimer ($k_{intra} = 10.4 \times 10^{-5}\ s^{-1}$). In contrast to the rather slow rates of intramolecular electron transfer observed in these three dinuclear metal systems, Miller, Calcaterra, and Closs[16] have observed extremely rapid (10^5–$10^9\ s^{-1}$) intramolecular rates involving strongly reducing organic free radicals. As recently discussed by Sandrini et al.,[14] numerous factors contribute to the slow rates of electron transfer of Co complexes as in the dinuclear metal systems. Nonetheless, it is clear that more work with both metal- and free-radical-containing systems will be necessary to determine the effect of distance on the rates of intramolecular electron transfer. For studying such reactions between metals, the approach outlined here has the distinct advantage that it can easily be extended to completely rigid bridging dioxime ligands having variable Os–Co separations. In addition, the reduction potentials of both metals and therefore the driving force can be readily varied by addition of substituents on the bipyridyl ligands. A systematic study of the rate of thermal *intra*molecular electron transfer between metals across a nonconjugated barrier as a function of the distance of separation and of the electrochemical driving force is now possible.

Acknowledgment. We gratefully acknowledge partial financial support from the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor D. L. Reger for helpful comments. J.H.D. is a Camille and Henry Dreyfus Teacher-Scholar, a Research Fellow of the Alfred P. Sloan Foundation, and a recipient of a NIH Research Career Development Award.

Registry No. I, 96041-27-9; I(Os^{II}–Co^{III},Os^{III}–Co^{II}), 96041-33-7; IIa, 96041-30-4; IIb, 96041-32-6; IIIa, 96041-28-0; IIIb, 96041-31-5; [*cis*-$(bpy)_2OsCl(H_2O)$]$^+$, 96041-29-1; [*cis*-$(bpy)_2CoI_2$]I, 96148-96-8.

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Received January 23, 1985

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(13) Kinetics experiments were performed in 0.2 M HCl at 25 °C. Absorbance measurements were begun 1 min after addition of 1 equiv of Ce(IV) to I in solution. Rate constants were determined from the slope of the linear least-squares fit of log $(A_\infty - A_t)_{442nm}$ vs. time. The reaction was followed in a concentration range of 1.00×10^{-5} to 7.41×10^{-5} M in I and was found to be first order with respect to [I]. The rate constants obtained from duplicate experiments at each of six concentrations of I ranged from 6.99×10^{-5} to $7.31 \times 10^{-5}\ s^{-1}$. The reactions were followed for at least 3 half-lives.

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(15) For the *inter*molecular experiments, the Os(III) complex (IIb) was generated in 0.20 M HCl by addition of 1 equiv of Ce(IV). The reaction between IIb and IIIa followed second-order kinetics where rate = k_{inter}[Os(III)–dioxime][Co(II)–dioxime] (25 °C, $\mu = 0.10$ M (LiCl)). The rate constant determined was $5.09 \times 10^{-4}\ M^{-1}\ s^{-1}$. From the values of k_{intra} and k_{inter}, it is possible to calculate that at the concentration of I used in our experiments[13] ($<10^{-4}$ M), intermolecular electron transfer contributes less than 2% to the observed rate.

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Hydroxide-Induced Reduction of (Tetraphenylporphinato)iron(III) in Pyridine

Sir:

In a recent investigation of the effects of axial ligands and solvents upon the electrochemistry for iron(III) porphyrins, we were surprised to find that the addition of hydroxide ion to a pyridine solution caused the iron(III) center to be reduced to iron(II).[1] Although our initial inclination was to attribute this base-induced reduction to impurities in the pyridine, the phenomenon has been confirmed after careful purification of reagents and has been observed in other workers' laboratories.[2,3] This has prompted a systematic study of the essential elements for the redox process.

Figure 1 illustrates the cyclic voltammograms for (*meso*-tetraphenylporphinato)iron(III) ($Fe^{III}TPP^+$) in dimethyl sulfoxide (Me_2SO) and in pyridine (Figure 1A,C). For solutions of $Fe^{III}TPP^+$ in Me_2SO the addition of OH^- results in axial binding

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(1) Jones, S. E.; Srivatsa, G. S.; Sawyer, D. T.; Traylor, T. G.; Mincey, T. C. *Inorg. Chem.* **1983**, *22*, 3903.

(2) Caughey, W. S., private communication, Department of Biochemistry, Colorado State University, 1983.

(3) Kadish, K. M., private communication, Department of Chemistry, University of Houston, 1984.