

Single Atom Bridged Porphyrin Dimers, and a Possible Carbon Sandwich

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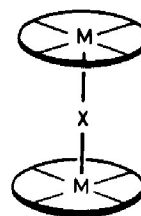
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Summary An orbital diagram constructed for $N_4M-X-MN_4$ where N_4 is a model for a porphyrin ring, M a transition metal, and X a monatomic bridge (O, N, or C) accounts for the electronic structure and bonding preferences of the $X = O$ and N species, and predicts a closed shell for the carbido bridged complex.

Two Schiff-base, porphyrin, or other macrocycle metal complexes may be linked at the metal through a single atom X , as illustrated schematically (1). The oxygen bridged dimers are well represented by $(Fe-salen)_2O$ or $(Fe-TPP)_2O$



(1)

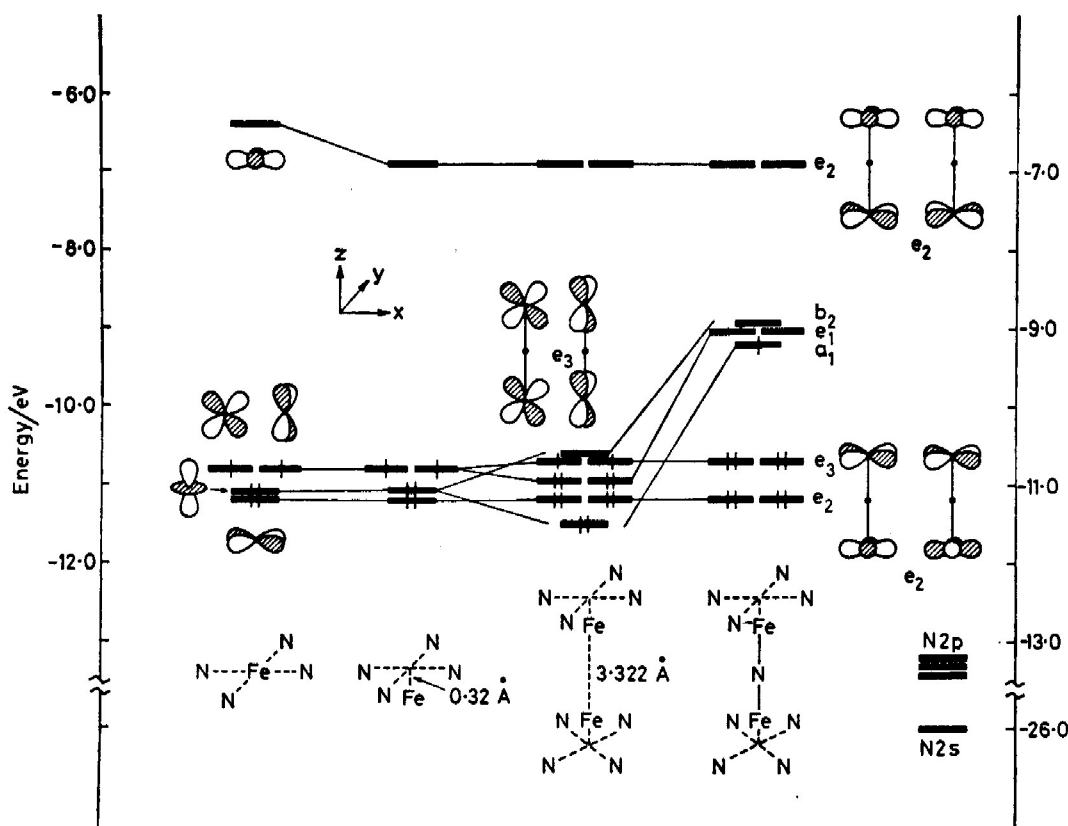


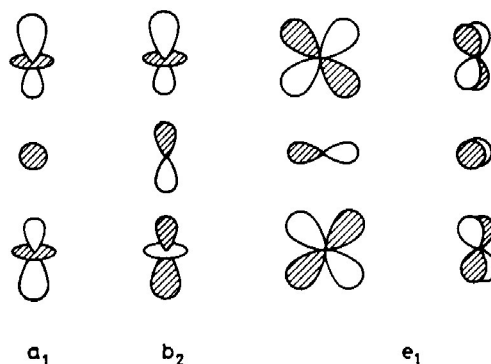
FIGURE 1. The building up of the orbitals of $N_4Fe-N-FeN_4$. From left to right: the orbitals of a square planar $N_4Fe=Fe(NH_4)_4^{2-}$; the N_4Fe pyramidalized by Fe moving 0.32 Å out-of-plane; two such pyramidal N_4Fe units brought to 3.322 Å separation; the orbitals of the composite nitrido complex; the valence orbitals of a N atom. The electron count shown is that appropriate to a low-spin Fe-N-Fe complex.

(salen = *o*-hydroxybenzylideneaminato, TPP = tetraphenylporphyrin).¹ For X = N we have, so far, a single example.² While severely constrained by the steric bulk of the macrocyclic ligand, these bridged molecules exhibit not only linearity but also a range of bending angles at X. They also show a remarkable range of magnetic behaviour. This paper suggests that a simple monatomic carbon bridge between two such metallomacrocycles is also a possibility.

The orbitals of a model $N_4FeXFeN_4$ are built up in Figure 1. The 'N₄' unit is a model $(NH_2)_4^{4-}$. It is the smallest reasonably reliable model of the porphyrin ligand that we have found, when in the course of a systematic study of porphyrin complexes³ we were driven by reasons of computational economy to examine progressive simplification of the porphyrin ring. The construction is for X = N, the iron atom 0.32 Å out of the plane of the four nitrogens, Fe-bridging N 1.661 Å. The symmetry is D_{4d} , with staggered N₄ units. The molecular geometry is derived from that of the known nitrido complex,² and the modifications of the level scheme that ensue for X = O or C will be discussed below.

The construction follows familiar lines.⁴ The lower d block orbitals of a square planar ML_4 complex are xy , z^2 and the degenerate pair xz , yz . The small out-of-plane displacement of the metal atom affects these orbitals but a little. The direct through-space overlap of these orbitals is not great, leading to the small splitting in the third

column of Figure 1. The orbitals are still easily recognized as in- and out-of-phase combinations of xy (e_2 in D_{4d}), z^2 (a_1 and b_2) and xz , yz ($e_1 + e_3$). Now the interaction with the bridging atom X is introduced. X bears orbitals of a_1 (2s) and $b_2 + e_1$ (2p) symmetry. In the high D_{4d} symmetry the e_2 and e_3 d-block combinations are left alone, and the a_1 , b_2 , e_1 molecular orbitals are destabilized by the orbitals of the bridging group.



For a bridging N atom these four levels are very nearly degenerate in our extended Hückel calculations. As the bridging group is varied the position of the a_1 remains relatively constant but the energy of the b_2 and e_1 orbitals

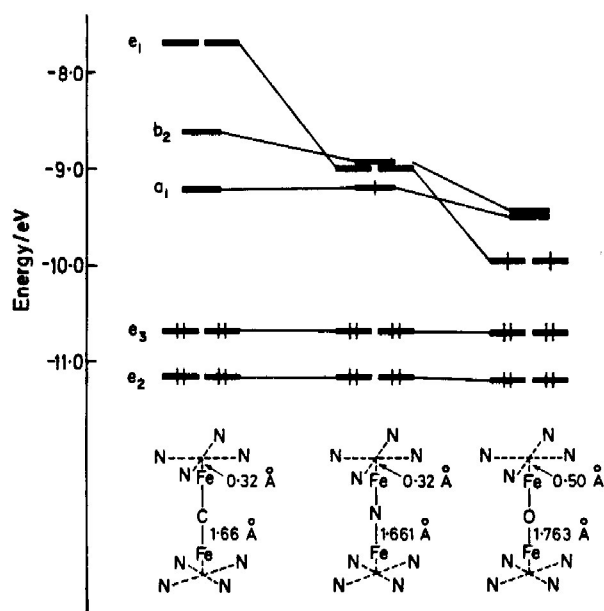


FIGURE 2. The valence orbitals of $N_4Fe-X-FeN_4$ for $X = C, N, O$. The electron count shown is for a low spin configuration.

varies significantly, as shown in Figure 2. As one proceeds from O to N to C the 2p are both closer in energy to and have a better overlap with the metal 3d, destabilizing the metal d-block orbitals, especially e_1 , to a greater extent. No wonder that the magnetic behaviour of the μ -oxo complexes is complicated,^{1,5} for there, four levels within 0.5 eV of each other are available for the two last electrons.

We have studied the bending of these molecules, *i.e.* variation of the M-X-M angle. The analysis will be

presented in the full paper,⁶ but the overall result is that the lower portion of the d-block ($e_3 + e_2$) resists bending, while the lowest energy orbital of the upper portion of the d-block ($a_1 + b_3 + e_1$) favours bending. The net balance is that the μ -oxo compound in its low-spin configuration has a very 'soft' surface for bending (where the steric demands of the ligand sphere allow it, as they do for our N_4 model). The M-X-M = 150° geometry, the 'most bent' geometry we calculated, is preferred to the 'linear' spine by less than 1 kcal/mol. For the μ -nitrido complex linearity is favoured, but not by much.

The most striking aspect of the level scheme of Figures 1 and 2 is that it suggests the existence of a low-spin complex with one electron less than μ -N, two electrons less than μ -O. Such a situation of eight electrons from μ -X and eight d-block electrons from the two metals can be achieved in three distinct ways. One can doubly oxidize an Fe^{III} ($Fe-TPP$)₂O,⁶ though the problem of the actual spin ground state of that system is not resolved, or one can move to another metal or ligand set, as in (Mn-pc)₂O·(py)₂⁷ or (RuCl₂)₂O·H₂O⁴⁻ (pc = phthalocyanine).⁸ Most interesting, however, is retention of the iron group metal atom but formal oxidation of the bridge, *i.e.* ($Fe-TPP$)₂C. We think this should be a stable diamagnetic molecule, with a linear M-C-M spine.

Carbides in which a carbon atom is encapsulated by a metal polyhedron are now well known.⁹ Simple carbon sandwiches have occasionally been proposed,¹⁰ but we know of no authentic example.¹¹ Perhaps here is an opportunity for making one.

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¹¹ There is an interesting report, accompanied by a crystal structure, of $Sn(TPP)[Re(CO)_2C]_2$ in which carbides are sandwiched between Re and Sn: I. Noda, S. Kato, M. Mizuta, N. Yasuoka, and N. Kasai, *Angew. Chem.*, 1979, 91, 85. Our calculations on this structure do not lead to a satisfactory electronic configuration, and we wonder if the carbide atom might really be O or CH₂.