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The Influence of Short Saturated Barriers on Electron Transfer Between Metal Ions

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Although the metal-ion-containing prosthetic groups of many electron-transport proteins lie at or very near the protein surface, some appear to be relatively inaccessible. Also, it is difficult to imagine how metalloproteins that are intermediate in the reaction sequence for mitochondrial oxidative phosphorylation could be attached to both sequence neighbors to allow direct-contact electron transfer. Hence, it has been reasonably assumed that electron transport metalloproteins are separated from each other by some distance along the membrane surface [1]. It is of interest to determine how the rate of electron transfer varies with separation distance of redox partners. In this presentation, we will discuss complexes formed from two bridging ligands that separate the metal atoms (Ru(II) and Co(III)) so that direct contact is not possible. One of these ligands, 1,4-dicyano-(2,2.2)-bicyclooctane, is rigid and provides a shortest-distance-beyond-the-first-coordination-sphere of 4 Å, while the other, *trans*-1,4-dicyanocyclohexane, is flexible and provides a shortest distance of 2 Å (Fig. 1).

The general scheme for the electron transfer reaction sequence we have used, involving initial reduction of Ru(III) to Ru(II) by a rapid reaction followed by the slow and irreversible reduction of Co(III) to Co(II), has been developed by Taube and coworkers [2]. The synthesis of the complexes, I and II, was accomplished by use of a labile Ru(III)-trifluoromethanesulfonate intermediate [3] using a method described by Sargeson and coworkers for Co(III) complexes [4] and by the *in situ* removal of Cl^- from Co(III) using $(CF_3SO_2)_2O$. Estimates for the expected rate of intramolecular electron transfer were made using Marcus' theory as described for ruthenium complexes by Brown and Sutin [5], with a statistical factor to account for the effective concentration of an intramolecular reaction [6].

The results are simple, but interesting nonetheless. Upon reduction of I or II by a stoichiometric or substoichiometric amount of $Ru(NH_3)_6^{2+}$ (in 0.10 *M* aqueous trifluoromethanesulfonic acid at 25 °C) the Ru(III) nitrile site is reduced to Ru(II) but no reduction of Co(III) to Co(II) is evident even after 20 hours (with concentrations of I or II less than 10^{-4} *M*, so that intermolecular reactions are slow). Addition of excess $Ru(NH_3)_6^{2+}$ leads to formation of $Co(H_2O)_6^{2+}$ at expected rates. Based on a rate reduction of $\exp\{-0.72(\Delta r)\}$ [7], one would predict rate reductions of 18 and 4, for I and II, respectively, rather than the observed factors of 10^3 and 10^4 (the $E_{1/2}$ values of I and II are different, leading to different predicted rates). The barrier due to a saturated bridge, whether rigid with the shortest distance through the organic structure, as in I, or flexible with the shortest possible distance through the solvent, as in II, is much higher than might have been expected.

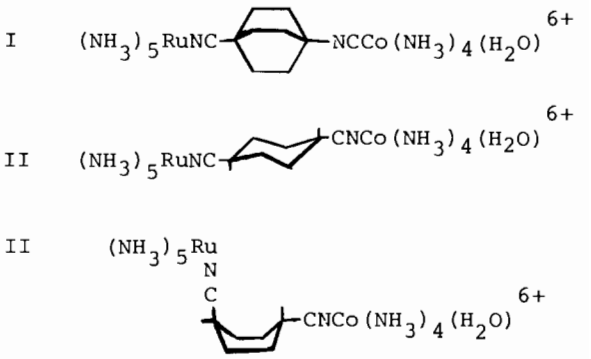

Fig. 1. μ-1,4-dicyano-(2.2.2)-bicyclooctane-pentaammineruthenium(III)-aquotetraamminecobalt(III) (6+) (I), and μ-*trans*-1,4-dicyanocyclohexane-pentaammineruthenium(III)-aquotetraamminecobalt(III) (6+) (II). Complex II is shown in its most probable chair form (upper) and in the boat form (lower) which provides the shortest distance between metal ions.

Acknowledgements. We gratefully acknowledge support for this work from the ACS-PRF (AC3-12197), the National Science Foundation (CHE 8006094) and the National Institutes of Health (GM 27179 and RR08176). We are indebted to Dr. J. C. Krause of DuPont de Nemours & Co. for 1,4-dichlorobicyclooctane for synthesis of the dicyano ligand and to Dr. John Petersen of Clemson University for 1,4-dicyano-(2.2.2)-bicyclooctane made by a different route.

1 D. DeVault, in 'Tunneling in Biological Systems', B. Chance *et al.*, (eds.), Academic Press, New York, 1979, pp. 303–316.
2 S. K. S. Zawacky and H. Taube, *J. Am. Chem. Soc., 103,* 3379 (1981) and references therein.
3 B. Anderes, S. T. Collins and D. K. Lavallee, submitted for publication.
4 N. A. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrance and A. M. Sargeson, *Inorg. Chem., 20,* 470 (1981).
5 G. M. Brown and N. Sutin, *J. Am. Chem. Soc., 101,* 883 (1979).
6 M. M. Kreitman and F. Hamaker, *J. Chem. Phys., 45,* 2396 (1966).
7 a) J. J. Hopfield, *Proc. Natl. Acad. Sci., U.S.A., 71,* 3640 (1974).

b) M. J. Potasek and J. J. Hopfield, *ibid.*, *74*, 229 (1977).
c) J. J. Hopfield, in 'Tunneling in Biological Systems', B. Chance *et al.* (eds.), Academic Press, New York, 1979, pp. 417–432.

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Monovalent Cation–A23187 Equilibria in MeOH–H_2O Solutions and on Phospholipid Vesicles

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Although the value of ionophore A23187 as a research tool arises from its transport specificity for divalent cations, the source and limits of this specificity have not been thoroughly studied. Previous work has shown that A23187 can complex monovalent cations [1], extract them to a bulk organic phase [2] and produce monovalent cation transport across certain biological membranes [3]. To elucidate the basis of the normal divalent cation specificity of this ionophore, detailed studies of the mechanism of monovalent cation transport will be necessary. In this communication we report equilibrium constants for complexation reactions involved in the transport of monovalent cations by this compound.

Experimental

Complexation constants in MeOH–H_2O mixtures were determined from absorbance measurements whereas fluorescence methods were employed for suspensions of small, unilamellar vesicles of dimyristoylphosphatidylcholine (DMPC). Nonaqueous pH* values in MeOH–H_2O mixtures were established and measured as described previously [4]. DMPC vesicles were prepared by sonication [5] and purified by ultracentrifugation [6].

Results

Table I shows 1:1 complexation constants of the ionophore with Li^+ and Na^+. The values in MeOH–H_2O mixtures were determined as conditional constants, K'_{MA}, by titration of A23187 with excess metal ion over the pH* range of 6–10. The equilibrium constants, K^*_{MA}, for the reaction $M^+ + A^- \rightleftarrows MA$ were obtained from the conditional values utilizing the relationship $K'_{MA} = K^*_{MA}(1 + K^*_{H1}a^*_H)$, where K^*_{H1} and a^*_H are the mixed-mode protonation constant and hydrogen ion activity in a given solvent, respectively. The complexation constant in suspensions of DMPC vesicles, K^b_{MA}, is defined by the reaction $M^+_{aq} + A^-_b \rightleftarrows MA_b$ where the subscripts aq and b denote solution and membrane-bound species, respectively. Constants for the bound compound were determined under conditions where the fraction of ionophore in the aqueous phase is small. The species A^-_b was generated by utilizing a high aqueous phase pH and then titrated with excess metal ion.

TABLE I. Complex Formation Constants of Ionophore A23187 with Li^+ and Na^+ at 25 °C.[a]

Medium	log K_{MA}	
	M = Li^+	M = Na^+
65% MeOH–H_2O[b]	2.53 ± 0.04[c]	1.95 ± 0.08
80% MeOH–H_2O	3.08 ± 0.05	2.36 ± 0.07
95% MeOH–H_2O	3.54 ± 0.03	–
100% MeOH[d]	4.1	3.4
DMPC vesicles	3.22 ± 0.04	–

[a]Ionic strength maintained at 0.05 *M* with $(C_2H_5)_4NClO_4$, buffer composition similar to that cited in Ref. 4. [b]Weight % MeOH. [c]Error given as 1 std. dev. [d]Taken from Ref. 1, $\mu \sim 0$.

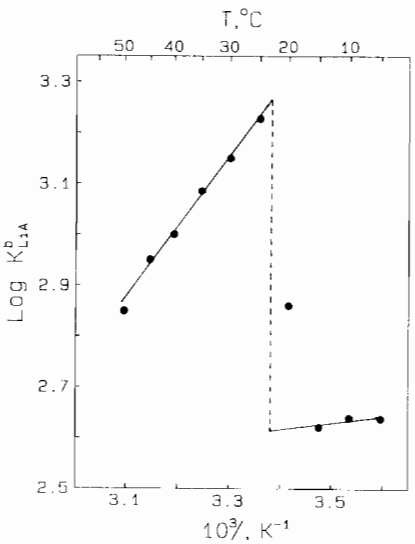

Fig. 1. The effect of temperature on log K_{LiA} values was determined as described in the text. The dashed line shows the location of the gel to liquid phase transition temperature of DMPC vesicles.

The effect of temperature on K^b_{LiA} is shown in Fig. 1 as a Vant'Hoff plot. The pronounced discontinuity in these data is located near the gel to liquid phase transition temperature (T_c) of DMPC vesicles (23 °C). The ΔH and ΔS values obtained from these data above T_c, are equal to –6.4 Kcal/mol and –6.7 cal/degree mol, respectively.