

Figure 3. Shape changes of helices into vesicles via tubular structures. $2C_{12}\text{-L-Glu-C}_{11}\text{N}^+$, 1×10^{-3} M. Micrographs (a) and (b) are obtained within an interval of 1 s during slow heating of the solution beyond T_c . Noticeable shape changes are denoted by arrows. Magnification 1300 times (scale bars, 10 μm).

Enantiomeric $2C_{12}\text{-D-Glu-C}_{11}\text{N}^+$ produces similar helical structures. The sense of the helix of the L amphiphile is always right handed, and that of the D amphiphile is left handed. They do not change, even when the helix is bent. Helices are not found for aqueous dispersions of racemic $2C_{12}\text{-DL-Glu-C}_{11}\text{N}^+$; instead, elastic fibers are present.

The helical superstructures are stable only at temperatures below the phase transition temperature (T_c) of the respective bilayers ($T_c = 34$ °C for helical $2C_{12}\text{-L-Glu-C}_{11}\text{N}^+$).⁵ The helices of Figure 1 change instantaneously to spherical vesicles and flexible filaments, when the solution is warmed to 40–50 °C. The conversion processes can be seen more clearly by slower heating. At temperatures near T_c , the pitch of a long helix of $2C_{12}\text{-L-Glu-C}_{11}\text{N}^+$ becomes shorter (from 3.2 to 2.8 μm) from one end (Figure 3a, I). The helices are then transformed into tubes (Figure 3a, II), which are immediately constricted and separated into vesicles. Figure 3, parts a and b are photographed within an interval of 1 s, and the rapid constriction process is apparent from comparisons of II with II', III with III', and IV with IV'. Some flexible filaments remain intact. All helices are eventually transformed into vesicles or flexible filaments.

The chemical structure of component amphiphiles in addition to their chirality plays crucial roles in morphology. $2C_{14}\text{-L-Glu-C}_{11}\text{N}^+$ gives helical aggregates, whereas $2C_{12}\text{-L-Glu-C}_2\text{N}^+$ and $2C_{14}\text{-L-Glu-C}_2\text{N}^+$ form spherical vesicles (diameter, several micrometers) at all temperatures. Long spacer methylenes (C_m) are required for helix formation.

It is known that biological lipids (lecithins) form helical myelin figures.^{7–9} Lin et al. reported the induction of helical liposomes

by Ca^{2+} , and Sakurai and Kawamura studied the growth mechanism of myelin figures. These results are in sharp contrast with ours in that helices are formed only in the chain-melting phase (above T_c) and do not exhibit enantiomorphism.

Recently, however, Weis et al.¹⁰ reported two-dimensional chiral crystals of phospholipid at the air/water interface. In the case of non-bilayer-forming amphiphiles, helix formation has already been reported from 12-hydroxystearic acid, both in organic gel state^{11,12} and from a collapsed monolayer.^{13–15}

In conclusion, helical superstructures are formed from synthetic, chiral bilayer membranes. The physical state and the chemical structure are crucial for generation and transformation of these helices. It is now possible to prepare helical superstructures from *designed* component amphiphiles. Electron microscopic studies of these and related systems are published elsewhere.^{5,16}

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Magnetic and Spectroscopic Properties of the $\delta\delta^*$ Excited States of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ and $\beta\text{-Mo}_2\text{Cl}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$: Experimental Determination of the Energy of a Triplet $\delta\delta^*$ State

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The lowest lying electronic excited state of complexes containing quadruple metal–metal bonds is a spin triplet of configuration $[\sigma^2\pi^4\delta\delta^*]$. Although the energy of this state has yet to be directly determined by magnetic or spectroscopic measurements, simple theoretical considerations of weakly interacting orbitals,^{1–3} as well as indirect experimental evidence,^{1,4} suggest that it lies much closer to the (δ^2) ground state than to its singlet $(\delta\delta^*)$ counterpart. Ab initio generalized valence bond calculations on $\text{Re}_2\text{Cl}_8^{2-}$ have borne this out, placing the $^3(\delta\delta^*)$ state of this complex 3200 cm^{-1} above the ground state and 11 200 cm^{-1} below $^1(\delta\delta^*)$.⁵ Over the past several years, a number of $d^4\text{-}d^4$ dimers have been reported in

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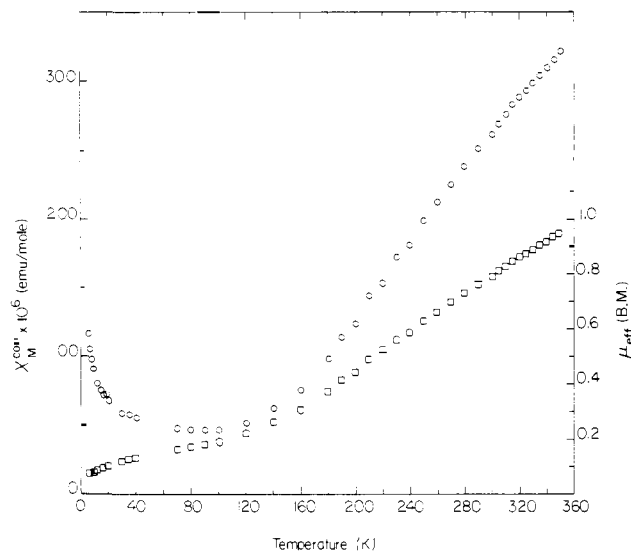
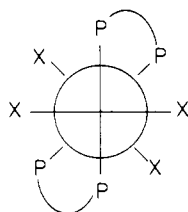


Figure 1. Temperature dependence of the corrected magnetic susceptibility (○) and magnetic moment (□) of a powdered sample of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ (SQUID detection, 10-kG field). The room temperature magnetic susceptibility of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ was used as the diamagnetic correction.

which the two ML_4 units that make up these complexes are partially or completely staggered with respect to each other due to bridging-ligand-induced rotation about the metal-metal bond.^{6,7}



While the rotationally symmetric $[\sigma^2\pi^4]$ triple-bond core remains intact in these twisted systems, the extent of δ -interaction between adjacent d_{xy} functions is progressively reduced, relative to that found in eclipsed dimers, as the torsional angle increases, with no overlap remaining at 45° .⁷ Herein we report the magnetic and spectroscopic properties of two d^4 - d^4 complexes that nearly span the range of δ -interactions: β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), with a twist angle of 40° , and $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$, its eclipsed "rotamer".⁸⁻¹⁰

While $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ displays the rigorous diamagnetism ($\chi_m = -280 \times 10^{-6}$ emu/mol; crystalline sample, Faraday balance, 300 K) typical of eclipsed d^4 - d^4 dimers of this type, β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ is paramagnetic under the same conditions. The temperature dependence of the magnetic susceptibility of the latter complex (Figure 1) is consistent with an antiferromagnetically coupled two-spin system. Although the Néel point is not observed

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(9) Structural comparison of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ ¹⁰ and $(\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2)^7$: $d(\text{MoMo})$, 2.13 (2.18) Å; $d(\text{MoCl})$, 2.41 (2.40) Å; $d(\text{MoP})$, 2.55 (2.53) Å; $\angle(\text{MoMoCl})$, 112 (111)°; $\angle(\text{MoMoP})$, 102 (98)°; $\angle(\text{MoMo, torsion})$, 0 (40)°.

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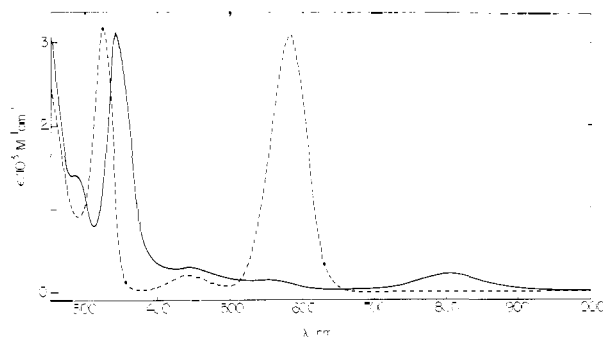


Figure 2. Electronic absorption spectra of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ (—) and $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ (---) in tetrahydrofuran solution at room temperature.

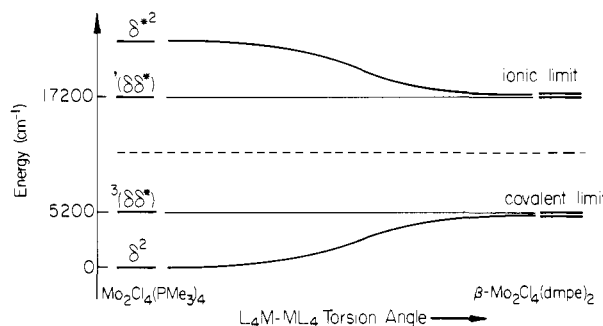


Figure 3. Energies of the lowest electronic states of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ and β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$.

within the temperature limits of the experiment,¹¹ a crude fit of the data (employing standard approximations of the limiting magnetic moment and correcting for the paramagnetic impurity)¹² places the energy (-2 J) of the thermally populated triplet state in the 400 – 500-cm^{-1} range, which is roughly an order of magnitude less than that anticipated for the eclipsed rotamer.^{4,5} This marked deviation in the electronic properties of the two complexes is also manifested in their electronic spectra (Figure 2). Aside from the expected⁸ insensitivity to torsion angle of the phosphine-to-molybdenum charge-transfer band (340 nm),¹³ the metal-metal-localized $1(\delta \rightarrow \delta^*)$ transition of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ is, like its triplet counterpart, lower in energy than that of its analogue in $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$,¹⁴ as well as being lower in intensity ($\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ λ_{max} 583 nm, ϵ_{max} $3110\text{ M}^{-1}\text{ cm}^{-1}$; β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ λ_{max} 803 nm, ϵ_{max} $210\text{ M}^{-1}\text{ cm}^{-1}$).¹⁵

The energetic differences between the $\delta\delta^*$ states of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ and β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ can be readily attributed to the orbital overlap dependence of the one- and two-electron interactions in these systems. It has previously been shown that a 40° torsion angle reduces δ -interaction to 0.17 times that found at 0° .⁷ Inasmuch as the δ -overlap of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ is on the order of $S \sim 0.1$,¹⁶ the energetic splitting of the one-electron δ and δ^* levels of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ is clearly quite small. Specifically, the covalent (δ^2) and $3(\delta\delta^*)$ states of the former species should collapse to a nearly degenerate pair of spin states derived from the weakly coupled d_{xy} functions of each metal of the latter complex. This is reflected in the substantial population of both spin states of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$ at room temperature. In contrast, the energy of the ionic $1(\delta\delta^*)$ state is dominated by an electron repulsion term (twice the electron exchange integral)³ that is roughly invariant over the range of overlaps ($0.01 \leq S \leq 0.1$) and distances spanned by these species (Figure 3). Thus, even near the zero-overlap

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limit, $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$ displays a ${}^1(\delta \rightarrow \delta^*)$ transition at $12\,500\text{ cm}^{-1}$, only 4700 cm^{-1} red shifted from that of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$. The sum of this red shift and the ${}^3(\delta\delta^*)$ energy of $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$, $\sim 5200\text{ cm}^{-1}$ (15 kcal/mol), which approximates the position of the ${}^3(\delta\delta^*)$ state of $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ (Figure 3), is an experimental measure of the δ -bond component of the barrier to rotation about a quadruple bond.

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Registry No. $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$, 67619-17-4; $\beta\text{-Mo}_2\text{Cl}_4(\text{dmpe})_2$, 85115-86-2.

Mechanism of "Oxygen Atom" Transfer to (Tetraphenylporphinato)chromic Chloride

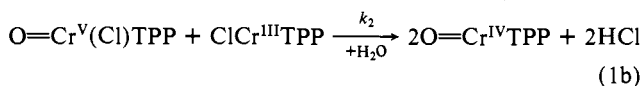
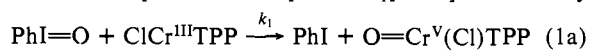
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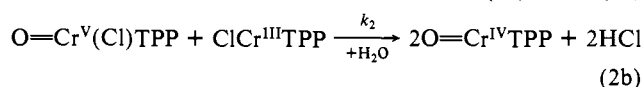
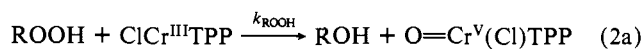
Herein are described results obtained in a study of the reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with a variety of oxygen-donor molecules. This investigation is an extension of studies of oxygen transfer from aniline *N*-oxides to (porphinato) $\text{Fe}^{\text{III}}\text{X}$ and (porphinato) $\text{Mn}^{\text{III}}\text{X}$ salts¹⁻³ and to cytochrome P-450 enzymes.⁴ The objectives of the present study are to ascertain the effect of donor structure on the ease and the mechanism of oxygen transfer.

The reaction of iodosylbenzene with $\text{ClCr}^{\text{III}}\text{TPP}$ is not well understood.⁵⁻⁸ In this study, the reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with PhIO was initiated (spectral grade dichloromethane, 25 °C, N_2 atmosphere) by mixing various volumes of a freshly prepared solution saturated in PhIO with a solution of $\text{ClCr}^{\text{III}}\text{TPP}$ ($1 \times 10^{-5}\text{ M}$). As the ratio of PhIO/ $\text{ClCr}^{\text{III}}\text{TPP}$, present at the time of mixing, was increased from 1 to 20 the Soret band of the product was found to shift from 429 ($\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$) to 415 nm ($\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$). Thus, at high concentrations of PhIO relative to $\text{ClCr}^{\text{III}}\text{TPP}$, there is obtained as product $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. An investigation of the kinetics of the reaction was not attempted due to the known polymeric nature of PhIO etc.⁹ Nevertheless, it would appear that the logical explanation for these experimental results is found in eq 1. When the product $k_1[\text{PhIO}]$ is sufficiently



large, all $\text{ClCr}^{\text{III}}\text{TPP}$ is converted into $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. At lower concentrations of PhIO the oxidant $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$ competes with PhIO for $\text{ClCr}^{\text{III}}\text{TPP}$ and a disproportionation reaction ensues to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$. (Traces of moisture in the solvent were

sufficient to supply the water molecules for the disproportionation reaction.) Thus, $\text{ClCr}^{\text{III}}\text{TPP}$ may be used as a trap for $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$. The rapid trapping of the chromium(V) species by the chromium(III) species has allowed us to study oxygen transfer from percarboxylic acids and hydroperoxides to $\text{ClCr}^{\text{III}}\text{TPP}$ (eq 2).



The kinetics of the reactions of percarboxylic acids and hydroperoxides with $\text{ClCr}^{\text{III}}\text{TPP}$ were carried out in CH_2Cl_2 (25 °C, N_2 atmosphere), under the pseudo-first-order conditions of $[\text{ROOH}] \gg [\text{ClCr}^{\text{III}}\text{TPP}]$. The reactions were monitored by observing the decrease in $\text{ClCr}^{\text{III}}\text{TPP}$ at 446 nm and were found to follow the first-order rate law to 6 to 7 half-lives. Plots of initial $[\text{ROOH}]$ vs. the determined pseudo-first-order rate constant (k_{obsd}) were linear. The slopes of such plots provided the second-order rate constants k_{ROOH} of eq 2a. In Figure 1 there is plotted the $\log k_{\text{ROOH}}$ values for the reaction of ROOH species with $\text{ClCr}^{\text{III}}\text{TPP}$ vs. the $\text{p}K_a$ of ROH. The lack of a break in the plot is in accord with consistency of mechanism for species of great monoxygen-donation potential (*m*- $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$) and little oxygen-donation potential (*t*-BuOOH). That this mechanism involves RO-OH bond heterolysis follows from the recovery of >90% phenylacetic acid (as methyl ester with CH_2N_2) when ROOH is phenylperacetic acid. Homolysis would yield phenylacetoxyl radical which decarboxylates rapidly.¹¹

The log of the second-order rate constants (k_{Nuc}) for heterolytic-nucleophilic cleavage of the O-O bond of a series of hydroperoxides and percarboxylic acids $[\text{ROOH}]$ have previously been shown to be a linear function ($\beta_{1g} = -0.6$) of the $\text{p}K_a$ of the leaving groups (ROH) when the nucleophilic species are thioxane, *N,N*-dimethylbenzylamine, and I^- .¹⁰ The reaction of $\text{ClCr}^{\text{III}}\text{TPP}$ with ROOH follows the same linear free energy relationship with $\beta_{1g} = -0.34$. If one wishes to ignore the difference in solvent for nucleophilic attack by I^- , :N^- , :S^- (*t*-BuOH) and by $\text{ClCr}^{\text{III}}\text{TPP}$ (CH_2Cl_2), though probably not wise, one would conclude that O-O bond cleavage has not proceeded as far in the transition state in the instance where the Cr^{III} moiety of $\text{ClCr}^{\text{III}}\text{TPP}$ is the nucleophile. With the percarboxylic acids the product is a mixture of porphinato Cr^{IV} and Cr^{V} species, whereas with all the hydroperoxides the λ_{max} of the Soret peak at t_∞ corresponds to the Cr^{IV} species. This result is as should be expected from the results with iodosylbenzene. As the $\text{p}K_a$ of ROH increases the ease of oxygen-oxygen bond breaking in RO-OH decreases as does the value $k_{\text{ROOH}}[\text{ROOH}]$ (eq 2a) and this allows the term $k_2[\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}]$ to compete for the $\text{ClCr}^{\text{III}}\text{TPP}$ species to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$.

2-(Phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine (Oxa) has been employed in the epoxidation of alkenes¹² (60 °C, CHCl_3) and on this basis would appear as a worthy agent to explore as an oxygen donor to metalloporphyrins. The kinetics of reaction of Oxa (1.9×10^{-2} to $1.9 \times 10^{-3}\text{ M}$) with $\text{ClCr}^{\text{III}}\text{TPP}$ ($1.3 \times 10^{-5}\text{ M}$) to provide $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$ were followed at 429 nm (CH_2Cl_2 , 20 °C). Reactions were first order to at least 6 half-lives and plots of k_{obsd} vs. $[\text{Oxa}]$ were linear with slope $8.25\text{ M}^{-1}\text{ s}^{-1}$. The appearance of $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$ rather than $\text{O}=\text{Cr}^{\text{V}}(\text{Cl})\text{TPP}$ as product is expected since the rate constant is but ~ 2 times greater than that for the reaction of triphenylmethyl hydrogen peroxide with $\text{ClCr}^{\text{III}}\text{TPP}$ (Figure 1).

Though *p*-cyano-*N,N*-dimethylaniline *N*-oxide (*p*-CNDMA-NO) is comparable to PhIO as an oxygen donor to $\text{ClFe}^{\text{III}}\text{TPP}$ in the epoxidation of alkenes,² it does not react with $\text{ClCr}^{\text{III}}\text{TPP}$ (25 °C, CH_2Cl_2 solvent, N_2 atmosphere). With photoexcitation of the reaction mixture, *p*-CNDMA-NO does transfer an oxygen to yield $\text{O}=\text{Cr}^{\text{IV}}\text{TPP}$. The photoreaction is presumably associated

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