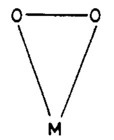
Oxygen Binding to Manganese Porphyrin. An ab Initio Calculation

Sir:

There have been recent reports of an adduct formation in solution between dioxygen and the manganese(II) tetraphenylporphyrin[1-3] ($Mn^{II}TPP$[4]). From the results of an optical and of an ESR study[2] an extensive Mn → O_2 charge transfer has been found. The dioxygen adduct has been formulated as $Mn^{IV}(O_2^{2-})$ ($S = 3/2$) in which the Mn^{IV} is in the $^4(t_2^3)$ ground state.[2] On this basis, the perpendicular structure **1** has been suggested[2] (rather than the bent structure **2**), in analogy with other peroxo complexes.[5] However, an x-ray crystal structure is still lacking for a dioxygen adduct of a manganese porphyrin. We present here results of ab initio calculations for the system $Mn(P)O_2$ which are at variance with the conclusions of the experimental study[2] for the electronic structure and geometry of the Mn-O_2 unit.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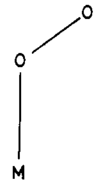
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The perpendicular structure **1** seems to occur in the dioxygen adducts of porphyrins of early transition metals such as Ti or of porphyrins of second row transition metals such as Mo, as shown by the x-ray crystal structures of the $Ti(OEP)O_2$[6] and $Mo[T(p\text{-Tol})P](O_2)_2$[7] systems. The same result has been found through ab initio calculations for the $Ti(P)O_2$ molecule.[8] On the other hand x-ray crystal structures[9] for the dioxygen adduct of iron porphyrins and cobalt Schiff bases (which are very similar to dioxygen adduct of cobalt porphyrins) and calculations[12] indicate a bent M-O-O unit, **2.**

For the $Ti(OEP)O_2$ molecule[6] the O-O bond length and the dioxygen stretching frequency indicate a $Ti^{IV}(O_2^{2-})$ formulation which is in agreement with our calculations.[8] A consequence of this peroxo-type formulation is the assignment of a formal oxidation state IV for the metal. This high oxidation state is unexpected in the case of manganese porphyrins[16] and has not been found experimentally for dioxygen adducts of porphyrins of Cr,[17] Fe,[18] and Co.[19] Our calculations on $Fe(P)O_2NH_3$[13,14] and on $Co(P)O_2NH_3$[20] give a formal oxidation state of II[21] and III for Fe and Co, respectively.

We have carried out ab initio calculations for the bent (**1**) and perpendicular (**2**) structures of the $Mn(P)O_2$ system.[23] We restricted ourselves to the $S = 3/2$ spin state (as experimentally found[2]). Given the assumption that the $3d_{x^2-y^2}$ orbital is not occupied in $Mn(P)O_2$ (which is likely to be the case), there are then 14 probable configurations for the ground state of $Mn(P)O_2$ of which the first three (denoted I-III in Table I) correspond to a $Mn^{IV}(O_2^{2-})$ formalism, five (IV-VIII) to a $Mn^{III}(O_2^-)$ formalism, and the last six (IX-XIV) to a $Mn^{II}(O_2)$ formalism. The corresponding energy values are given in Table I. We denote $\pi_g{}^a$ and $\pi_g{}^b$ the two $1\pi_g$ antibonding orbitals of dioxygen, which are degenerate for the free ligand (for the bent and perpendicular structures the $\pi_g{}^a$ orbital is symmetric with respect to the MnO_2 plane, whereas $\pi_g{}^b$ is antisymmetric). Inspection of Table I reveals that no stationary value of the energy of the first three configurations (of the $Mn^{IV}(O_2^{2-})$ type) was achieved, neither for the perpendicular nor for the bent structure. On the contrary, through the SCF iterations a stable configuration of the same symmetry but corresponding to a $Mn^{III}(O_2^-)$ formalism was obtained. (For instance using configuration I as a starting point for the perpendicular structure led to the configuration VII.[27]) Therefore, on the basis of these calculations, the $Mn^{IV}(O_2^{2-})$ formalism appears to be unlikely for the dioxygen adduct of manganese porphyrins. This result is traced to the fact that the π_g antibonding dioxygen orbitals *do not* lie below the set of 3d orbitals of Mn, even if the 3d orbitals would be destabilized on going from Co to Mn as it has been postulated in ref 2.[28] Moreover, in the case of a $Mn^{IV}(O_2^{2-})$ formalism, the high positive charge on Mn would stabilize the d orbitals, whereas the negative charge on O_2 would destabilize the π_g antibonding orbitals.

From the values reported in Table I, the lowest energy configuration is $(\pi_g{}^a)^2(\pi_g{}^b)^1(xy)^2(yz)^1(z^2)^1$ (configuration VI) for the perpendicular structure and $(\pi_g{}^a)^2(\pi_g{}^b)^1(xy)^2(yz)^1(xz)^1$ (configuration IV) for the bent structure. Both correspond to a $Mn^{III}(O_2^-)$ formalism in which the Mn^{III} is of intermediate spin (d^4, $S = 1$). The configurations IX-XIV are close in energy to the configuration IV-VIII.[29] These configurations correspond to a $Mn^{II}(O_2)$ formalism in which the manganese is also of intermediate spin (d^5, $S = 3/2$). That the lowest energy configuration corresponds to a $Mn^{III}(O_2^-)$ formalism does not agree with the experimental observation[2] that no spin transfer to dioxygen has been found in the experiments with 50% ^{17}O-enriched O_2. However, the authors of ref 2 have pointed out the similarity of the optical spectra of $Mn(TPP)O_2$ and of the $Mn^{III}TPP$ (X) porphyrins. As they also suggest, the optical spectra may simply indicate some charge transfer from Mn to O_2. Such charge transfer can occur by covalent interaction in a formal $Mn^{II}(TPP)(O_2)$ complex[30] (for instance, the results of the population analysis for the

Table I. Energy Values (in au) for the Electronic Configurations ($S = 3/2$) and the Two Geometric Structures of $Mn(P)O_2$[a]

		Geometric structure and state			
	Electronic configuration	Perpendicular (C_{2v})		Bent (C_s)	
I	$(\pi_g{}^a)^2(\pi_g{}^b)^2(xy)^1(xz)^1(yz)^1$	*b*	$^4A_1$	*b*	$^4A'$
II	$(\pi_g{}^a)^2(\pi_g{}^b)^2(xy)^1(xz)^1(z^2)^1$	*b*	$^4B_2$	*b*	$^4A''$
III	$(\pi_g{}^a)^2(\pi_g{}^b)^2(xy)^1(yz)^1(z^2)^1$	*b*	$^4B_1$	*b*	$^4A'$
IV	$(\pi_g{}^a)^2(\pi_g{}^b)^1(xy)^2(yz)^1(xz)^1$	−2273.041	$^4A_1$	$\underline{-2273.129}$	$^4A'$
V	$(\pi_g{}^a)^2(\pi_g{}^b)^1(xy)^2(xz)^1(z^2)^1$	−2272.992	$^4B_2$	−2273.080	$^4A''$
VI	$(\pi_g{}^a)^2(\pi_g{}^b)^1(xy)^2(yz)^1(z^2)^1$	$\underline{-2273.077}$	$^4B_1$	*b, c*	$^4A'$
VII	$(\pi_g{}^a)^1(\pi_g{}^b)^2(xy)^1(yz)^1(xz)^2$	−2272.973	$^4A_1$	−2273.105	$^4A'$
VIII	$(\pi_g{}^a)^1(\pi_g{}^b)^2(xy)^1(xz)^2(z^2)^1$	−2272.920	$^4B_2$	−2273.055	$^4A''$
IX	$(\pi_g{}^a)^2(xy)^2(xz)^1(yz)^1(z^2)^1$	−2272.958	$^4A_2$	−2273.057	$^4A''$
X	$(\pi_g{}^a)^2(xy)^1(xz)^2(yz)^1(z^2)^1$	−2272.869	$^4B_1$	−2273.036	$^4A'$
XI	$(\pi_g{}^a)^2(xy)^1(xz)^1(yz)^2(z^2)^1$	−2272.918	$^4B_2$	−2273.057	$^4A''$
XII	$(\pi_g{}^b)^2(xy)^2(xz)^1(yz)^1(z^2)^1$	−2272.999	$^4A_2$	−2273.061	$^4A''$
XIII	$(\pi_g{}^b)^2(xy)^1(xz)^2(yz)^1(z^2)^1$	−2273.056	$^4B_1$	−2273.053	$^4A'$
XIV	$(\pi_g{}^b)^2(xy)^1(xz)^1(yz)^2(z^2)^1$	−2272.982	$^4B_2$	−2273.050	$^4A''$

[a] Underlined values correspond to the lowest energy configuration for each structure. [b] No stationary value of the energy was achieved. [c] SCF iterations have led to the configuration IV.

configuration XIII indicate a net charge of 0.20 e on the dioxygen ligand in the bent structure and 0.36 e in the perpendicular structure). These $Mn^{II}(O_2)$-type (Mn^{II}, d^5, $S = 3/2$) configurations have not been considered in ref 2, although there is no feature of the ESR spectra which in principle is incompatible with this formalism.[30] They also meet the requirement of no spin density on O_2. If the vast majority of Mn^{II} complexes are high spin (including Mn(TPP)), there are at least two systems of Mn^{II} with a quartet ground state[31,32] including manganese phtalocyanine.[32] We also do not expect more refined calculations (of a double-ζ basis set quality or the introduction of configuration interaction between configurations of the same symmetry) to give a stationary value of the energy for the first configurations of the $Mn^{IV}(O_2^{2-})$ type. However, they could modify the relative stabilities of the $Mn^{II}(O_2)$- and $Mn^{III}(O_2^-)$-type configurations. Such calculations are now in progress.

From Table I, it also appears that for all configurations but one the bent structure is more stable than the perpendicular one. The two structures are of comparable stability (to the precision of the calculations) for the configuration XIII. However, introduction of configuration interaction will mix this configuration with the configurations IV, VII, and X for the bent structure (since IV, VII, X, and XIII belong to the $^4A'$ symmetry) and with the configurations VI and X for the perpendicular structure (VI, X, and XIII belong to the $^4B_1$ symmetry). Since the configurations IV, VII, and X of the bent structure are lower in energy than the configurations VI and X of the perpendicular structure, the same ordering is likely for the corresponding states $^4A'$ and $^4B_1$. We can therefore predict that the bent structure is more stable than the perpendicular one. This result (opposite to the conclusions of ref 2) is not unexpected since we did not find any stable configuration with dioxygen bonded as a peroxo (O_2^{2-}) ligand. If we compare the energy value of the most stable configuration for each of the two states $^4A'$ and $^4B_1$ (cf. Table I), the stabilization amounts to 33 kcal/mol.

In summary our conclusions are at odds with the interpretation of the experimental results for the Mn(TPP)O_2 system. We look forward to a more detailed experimental study of the system,[33] especially an x-ray structural determination. We are also carrying more refined calculations on this system.

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Preparation of a Tetraphosphine Macrocyclic Ligand

Sir:

The preparation of synthetic macrocycles and their subsequent ligation to various transition metals has been a fruitful area of research.[1] Macrocycles having oxygen, nitrogen, and/or sulfur donor atoms have been prepared and the chemical reactivity of their metal complexes studied.[2] To date, however, there is only one example of a macrocyclic ligand that contains a phosphorus atom[3] and the chemical reactivity of its metal complex is very much controlled by the nitrogen atoms