The effect of axial ligands on M–M distances has been well documented in connection with $Cr_2(O_2CR)_4$,[11] $Mo_2(O_2CR)_4$,[14] and $Re_2Cl_8^{2-}$[15] and naturally requires consideration here. In the $M_2(DMP)_4$ and $M_2(TMP)_4$ molecules the axial positions are rather effectively blocked by the uncoordinated methoxy groups and there is no axial coordination whatever. However, in the present case, no such blocking occurs, and there are Br^- ions along the axial directions, but these Br^- ions remain very distant. This could, of course, be due simply to the fact that the anionic $[Cr_2(C_6H_4O)_4]^{4-}$ unit as a whole repels the Br^- ions. In other words, the axial positions might be protected electrostatically though not sterically. Thus, we do not yet know what, if any, role axial ligands, or their absence, have to play in these compounds with exceedingly short Cr–Cr bonds.

It is pertinent to note that a "naked" Cr_2 species has been observed in an argon matrix[16] and possibly in the thermal decomposition of $Cr(CO)_6$.[17] If the species Cr_2 has been correctly identified as such under the latter conditions, it can be inferred from its rotational energy levels that the Cr–Cr distance is 1.71 Å. The bond in this case might, as suggested for Mo_2,[18] be of order 6.

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Registry No. $Li_6Cr_2(o\text{-}C_6H_4O)_4Br_2\cdot 6(C_2H_5)_2O$, 66323-53-3; $Cr_2(O_2CCH_3)_4$, 15020-15-2.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Dêpartement de Recherche Fondamentale
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Conformation of Triangular Peroxo d^0 Metalloporphyrins

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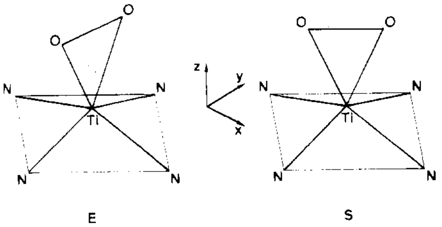
The detailed nature of the bonding of molecular oxygen to transition-metal complexes has been a subject of increasing interest because it represents a basic step in the function of oxygen carrying and activating metalloproteins in biological systems.[2] Recently, x-ray structures have been reported for titanium[3,4] and molybdenum[5] porphyrin complexes containing dioxygen ligands. It has been found that the MO_2 system adopts a triangular edge-on structure, the dioxygen moiety eclipsing two opposite nitrogens of the macrocycle. In the case of the bis(dioxygen)molybdenum complex each N–N diagonal is eclipsed by a dioxygen unit, one above the molecular plane and the other below. Dynamic NMR measurements on the titanium complex[4] support the view that these features of the solid-state structures are not imposed by crystal packing constraints but rather that they reflect the preferential conformation of the isolated molecules. The aim of this paper is to present a qualitative theoretical model to account for the preferential conformation of these edge-on adducts.

We start with the interaction of a diatomic O_2 with a pyramidal TiN_4 fragment. On the basis of the assumptions previously made by Hoffmann, Chen, and Thorn[6] the orbitals of the metal and of the dioxygen ligand to be taken into account are the four d orbitals of the metal, z^2, xy, xz, and yz, and the $3\sigma_g$, π_u, and π_g levels of the ligand. The ligand contributions and core levels are omitted as well as the high-lying levels σ_u and $x^2 - y^2$.



In the complex, the two conformations E (eclipsed) and S (staggered) belong to the C_{2v} point group. The fundamental difference appears in the fact that the plane containing the metal and the O_2 moiety is the yz plane in E whereas it bisects the xz, yz dihedron in S. Then, the constitutive orbitals of the fragments are distributed among the different irreducible representations as shown in Table I. Indices ∥ and ⊥ characterize the π orbitals parallel and perpendicular to the z axis, respectively. According to experimental data[3,4] the complex is best described by a peroxotitanium(IV) electronic structure. The number n of electrons to be placed in the molecular levels of the complex are given for each symmetry besides the corresponding label.

Let us now focus on what is changed in going from one conformation to the other. It appears clearly that for B_1 and B_2 representations all interactions are retained along the deformation coordinate since the symmetry-adapted orbitals of the $[TiN_4]_S$ fragment can be deduced from those of $[TiN_4]_E$ by a unitary transformation in the subspace of the degenerate levels of the metal. As concerns the A_1 representation, interactions between z^2 and the $3\sigma_g$ and $\pi_u^{\parallel}$ orbitals are invariant during the rotation around the z axis, the orbitals being themselves symmetric with respect to the rotation axis. The supplementary interaction between xy and the $3\sigma_g$ and $\pi_u^{\parallel}$ orbitals which appears in S is small as a consequence of the large energy gap between the metal and diatomic levels and the weakness of their mutual overlaps.[6] The deciding difference can be found in the A_2 representation. In E, interaction

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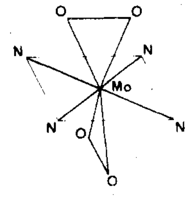
Table I

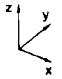
$[TiN_4]_E$	$[O_2]$	$[TiN_4]_S$	n	
z^2	$3\sigma_g; \pi_u^{\parallel}$	$z^2; xy$	4	A_1
xy	$\pi_g^{\perp}$		2	A_2
xz	$\pi_u^{\perp}$	$(xz - yz)$	2	B_1
yz	$\pi_g^{\parallel}$	$(xz + yz)$	2	B_2

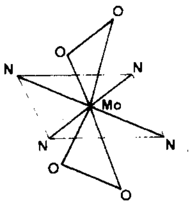
of xy and $\pi_g^{\perp}$ splits the levels into a bonding–antibonding pair, the lower combination $xy + \pi_g^{\perp}$ being occupied by two electrons. On the contrary in S, dioxygen $\pi_g^{\perp}$ finds no metal orbital with which to interact. The resulting loss of binding energy in the staggered conformation compared with the eclipsed one (Figure 1) clearly favors the latter conformation.

For the bis(dioxygen)molybdenum complex the problem is more complicated because the three plausible limiting conformations to be considered belong to different symmetry groups. In the E_xE_y conformation, the upper and lower oxygen molecules lie in the yz and xz planes, respectively. In the SS conformation the position of the two dioxygen ligands is obtained from the preceding conformation by rotation of $\pi/4$ around the z axis. In the E_yE_y conformation both ligands are in the yz plane.

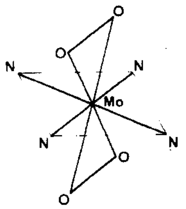


SS





E_xE_y



E_yE_y

Let us consider the interaction of the two diatomics O_2 with a planar MoN_4 fragment[7] in the E_xE_y and SS conformations. The projection of the constitutive orbitals of the interacting fragments in the different irreducible representations of the symmetry groups are shown in Table II. In order to simplify the problem we assume that interactions between the diatomics can be neglected. This seems reasonable in view of the large distance (3.66 Å) between the two O_2 units. If we adopt as a trial the above restriction, the situation offers no new features beyond those discussed for the titanium complex. The bonding constraints which are imposed by symmetry appear now in the B_1 and B_2 representations, all remaining interactions being unchanged during rotation. Again, one representation, here B_1, is determining. In the SS conformation xy interactions with $\pi_u^{\parallel}$ and σ_g levels are small for the same reason as in $[TiN_4O_2]_S$ while the $\pi_g^{\perp}$ levels do not interact with the metal in B_1. By contrast, they are strongly interacting with xy in the E_xE_y conformation in the same way as in $[TiN_4O_2]_E$ leading to a larger stabilization as compared to the SS conformation.

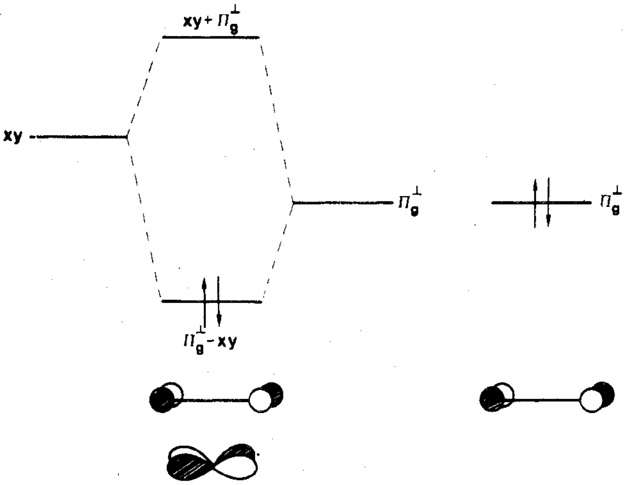


Figure 1. Simplified interaction diagram and schematic drawing of the occupied levels of A_2 symmetry for the dioxygen complex $[TiN_4O_2]$ in the eclipsed (left) and staggered conformations (right).

In the E_yE_y conformation, the complex belongs to D_{2h} symmetry so that the fragment orbitals are distributed as shown in Table III.

Comparison of the relative stability of E_xE_y and E_yE_y conformation can now be analyzed as follows. Interactions which combine z^2 and xy with the appropriate symmetry orbitals of the diatomics are unchanged with the assumption of noninteracting ligands. Symmetry orbitals belonging to A_2 and B_2 in E_xE_y and to A_u and B_{1u} in E_yE_y do not interact with the metal. Thus all these orbitals provide no energetic differential between the two conformations. The deciding difference between E_xE_y and E_yE_y comes from the symmetry properties of the four remaining levels of the ligands. In E_xE_y two ($\pi_u^{u\perp}$, $\pi_g^{l\parallel}$) are symmetric with respect to the xz plane, and two ($\pi_u^{l\perp}$, $\pi_g^{u\parallel}$) are symmetric with respect to the yz plane, each level involving only one of the two ligands. These two groups are equivalent and all the interactions of xz with one group are equal two by two to the interactions of yz with the other group, whereas the cross interactions are all zero. Each of these interactions leads to a bonding–antibonding pair of MO's involving a metal orbital and one of the two diatomics. In E_yE_y the levels of the ligands are distributed quite differently. Two (B_{2g}, B_{3u}) are symmetric with respect to the xz plane, two (B_{3g}, B_{2u}) are symmetric with respect to the yz plane, each level implying now the two ligands simultaneously. Let us focus on the $\pi_g^{\parallel}$ levels. One (B_{3g}) combines with yz to give bonding and antibonding MO's both involving the metal

Table II[a]

$[MoN_4]_{E_xE_y}$	$[O_2]$	$[MoN_4]_{SS}$	n	
z^2	$(\sigma_g^u + \sigma_g^l); (\pi_u^{u\parallel} - \pi_u^{l\parallel})$	z^2	4	A_1
	$(\pi_g^{u\perp} - \pi_g^{l\perp})$		2	A_2
xy	$(\pi_g^{u\perp} + \pi_g^{l\perp})$		2	B_1
	$(\sigma_g^u - \sigma_g^l); (\pi_u^{u\parallel} + \pi_u^{l\parallel})$	xy	4	B_2
xz	$\pi_u^{u\perp}; \pi_g^{l\parallel}$	$(xz + yz)$	8	E
yz	$\pi_u^{l\perp}; \pi_g^{u\parallel}$	$(xz - yz)$		

[a] The superior indices u and l refer to the upper and lower O_2 groups, respectively.

Table III. Fragment Orbitals in the E_yE_y Corformation

$[MoN_4]_{E_yE_y}$	$[O_2]$	n	
z^2	$(\sigma_g^{u} + \sigma_g^{l}); (\pi_u^{u\parallel} - \pi_u^{l\parallel})$	4	A_g
xy	$(\pi_g^{u\perp} + \pi_g^{l\perp})$	2	B_{1g}
xz	$(\pi_u^{u\perp} - \pi_u^{l\perp})$	2	B_{2g}
yz	$(\pi_g^{u\parallel} + \pi_g^{l\parallel})$	2	B_{3g}
	$(\pi_g^{u\perp} - \pi_g^{l\perp})$	2	A_u
	$(\sigma_g^{u} - \sigma_g^{l}); (\pi_u^{u\parallel} + \pi_u^{l\parallel})$	4	B_{1u}
	$(\pi_g^{u\parallel} - \pi_g^{l\parallel})$	2	B_{2u}
	$(\pi_u^{u\perp} + \pi_u^{l\perp})$	2	B_{3u}

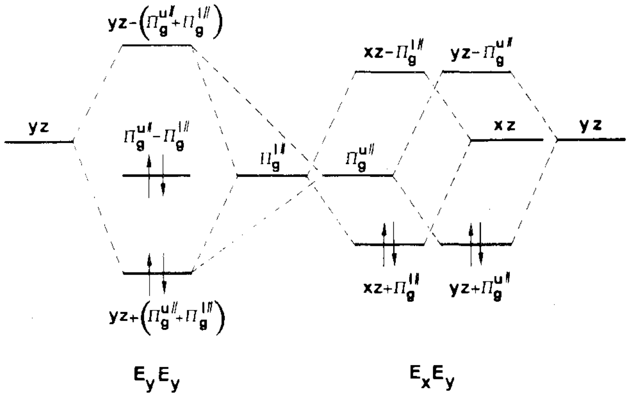


Figure 2.

orbital and the two diatomics. The remaining level (B_{2u}) is a typical nonbonding MO (i.e., no interaction with the metal). The resulting system is then formed by three molecular levels. The qualitative energy diagram arising from the combination of the $\pi_g^{\parallel}$ with their matching symmetry orbitals of the metal in the two conformations is presented in Figure 2.

In the bis(dioxygen) complex, the molybdenum d levels[8] will lie close to the ligand $\pi_g^{\parallel}$ orbitals.[9] Since d orbitals interact equally with the upper and lower molecules, one obtains a characteristic "allylic" type diagram for E_yE_y and two usual "ethylenic" type diagrams for E_xE_y. In both conformations, two of these levels are to be occupied by four electrons. The total energy is well-known[10] in that case to be lower for two ethylenic systems compared to an allylic one so that the E_xE_y conformation will be the favored one.

The preceding arguments similarly apply to the interactions involving the $\pi_u^{\perp}$ levels giving an "allylic" system for E_yE_y vs. two "ethylenic" ones for E_xE_y. Thus the eclipsed conformation found in the dioxygen complexes of titanium and molybdenum porphyrins are well accounted for by simple group-theoretical considerations.

Finally it should also be mentioned that a recent ab initio calculation by Rohmer and Veillard[11] found the eclipsed conformation of a dioxygen titanium porphyrin to be more stable than the staggered one. The calculated energy difference is 5 kcal/mol in agreement with the value of 10 kcal/mol evaluated from dynamic NMR measurements.[4]

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Facile Synthesis of the Lower Valent Halides of Gallium, Ga_2X_4 (X = Cl, Br, I) and Ga_4I_6

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The lower valent halides of gallium are usually prepared by the reduction of gallium(III) halides at temperatures in the region of 180 °C for the chloride and bromide and 212 °C for the iodide.[1,2] The temperatures are often critical since disproportionation reactions easily occur.

Very pure Ga_2Cl_4 and Ga_2Br_4 may be prepared by the rather tedious process of fractionally freezing the compounds at their melting points.[1] This method cannot be used for Ga_2I_4 since the following disproportionation reaction occurs at its melting point:[2] $3Ga_2I_4 \rightarrow Ga_4I_6 + Ga_2I_6$.

We have found that the halides Ga_2X_4 (X = Cl, Br, I) and Ga_4I_6 may be easily prepared by reducing the relevant gallium(III) halide with gallium metal at 60 °C in benzene solution.

Experimental Section

Preparation of Ga_2I_4. Stoichiometric amounts of gallium(III) iodide (4.73 g, 7.17 mmol) and gallium metal (0.25 g, 3.505 mmol) were shaken with benzene in an evacuated glass vessel at 60 °C in an oven. After 1 day all of the metal had been consumed and an insoluble yellow solid of Ga_2I_4 remained. After the mixture was cooled, the benzene was removed by vacuum distillation.

Anal. Calcd for Ga_2I_4: Ga, 21.5; I, 78.5. Found: Ga, 21.4; I, 78.1.

Raman spectrum: 143 (vs), 214 (w), 235 (w) cm^{-1}.

Preparation of Ga_4I_6. The method was identical with that described for the diiodide except that an excess of gallium metal was added to the gallium(III) iodide in benzene. For gram quantities of product the reaction was complete in 24 h. A yellow-green solid of Ga_4I_6 was formed.

Anal. Calcd for Ga_4I_6: Ga, 26.8; I, 73.2. Found: Ga, 26.9; I, 72.8.

Raman spectrum: 292 (s), 186 (w), 124 (vs), 79 (m) cm^{-1}.

Preparation of Ga_2Cl_4 and Ga_2Br_4. Gallium(III) halide and excess gallium metal were heated with benzene in an evacuated glass vessel at 60 °C for 24 h. After this time two liquid layers had formed. These layers are characteristic of the halides which form benzene complexes.[4] The benzene was removed by vacuum distillation and white crystalline solids remained.

Anal. Calcd for Ga_2Cl_4: Ga, 49.6; Cl, 50.4. Found: Ga, 49.4; Cl, 50.1. Calcd for Ga_2Br_4: Ga, 30.4; Br, 69.6. Found: Ga, 30.1; Br, 70.1. Melting points: Ga_2Cl_4, 172 °C; Ga_2Br_4, 166 °C.

Raman spectra: Ga_2Cl_4 377 (m), 347 (vs), 174 (w), 150 (m), 115 (w); Ga_2Br_4 273 (w), 269 (w), 210 (vs), 109 (m).

Drying of Benzene. Since the halides are very susceptible to moisture, "sodium dried" benzene was refluxed for 12 h with lithium hydride and fractionally distilled. The solvent was then tested by the addition of a small amount of gallium "dihalide". Minute traces of

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