The parameters were derived from room-temperature measurements on QSB, CIQSB, and six others with different acceptor groups providing a range from -0.06 to -2.5 eV. Fitting these data to eq 1 provided the solvent reorganization energy ($\lambda_s = 0.75$ eV for MTHF), the reorganization energy ($\lambda_s = 0.45$ eV) of the high-frequency vibrational modes, here represented by a single average skeletal vibration of 1500 cm$^{-1}$, and the coupling matrix element $V = 6.2$ cm$^{-1}$. The parameters were further confirmed by measuring the temperature dependence of $k_{	ext{obs}}$ of NSB ($N = 2$-naphthyl) and $\lambda_s$ of MTHF. However, because of the weak exoergicity ($\Delta G^\circ = -0.06$ eV), the high-frequency mode is restricted to $\omega = 0$, making the part of eq 1 that depends on temperature equal to the classical Marcus expression.

According to eq 1, the rates are very weakly dependent on temperature because of the quantum-mechanical nature of the high-frequency modes. These modes are "frozen" in their temperature range. Their Franck-Condon factors are not improved by increasing temperature in our range because of nuclear tunneling in these modes. The nuclear tunneling makes the high-frequency modes efficient at disposing the excess energy in these highly exergic reactions. In addition, $\lambda_s$ of MTHF increases by 20% from 100 to -94 °C, which is responsible for the slightly negative activation energies ($\approx -0.18$ kcal/mol for CIQSB). If $\lambda_s$ were independent of temperature, the rates would still have been predicted to be almost independent of temperature, but with a very weakly positive activation energy (0.5 kcal/mol).

For the same donor-acceptor pairs, the intermolecular rate constants (lower Figure 1) are quite sensitive to temperature but insensitive to $\Delta G^\circ$. This is because $k_{\text{obs}}$ is primarily determined by diffusion as demonstrated by the excellent fit of the data to the phenomenological VT equation:

$$k_s = k_0 \exp[-E_0/(T - T_0)]$$

with $E_0 = 0.40$ K$^{-1}$ and $T_0 = 100 \pm 20$ K. This is another demonstration of how the unique features of the inverted region are buried in rate-limiting transport processes in biomolecular reactions.

In conclusion, while the Marcus theory in its classical form describes the temperature dependence of ET at least qualitatively in the normal region, the present study finds it to be inadequate in the inverted region. Here, it is essential to include a quantum-mechanical treatment of high-frequency modes. In kinetic terms, the classical theory attributes the inverted region to an increasing activation energy in the exponential term of the rate equation, while because of nuclear tunneling it is the decreasing preexponential factor that is primarily responsible for the diminishing rate. Other evidence for the necessity of quantum modes in ET processes is abundant. The observations reported here resemble the temperature-independent ET processes in photo-synthetic reaction centers and may shed some light on the understanding of this important problem.

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In recent years we have been reporting our progress toward developing oxide-bridged Mn carboxylate chemistry. Efforts have been directed primarily toward di- and tetratric nuclear species to obtain potential models of the Mn units within certain Mn biomolecules. We, and others, have occasionally encountered higher nuclearity products, and structurally characterized species include Mn$_4$, Mn$_5$, Mn$_6$, and Mn$_{12}$. In parallel, other groups have reported high nuclearity Fe carboxylates, Fe$_7$, Fe$_8$, Fe$_9$, and Fe$_{10}$ (M = Co, Mn). In all cases, it is probably fair to say that serendipity has provided a helping hand, in that reactions were under thermodynamic control and the precise nuclearity could not have been predicted from the reagents employed. Higher nuclearity species are important for a variety of reasons, including providing insights into the assembly of the polynuclear core of the ferritin protein and understanding the variation of magnetic exchange interactions as a function of nuclearity and metal oxidation state. The latter has been particularly interesting for Mn where ferromagnetic interactions have occasionally led to high spin ground states. For example, Mn$_4$O$_4$(O$_2$CPh)$_6$(H$_2$O)$_4$ has an S = 14 ground state, and we have commented on the potential of such species as precursors to molecular ferromagnets. Given this importance of high-nuclearity species and the serendipitous nature of their discovery to date, we felt it important to overcome this lack of control and develop methodology for their rational synthesis. One attractive approach is to link together, in a controlled manner, smaller nuclearity "building blocks" derived from available smaller nuclearity species. Preliminary efforts have

Figure 1. Labeled structure and stereoview of complex 2. To avoid congestion, not all symmetry-equivalent atoms have been labeled. The $\mu_4$-O atoms are O5, O5', O6, and O6'. Selected distances (Å): Mn1-Mn2, 2.876 (7); Mn1-Mn3, 3.450 (7); Mn1-Mn4, 3.309; Mn2-Mn3, 3.248 (7); Mn2-Mn4, 3.300 (7); Mn1-O5, 1.932 (19); Mn2-O5, 1.863 (20); Mn3-O5, 1.872 (19); Mn1-O6, 1.904 (20); Mn2-O6, 1.882 (20); Mn4-O6, 1.859 (19); Mn1-O48, 2.236 (19); Mn4-O47, 1.946 (20); Mn3-N31, 2.060 (25); Mn4-N40, 2.038 (23); Mn3-O38, 1.905 (20); Mn1-O7, 1.956 (23); Mn1-O23, 1.939 (23); Mn1-O48, 2.222 (21); Mn4-O11, 1.997 (21); Mn2-O15, 2.061 (20); Mn4-O19, 1.947 (21); Mn3-O9, 2.134 (20); Mn3-O13, 2.213 (23); Mn2-O17, 1.970 (20); Mn4-O21, 2.337 (23); Mn4-O25, 2.216 (20); Mn4-O29, 1.927 (20).

Figure 2. The Mn/O/pic cores of complexes 1 and 2 emphasizing structural changes on dimerization of the $[\text{Mn}_4\text{O}_2\text{pic})_2]$ core and the interfragment connections.

The Mn/O/pic cores of complexes 1 and 2 emphasize structural changes on dimerization of the $[\text{Mn}_4\text{O}_2\text{pic})_2]$ core and the interfragment connections.
(Mn1-O48) and Mn1-O27 are the two axially elongated bonds (2.236 (19) and 2.222 (21) Å, respectively). The Mn1-O48 distance (2.236 (19) Å) is similar to the lengths of other JT-elongated Mn-O bonds in 2 (2.126 (20)-2.373 (23) Å). A comparison of the core structures of 1 and 2 is provided in Figure 2. The top half shows the Mn-O48 "butterfly" structure in 1 and the disposition of its pic ligands. The bottom half shows the Mn6O6(pic)2 portion of 2. Note that, in 1, both of the μ6-O atoms are trans to picolinate oxygens while, in 2, some μ5-O atoms are also trans to picolinate nitrogen atoms. This can be rationalized as a consequence of the need to accommodate the new interfragment Mn-O bonds. Also, the Mn4 units in 2 are no longer in a "butterfly" arrangement. Apart from these small structural changes, we emphasize that the [Mn402(OAc)6(pic)2] fragments oxidization level decreases and the two [Mn3(p3-O)] cores fuse to their original identity. This is distinctly different from the condensation" reaction\(^1\) with the [Mn30] fragment Mn-0 bonds. Also, the Mn4 units in Mn12O12(02CPh)16(H2O)4 (S = 1) are trans to picolinate oxygens while, in Mn12O12(02CPh)16(H2O)4 (S = 1), some p3-0 atoms are still possesses two pic 0 atoms not bound to Mn (0).

The conversion of 

\[
[Mn4(OAc)2(pic)2]^2- + 2MeSiCl \rightarrow [Mn4O6(OAc)2(pic)]^3+ + 2Me2SiOAc + 2Cl^- (1)
\]

can be rationalized as follows: removal of the carboxyly group bridging central Mn atoms Mn1 and Mn2 yields two five-coordinate centers, one of which is converted back to six-coordination via the new interfragment linkages (Mn1-O48 and its symmetry-related partner) (Figure 2) whereas Mn2 and Mn2' remain five-coordinate. Note that complex 2 still possesses two pic 0 atoms not bound to Mn (O39). In principle, carboxylate removal from 2 might yield further aggregation via conversion of O39 to a bridging mode (currently under investigation).

We recognize that formation of 2 from 1 relies on the picolinate and its flexibility in converting from \(\pi^2\) to \(\pi^2\)-\(\mu_3\). Since other Mn1-O/RCO\(_2\) complexes do not possess pic ligands, similar transformations are ruled out. Nevertheless, the aggregation of fragments generated from carboxylate abstraction has the potential for general application either with deliberately added bridging ligands or with bound RCO\(_2\) groups themselves converting from \(\mu_3\)-O to \(\mu_5\)-O, or for interfragment linking. With the feasibility of linking Mn60 units established, we are investigating application of this approach to the linking of ferromagnetically coupled species such as Mn14O36Cl4(OAc)4(pyz)6 (6 = 9/2) and Mn12O12(C6PBP)12Cl4(H2O)4 (S = 14) and determining the magnetic properties of higher nuclearity products.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and bond distances and angles of 2 (8 pages). Ordering information is given on any current masthead page. A complete MSC structure report is available on request from the Indiana University Chemistry Library.

Shape-Selective Olefin Epoxidation Catalyzed by Manganese Picnic Basket Porphyrins

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We have previously described the synthesis and characterization of the "picnic-basket" porphyrin complexes, which possess a rigid but variable dimension on one face of the porphyrin ring.\(^1\) Using ruthenium derivatives, we were able to control the reactivity of axial ligand coordination and to prepare stable dioxigen and dinitrogen complexes.\(^2\) However, the picnic basket system was designed to effect catalytic, shape-selective oxygenations and thus to mimic the enzyme family cytochrome P-450. Our early attempts to epoxidize olefins using manganese derivatives and dioxygenized failed to achieve shape selectivity. We were unable to seal the outside of the cavity by blocking the open face of the porphyrin with bulky neutral axial ligands such as 3,5-disubstituted imidazoles. Olefins were epoxidized on the open face of the porphyrin. Thus, these catalysts failed to show shape selectivity in the competitive epoxidation of olefin pairs.

We now describe conditions that result in catalytic olefin epoxidation within the cavities of a series of manganese picnic basket porphyrins. We have achieved substrate selectivities that reflect an interplay between the dimensions of the cavity size and the shape of the olefin substrate. The solution to this problem involves the use of a bulky, anionic axial ligand and acetoneil as a solvent with iodosylbenzene as the oxidant (eq 1).

\[
\frac{1}{\Phi_{\text{IO}^+}} = \frac{1}{\Phi_{\text{IO}^2-}} + \frac{1}{\Phi_{\text{IO}^{-}}} (\text{eq 1})
\]

Our results are summarized in Table I. Very slow epoxidation is observed when the C2 and C4 baskets 1 and 2 are used (Figure 1). Apparently, a small amount of reaction occurs at the open face. In these cases the cavities are too restricted for reaction to occur inside. The C3 basket, 3, shows a dramatic selectivity as illustrated for cis-2-octene competing with trans-β-methylstyrene (70:1) and cis-2-octene with cis-cyclooctene (67:1). The flat, rigid xylil basket, 6, shows a slightly lower selectivity with cis-2-octene versus trans-β-methylstyrene (29:1) but dramatic shape selectivity for cis-2-octene versus sub-shaped cis-cyclooctene (>1000:1). The modest, inverted selectivities of the hindered open face tetrarmitylporphyrin are provided for contrast. The selectivity within the C3 basket, 4, falls sharply, giving ratios of 12:7:1.

(6) To a solution of Mn(Por)X (X = Br, Cl) in 2.5 mL of CH2CN was added 20 equiv of {Et3O}2(0Ac)4. The solution was stirred at room temperature until the Soret band at 454 nm completely developed. Olefin (125 equiv), olefin (125 equiv), and PhO (55 equiv) with a GC standard (nonane (6.5 equiv). The olefin conversion rate for the catalyst Mn(C6PBP)(OAc) and Mn(C6PBP)(OAc) and Mn(C6PBP)(OAc) at least 15 times slower than with Mn(C6PBP)(OAc).