cannot effect the N–N bond length. Thus, the character of the 2e MO must control the strength of the M–N and N–N bonds. The Ru dimer has the shortest N–N bond length due to less M → N_2 $1\pi_g$ donation, which results from less N_2 participation in the 2e MO. More electrons are donated into the μ-N_2 π^* system in the mixed-metal Re–Mo dimer, the Nb dimer, and the Zr dimer because the two unoccupied dπ orbitals located at higher energy than the two occupied dπ orbitals stabilize the μ-N_2 $1\pi_g$ MO. This allows the $1\pi_g$ MO to participate more strongly in the 2e MOs. In the Re–Mo case both high-energy dπ orbitals are primarily Mo dπ in character. The Nb and Zr dimers have one occupied and one unoccupied dπ orbital localized on each metal center. As a result, M → N_2 $1\pi_g$ → M electron flow can occur without charge depletion or charge buildup. Synergetic σ donation is observed for the Nb dimer, which strengthens the M–N bond and weakens the N–N bond.

The key to ambient-temperature nitrogen fixation may lie in d^2 systems like those of Zr and Ta, where the N–N bond is lengthened by π-type synergism.

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Registry No. $[\{Ru(NH_3)_5\}_2(N_2)]^{4+}$, 25754-89-6; $[\{Nb(PH_3)_2(CH_2)(CH_3)\}_2(N_2)]$, 93383-47-2; $[\{Zr(C_5H_5)_2(N_2)\}_2(N_2)]$, 93383-48-3; $[\{Re(PH_3)_4Cl\}\{MoCl_4(OH)\}(N_2)]$, 93383-49-4.

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Generalized Molecular Orbital Calculations on Transition-Metal Dioxygen Complexes. Models for Iron and Cobalt Porphyrins

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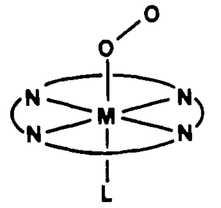
Generalized molecular orbital calculations with configuration interaction are reported for the dioxygen complexes of Co and Fe. The other ligands include a model ligand to represent the porphyrin ring system and a trans ammonia. The Co–O_2 system is best described as a superoxide complex, Co^{3+}–O_2^-, with the unpaired electron in a nearly pure π_g O_2 orbital. The Fe–O_2 system is best described as a singlet dioxygen, O_2 ($^1\Delta_g$) σ donating to and π accepting from an Fe^{2+}. All of the experimental results for both systems can be rationalized with these descriptions. The calculations predict a low-lying triplet state for the FeO_2 system, but not low enough in energy to explain the recently reported paramagnetism of hemoglobin.

Introduction

Transition-metal dioxygen complexes continue to generate considerable interest.[1] Although relatively few of these complexes are biologically active, studies on model systems of both iron and cobalt have increased our understanding of the chemistry and structure of the biological systems. Evidence accumulated from X-ray studies on iron[2] and cobalt[3] model compounds and structural work on oxymyoglobin[4] lead to the conclusion that in these and oxyhemoglobin the metal is six-coordinate with an end-on, bent MO_2 linkage, **1**, where it can be accurately determined the O–O distance in iron porphyrins is 1.23–1.25 Å, while in cobalt complexes it is 1.26–1.30 Å. The metal to oxygen distances are substantially different; Fe–O distances are 1.70–1.75 Å while Co–O distances are 1.86–1.89 Å. The M–O–O angles are larger for Fe(135–130°) than for Co (120–115°).



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The vast amount of experimental work on both metals, which will not be reviewed here, can be accommodated with either a M^{2+}–O_2^0 (dioxygen) or a M^{3+}–O_2^- (superoxide) description. Recent theoretical work has included extended Pariser–Parr–Pople and Xα multiple scattering calculations,[5] which suggest that the FeO_2 unit could be viewed as an equal mixture of Fe^{2+} (S = 0)–O_2^0 (S = 0) and Fe^{2+} (S = 1)–O_2^0 (S = 1). The latter description, which resembles ozone, was suggested as the major contributor by generalized valence bond calculations.[6] However, other ab initio calculations suggest that Fe^{2+} (S = 0)–O_2^0 (S = 0) plays the dominant role in the ground state.[7] Further confusion is added by recent INDO–SCF–CI calculations which suggest that the ground state has considerable Fe^{3+} (S = $^1/_2$)–O_2^- (S = $^1/_2$) character.[8] Pauling

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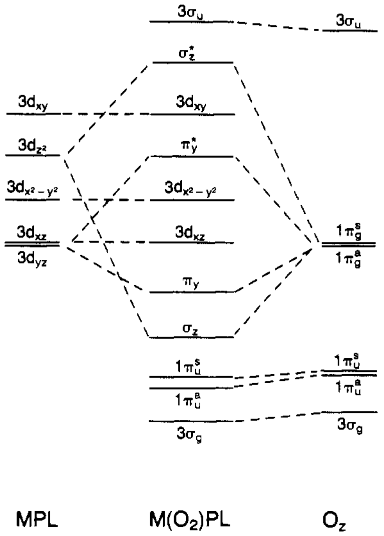

Figure 1. Qualitative molecular orbital diagram for the $M(O_2)PL$ molecule. The $M-O_2$ σ bonding and antibonding MO's formed from $3d_{z^2}$ and $1\pi_g{}^s$ are labeled σ_z and $\sigma_z{}^*$, respectively. The $M-O_2$ π bonding and antibonding MO's formed from $3d_{yz}$ and $1\pi_g{}^a$ are labeled π_y and $\pi_y{}^*$, respectively. The other MO's can usually be identified with one of the MO's of the isolated fragments. The N atoms of the porphyrin model, P, bisect the x and y axes, and $M-O_2$ lies in the xz plane. Thus, antisymmetric $1\pi_u{}^a$ and $1\pi_g{}^a$ are formed from O $2p_y$ atomic orbitals. The point group symmetry is C_s, the a′ orbitals include $3\sigma_g$, $1\pi_u{}^s$, σ_z, $3d_{xz}$, $3d_{x^2-y^2}$, $\sigma_z{}^*$, and $3\sigma_u$, and the a″ orbitals include $1\pi_u{}^a$, π_y, $\pi_y{}^*$, and $3d_{xy}$.

originally suggested the $Fe^{2+}-O_2{}^0$ view,[9] while Weiss suggested the $Fe^{3+}-O_2{}^-$ view.[10] Although considerable progress in our understanding of oxyhemoglobin has been made since these original suggestions, neither description has proved to be dominant. The situation for Co is only slightly less confusing. Ab initio calculations suggest a Co^{3+} ($S = 0$)–$O_2{}^-$ ($S = {}^1/_2$) interpretation of the ground state. Drago, however, prefers a Co^{2+} ($S = {}^1/_2$)–$O_2{}^0$ ($S = 1$) description of this system.[11] The spin-pairing model of Drago can also be applied to other dioxygen complexes.

In spite of the progress in the chemistry and structure of dioxygen complexes, there remains serious differences of opinion on the nature of the electronic structure in both iron and cobalt complexes. Some of these differences are more semantic than real while others are more formal than actual. In this work we report the results of ab initio calculations including configuration interaction on model iron and cobalt systems. These calculations, which are more accurate than previous ones, resolve many of the problems in the description of the electronic structure.

Problem

Figure 1 shows a qualitative molecular orbital (MO) diagram for a molecule such as **1**. All of the models for both iron- and cobalt–dioxygen bonding can be accommodated within this general MO model. The differences in the description arise from the relative amounts of metal or dioxygen character in the σ_z and π_y molecular orbitals, the strength of the interaction between the metal and dioxygen, and the importance of mixing of the $1\pi_u$ and $3\sigma_g$ into the π_y and σ_z molecular orbitals.

The case for cobalt is perhaps simpler. The electronic configuration would be $(\sigma_z)^2(\pi_y)^2(d_{xz})^2(d_{xy})^2(\pi_y{}^*)^1$. ESR experiments firmly establish that $\pi_y{}^*$, the orbital containing the unpaired electron, is nearly a pure O_2 π_g orbital.[12] Therefore, the π_y MO must be nearly pure Co d_{yz}. The difference between the $Co^{2+}-O_2{}^0$ and the $Co^{3+}-O_2{}^-$ description involves the electron distribution in the σ_z orbital. If this orbital is nearly an equal mixture of Co and O_2, then $Co^{2+}-O_2{}^0$ would be the best description, while if it is mostly O_2 in character, $Co^{2+}-O_2{}^-$ would be preferred. For $Co^{2+}-O_2{}^0$ the bond could be a strong covalent one or simply spin coupling of the two electrons, one in d_{z^2} and one in $\pi_g{}^s$.

In our description of the bonding we will reserve the term "spin coupling" for situations in which the interaction of the two fragment orbitals is weak. If two fragment orbitals have similar energy, the bonding MO will be an equal mixture of both fragment orbitals, and if their interaction is weak, the electronic structure is not properly described by a single configuration as in ordinary MO theory. In this situation the correct qualitative description involves a mixture of two configurations, such as $(\sigma)^2-\lambda(\sigma^*)^2$. The mixing of the configuration with the antibonding orbital occupied served to spacially separate the two electrons involved in this weak bond. In other words, a valence bond description of the two electrons in this bond is substantially better than the MO description. This situation arises in the dissociation of even a simple molecule like H_2,[13] in the π system of ozone,[14] and in the δ bond of quadruply bonded chromium.[15] If this situation also prevails for the σ $Co-O_2$ bond, then one must describe this bond with two configurations and the bond would be very close to pure spin coupling. Otherwise the bond would be described better as a typical covalent bond.

The iron-to-dioxygen bond is more complicated. In addition to the problem of the σ system described for cobalt, the π system presents a similar problem. Thus, the π system could be described as one electron in the d_{yz} orbital of Fe bonding with one electron in the $\pi_g{}^a$ orbital of O_2. If the σ system also involves little charge transfer, then the system would be described as Fe^{2+} ($S = 1$)–$O_2{}^0$ ($S = 1$) or ozone-like. However, if the σ system was primarily on O_2, a dative bond formed from $(\pi_g{}^s)^2$ donating to d_{z^2}, then the system would be described as Fe^{3+} ($S = {}^1/_2$)–$O_2{}^-$ ($S = {}^1/_2$) or superoxide-like. This latter case would correspond to the Weiss model.

A reasonable alternative for the π system would be an empty $\pi_g{}^a$ accepting electron density from $(d_{yz})^2$, i.e., O_2 being viewed as a strong π acceptor. Again, this leads to two situations for the two choices for the σ system, an Fe^{2+} ($S = 0$)–$O_2{}^0$ ($S = 0$) system if the σ bond was dative, $(\pi_g{}^s)^2$ to d_{z^2} donation, or Fe^+ ($S = {}^1/_2$)–$O_2{}^+$ ($S = {}^1/_2$) if the σ system was essentially a neutral covalent bond. The former is one of the primary resonance structures of the Pauling model, while the latter is rather unlikely in this molecule because of the high ionization energy of O_2.

There are still other possibilities, some leading to an even more highly reduced Fe and others that involve Fe^{4+} and $O_2{}^{2-}$ or a peroxide-like model. Although the latter model may be

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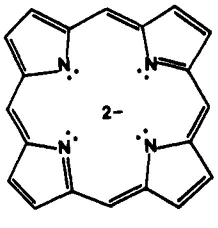
Table I. Comparison of Approximate MO Calculations for $Fe(O_2)PL$

	porphyrin (2)–imidazole		model (6)–ammonia	
sym	energy, eV	character	energy, eV	character
a′	7.26	52% $3d_{z^2}$, 17% L, 14% P	5.19	55% $3d_{z^2}$, 14% L
a″	7.23	54% $3d_{xy}$, 44% P	3.48	54% d_{xy}, 39% P
a″	−4.38	21% $3d_{yz}$, 28% $1\pi_g$, 45% P	−4.76	28% $3d_{yz}$, 68% $1\pi_g$
a″	−5.57	5% $3d_{yz}$, 41% $1\pi_g$, 49% P		
a′ (HOMO)	−6.86	21% $3d_{xz}$, 55% $1\pi_g$, 12% P	−6.45	31% $3d_{xz}$, 54% $1\pi_g$
a′	−9.92	90% $3d_{x^2-y^2}$, 8% P	−7.39 −14.61	50% $3d_{x^2-y^2}$, 32% P 35% $3d_{x^2-y^2}$, 41% P
a′	−10.16	15% $3d_{xz}$, 10% $1\pi_g$, 56% P	−9.13	18% $3d_{xz}$, 33% $1\pi_g$, 46% P
a′	−10.36	20% $3d_{xz}$, 16% $1\pi_g$, 53% P		
a″	−10.47	31% $3d_{yz}$, 18% $1\pi_g$, 43% P	−9.74	44% $3d_{yz}$, 28% $1\pi_g$, 24% P
a″	−13.66	18% $3d_{yz}$, 48% P		
a′	−13.71	20% $3d_{xz}$, 54% P	−13.57	41% $3d_{xz}$, 11% $1\pi_g$, 43% P
a″	−16.83	12% $3d_{xy}$, 63% P	−17.28	37% $3d_{xy}$, 56% P
a″	−19.43	22% $3d_{xy}$, 76% P		

useful in a formal way if one wishes to view all transition metal to ligand bonds as dative with ligand to metal donation,[16] it is unlikely that the actual charge distribution in the molecule is this highly polarized. Since our emphasis in the present study is on the actual charge distribution in the complex, the highly reduced or oxidized iron situations will not be given further consideration.

Theoretical Section

Porphyrin Model. Because we wished to use a better basis set than those previously employed and to include electron correlation in our calculation, we found it necessary to replace the porphyrin ring system, **2**, with a simpler model. In order to choose between the various possibilities, $[NH_2]_4^{2-}$ (**3**), $[NHCH_2]_4^{2-}$ (**4**), $[(NH)_2(CH)_3]_2^{2-}$ (**5**), and $[(NH)_2CH]_2^{2-}$ (**6**), we performed approximate molecular orbital calculations[17] on FeP and $Fe(O_2)PL$, where P = porphyrinato(2−) or model and L = imidazole or ammonia terminal ligand. The porphyrin ligand is, of course, an aromatic ring system with the nitrogen π electrons delocalized through the carbon framework. Our calculations indicate that his delocalization, present in **2**, is absent in **3** but partially accounted for in **4**, **5**, and **6**. Overall the last model, **6**, provides a reasonable balance between accuracy and economy. Although not required by symmetry in this simple model, the d_{xz} and d_{yz} orbitals are nearly degenerate in FeP, P = **6**. Evidence that **6** is an adequate model is presented in Table I, where we compare $Fe(O_2)PL$ for two situations: first where P = **2**, L = imidazole and second where P = **6**, L = ammonia. Except for some splittings due to near-degenerate mixing with the porphyrin model, which are denoted by braces, the O_2 and Fe character of the upper valence orbitals is remarkably similar. The geometries and basis sets used for these calculations and the results of the other models are described elsewhere.[18] We do not suggest that these approximate results will produce a definitive description of the Fe to O_2 bond but only that since **6** is a reasonable model in the approximate calculation it should be a reasonable model in the ab initio calculations. The Results and Discussion will refer to the ab initio calculations.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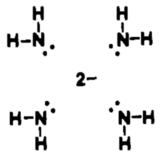
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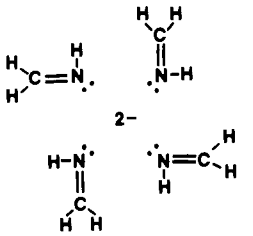
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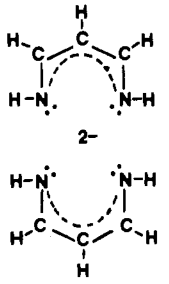
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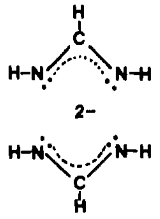
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Geometry. The model **6** has N–C, N–H, and C–H bond lengths of 1.40, 0.915, and 1.078 Å, respectively. The N–C–N angle is 125.6°. The N atoms of **6** are placed 1.96 Å from both Fe and Co, and the ammonia ligand is 2.07 Å from both metals. The M–O and O–O bond distances were respectively 1.75 and 1.24 Å (and 1.75 and 1.21 Å in a second calculation) in the Fe system and 1.86 and 1.27 Å in the Co system. The corresponding M–O–O angle was 136.0° in the Fe system and 117.4° in the Co system. These geometries were estimated from the average values of a number of structures[2,3] and correspond closely to geometries used in other calculations.[7]

Basis Set. The basis set is essentially double-ζ in the outer valence of the metal and dioxygen and minimal for the other atoms. The functions used in the ab initio calculations were obtained from a least-squares fit of a linear combination of Gaussians to near-Hartree–Fock-quality Slater-type orbitals.[19] The program, GEXP, processes the functions from the 1s orbital outward keeping each orbital of higher *n* quantum number orthogonal to the previous ones. This procedure results in an efficiently nested representation.[20] The number of Gaussians used for each atomic orbital was increased until the integral error of the fit was $<10^{-3}$. It was found that three Gaussians per atomic orbital were sufficient except for the O 2p, Fe 3d, and Co 3d orbitals. A 4-31G-type basis was used for O 2p, and a 5-41G-type basis was used for metal 3d. These were obtained by splitting off the most diffuse component of the fully contracted set. Metal 4s and 4p functions were included with exponents of 0.20 and 0.25. This process results in a [10s,7p,5d]/(4s,3p,2d) basis for the metals, [6s,4p]/(2s,2p) for oxygen, [6s,3p]/(2s,1p) for nitrogen and carbon and [3s]/(1s) basis for hydrogen.

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Calculations. The molecular orbitals, first determined by the generalized molecular orbital (GMO) approach, are subsequently subjected to a configuration interaction (CI) calculation, and "natural" orbitals are determined from this CI calculation. Details of the GMO approach have been presented elsewhere.[21] Conceptually the approach divides the orbital space into five shells (doubly occupied, strongly occupied, singly occupied, weakly occupied, and unoccupied) rather than the usual three (doubly occupied, singly occupied, and unoccupied). The two new shells, strongly and weakly occupied, are composed of the orbitals containing electron pairs to be correlated and the orbitals that will be used to correlate these electron pairs. The GMO procedure solves for these orbitals with a limited type of multiconfiguration self-consistent-field calculation. The subsequent CI calculation usually includes at least all those configurations one can make from single and double excitations out of the strongly occupied into the weakly occupied.

All calculations were performed on an AMDAHL 470/V6 computer at the Data Processing Center of Texas A&M University. The ATMOL3 integral-SCF package was modified by addition of a GMO module to the SCF program. The CI calculations were performed with a bonded function program[23] modified by T. E. Taylor for the AMDAHL-ATMOL3 system. Orbital plots were prepared by the program MOPLOT.[24]

Results

Iron–Dioxygen System. The orbitals in the strongly occupied set were the $3\sigma_g$, $1\pi_u{}^a$, $1\pi_u{}^s$, σ_z, π_y, $3d_{xz}$, and $3d_{x^2-y^2}$, i.e. the upper valence orbitals of the FeO_2 moiety that would be doubly occupied in a standard MO calculation (see Figure 1). The weakly occupied orbitals were $\pi_y{}^*$, d_{xy}, $\sigma_z{}^*$, and $3\sigma_u$; i.e. the antibonding counterparts of the occupied orbitals. The initial orbital space consists of all those molecular orbitals that are formed from the five Fe 3d and six O 2p orbitals. During the cycling of the GMO-SCF calculation $1\pi_u{}^s$ interacted strongly with both the $2\sigma_u$ and $2\sigma_g$ orbitals of O_2, eventually causing the primary $1\pi_u{}^s$ character to revert to the doubly occupied shell. However, $1\pi_u{}^s$, $2\sigma_u$, and $2\sigma_g$ were doubly occupied in all the important configurations so this apparent change is not significant. At self-consistency the GMO calculation had a total energy of −1748.156 au.

The strongly and weakly occupied orbitals generated in the GMO step were then used in a CI calculation on the lowest $^1A'$ state. All single and double excitations from the strongly occupied orbitals to the weakly occupied orbitals were included. The lowest root of this 289-configuration CI matrix yielded a total energy of −1748.286 au. The HF configuration, $(3\sigma_g)^2(1\pi_u{}^a)^2(1\pi_u{}^s)^2(\sigma_z)^2(\pi_y)^2(3d_{xz})^2(3d_{x^2-y^2})^2$ (see Figure 1), represents 91% of the wave function. The next most important configuration (3%) involves a double excitation from π_y to $\pi_y{}^*$, i.e., two electrons leaving the bonding Fe–O_2 π combination and entering its antibonding counterpart. The remainder of the wave function is composed of small contributions (1% or less) from a large number of configurations; many of the more important of these involve one of the two electrons excited from π_y to $\pi_y{}^*$.

The natural orbitals of this CI wave function were determined and their occupation numbers are

$$(3\sigma_g)^{1.96}(1\pi_u{}^s)^{2.00}(\pi_y + 1\pi_u{}^a)^{1.99}(\sigma_z)^{1.99} \times \\ (\pi_y - 1\pi_u{}^a)^{1.90}(3d_{xz})^{2.00}(3d_{x^2-y^2})^{2.00} \times \\ (\pi_y{}^*)^{0.11}(3d_{xy})^{0.01}(\sigma_z{}^*)^{0.01}(3\sigma_u)^{0.04}$$

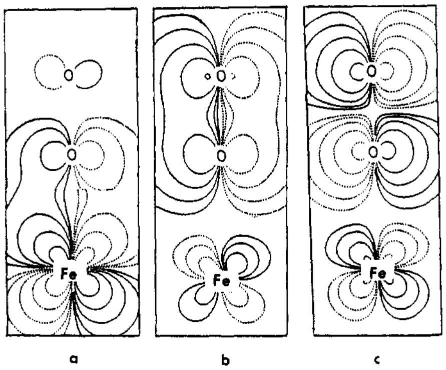

Figure 2. Plots of the FeO_2 π orbitals: (a) the bonding MO π_y mixing with $1\pi_u{}^a$; (b) out-of-phase mixture of π_y and $1\pi_u{}^a$; (c) $\pi_y{}^*$. These orbitals have a″ symmetry (C_s) and are plotted in a folded plane that contains Fe–O_1–O_2 and is perpendicular to the *xz* reflection plane.

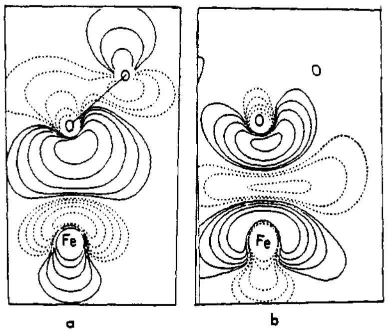

Figure 3. Plots of the FeO_2 σ orbitals: (a) the bonding MO σ_z; (b) the antibonding MO $\sigma_z{}^*$. These orbitals are plotted in the *xz* plane, which contains the Fe–O_1–O_2 unit.

As we have indicated in our notation for the orbitals, there has been rather strong mixing between $1\pi_u{}^a$ and π_y; the latter is the bonding combination of $3d_{yz}$ and $1\pi_g{}^a$.

The π (a″) orbitals, $(\pi_y + 1\pi_u{}^a)$, $(\pi_y - 1\pi_u{}^a)$, and $\pi_y{}^*$, are plotted in Figure 2. The most highly occupied orbital is primarily $3d_{yz}$ strongly delocalized onto the closest O of the O_2 molecule. The next most highly occupied orbital is mainly $1\pi_u{}^a$ with an antibonding Fe–O_2 interaction. The weakly occupied orbital, $\pi_y{}^*$, is a nearly equal mixture of Fe and the two O orbitals with a node between each. This system of orbitals resembles a localized version of a three-center, four-electron π bond, such as one might find on ozone.

The Fe–O_2 σ bond is dominated by the strongly occupied σ_z, and there are only small contributions to the wave function from the very weakly occupied $\sigma_z{}^*$. These two orbitals are plotted in Figure 3. The bonding orbital (Figure 3a) involves donation from an O_2 molecular orbital, which is a mixture of $1\pi_g{}^s$, $1\pi_u{}^s$, and $3\sigma_g$, to an Fe hybrid that contains $3d_{z^2}$, 4s, and $4p_z$ character. The mixing of $1\pi_u{}^s$ and $3\sigma_g{}^s$ into $1\pi_g{}^s$ causes the lobe on the closest oxygen to enlarge and rotate toward the Fe. The orbital is in phase with $3d_{z^2}$, 4s, and $4p_z$, but because $4p_z$ must be orthogonal to $3p_z$, a node arises close to the Fe. The antibonding Fe–O_2 orbital therefore has two nodes, one closer to the midpoint of the Fe–O bond and one close to the Fe. Similar behavior has been in Cr–CO bonds.[25] In both orbitals the contribution of the more distant O is substantially smaller.

A second calculation with a shorter O–O distance of 1.21 Å resulted in essentially the same qualitative wave function. The total energy at the CI level was −1748.279 au. Because so many of the excited states of oxyhemoglobin involve the porphyrin π system, we have not attempted to investigate them.

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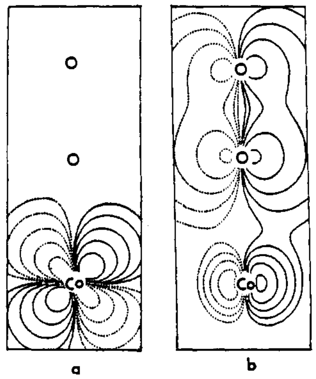

Figure 4. Plots of the CoO_2 a″ orbitals in the same plane as Figure 2: (a) nearly pure $3d_{yz}$; (b) nearly pure $1\pi_u{}^a$; (c) nearly pure $1\pi_g{}^a$.

However, the lowest energy excitations at 0.95 and 1.08 eV involve excitation into the $\pi_y{}^*$ orbital.[26] Recent magnetic results suggest a low-lying triplet 146 cm^{-1} above the ground state.[27] This result has been questioned on several grounds[5,28] but supported by INDO–SCF–CI calculations.[8] We have attempted a direct calculation of this energy difference. Preliminary CI calculations suggest that the most likely candidate for a low-lying triplet was $^3A'$ corresponding to a $\pi_y{}^* \leftarrow \pi_y$ transition. A similar state, $^3B_2$, in ozone lies lower than $^1A_1$ in the Hartree–Fock approximation. In order to keep the calculation of these two states, $^1A'$ and $^3A'$, at the same level of accuracy, $^3A'$ was treated as a single determinant

$$(\sigma_z)^2(d_{xz})^2(d_{x^2-y^2})^2(\pi_y)^1(\pi_y{}^*)^1$$

and $^1A'$ was treated as two determinants

$$(\sigma_z)^2(d_{xz})^2(d_{x^2-y^2})^2[(\pi_y)^2 + \lambda(\pi_y{}^*)^2]$$

Self-consistent-field calculations on these two states yield total energies of −1748.2091 au for the ground state $^1A'$ and −1748.2052 au for the excited state $^3A'$. Although the energy difference, 0.11 eV or 850 cm^{-1}, is small, it is much too large for the $^3A'$ state to be populated thermally.

Cobalt–Dioxygen System. As in the iron calculation we formed the strongly occupied set of orbitals from $3\sigma_g$, $1\pi_u{}^a$, $1\pi_u{}^s$, σ_z, π_y, $3d_{xz}$, and $3d_{x^2-y^2}$. $\pi_y{}^*$ was singly occupied, and $3d_{xy}$, $\sigma_z{}^*$, and $3\sigma_u$ were weakly occupied. After the orbitals were optimized by the GMO procedure, we calculated the $^2A''$ ground state from a CI calculation, which allowed all single and double excitations from the strongly and singly occupied orbitals to the singly and weakly occupied orbitals. This procedure results in a 383-configuration wave function and a total energy of −1866.462 au. The HF configuration, $(3\sigma_g)^2(1\pi_u{}^a)^2(1\pi_u{}^s)^2(\sigma_z)^2(\pi_y)^2(3d_{xz})^2(3d_{x^2-y^2})^2(\pi_y{}^*)^1$ (see Figure 1), represents 94% of the wave function. There is no single configuration that dominates the rest of the wave function.

The natural orbitals of this CI wave function were determined, and their occupation numbers are

$$(3\sigma_g)^{1.96}(1\pi_u{}^s + \sigma_z)^{2.00}(1\pi_u{}^a)^{1.99}(1\pi_u{}^s - \sigma_z)^{1.97} \times (3d_{yz})^{1.99}(3d_{xz})^{2.00}(3d_{x^2-y^2})^{1.99}(1\pi_g{}^a)^{1.01} \times (3d_{xy})^{0.02}(\sigma_z{}^*)^{0.03}(3\sigma_u)^{0.04}$$

The π (a″) orbitals are plotted in Figure 4. They are nearly completely separated into $3d_{yz}$, $1\pi_u{}^a$, and $1\pi_g{}^a$. $1\pi_u{}^a$ has mixed some with the Co, but the singly occupied $1\pi_g{}^a$ is nearly pure O_2 in character. The a′ orbitals are plotted in Figure 5. $3\sigma_g$ mixes slightly with the π orbitals in order to rotate away from the Co (Figure 5a). The main Co–O_2 bonding interaction is split between donation to a hybrid formed from $3d_{z^2}$, 4s, and $4p_z$ from both $1\pi_u{}^s$ (Figure 5b) and $1\pi_g{}^s$ (Figure 5c). Both have mixed slightly with $3\sigma_g$ to point their lobes toward the Co. One can easily imagine adding and subtracting these two orbitals to form a localized Co–O_2 bond and a O_2 lone pair, respectively. Again a node close to the Co occurs because of orthogonality to 3p. The Co–O_2 antibonding orbital (Figure 5d) is primarly Co $3d_z$ in character with a node near the midpoint of the Co–O_1 bond.

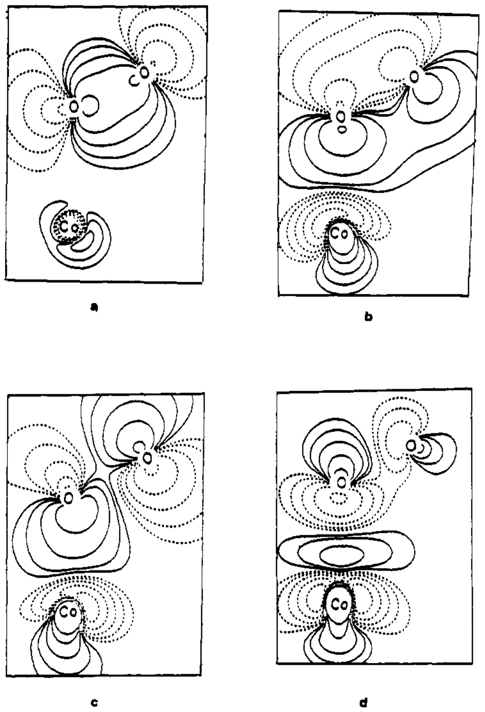

Figure 5. Plots of the CoO_2 a′ orbitals in the same plane as Figure 3: (a) $3\sigma_g$; (b) the Co σ hybrid mixing with $1\pi_u{}^s$; (c) the Co σ hybrid mixing with $1\pi_g{}^s$; (d) $3d_{z^2}$ out of phase with a mixture of $1\pi_u{}^s$ and $1\pi_g{}^s$.

Discussion

As in the Problem section, we will deal with the Co–O_2 system first. Clearly the calculations are in agreement with the ESR[12] results, which suggest that the unpaired electron remains essentially in a $1\pi_g$ orbital on O_2. Our results show almost no direct delocalization of the spin density onto the cobalt, a result that supports the interpretation of Drago et al.[11] Furthermore, the more distant oxygen, O_2, carries about 1.5 times as much spin density as the closer oxygen, O_1 a result that is in total agreement with the experimental results.

The Co–O_2 σ bond, about which there is more controversy, consists of a mixture of $3\sigma_g$, $1\pi_u$, and $1\pi_g$ donating to a Co hybrid formed from $3d_{z^2}$, 4s, and $4p_z$. The net bond is essentially an sp^2 O_2 lone pair being donated to the Co. The fact that this bond is a mixture of O_2 molecular orbitals localized toward the O_2 ligand precludes the description as spin coupling. Our results are wholly consistent with previous ab initio results on Schiff-base systems[7] and suggest that the O_2 in the cobalt system is best described as a superoxide, $O_2{}^-$, forming a dative σ bond by donating electrons to an empty Co^{3+} orbital.

The situation with the Fe–O_2 bonds is clearly more complicated. The π bond (Figure 2) looks very much like a localized three-center, four-electron bond. The usual treatment

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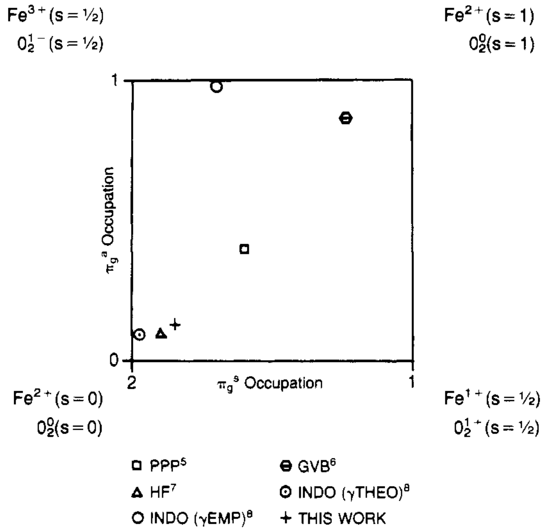

Figure 6. Qualitative representation of the charge distribution predicted by various theoretical methods.

for a three-center, four-electron bond such as found in the π system of ozone begins with three orbitals a, b, and c, of equal energy which form the molecular orbitals

$$\psi_1 = a + b + c \qquad \psi_2 = a - c \qquad \psi_3 = a - b + c$$

What makes ozone unusual is that the triplet configuration $\psi_1^2\psi_2^1\psi_3^1$ is of lower energy than the ground-state singlet $\psi_1^2\psi_2^2$ unless CI is taken into account by allowing the singlet to mix in the configuration $\psi_1^2\psi_3^2$. Our FeO_2 system has some similarities. Our $^3A'$ corresponds to $\psi_1^2\psi_2^1\psi_3^1$ with a total energy −1748.205 au. the singlet configuration $\psi_1^2\psi_2^2$ has an energy of −1748.156 au, but the two-configuration result $(\psi_1^2\psi_2^2 + \lambda\psi_1^2\psi_3^2)$ has an energy of −1748.209 au. Thus, for FeO_2, like O_3, electron correlation must be introduced in order to obtain the correct ground state. However, the weight of the configuration $\psi_1^2\psi_3^2$ is rather small and in a qualitative sense $\psi_1^2\psi_2^2$ remains a fairly good description of the overall wave function. The plots in Figure 2 resemble the following linear combination of ψ_1, ψ_2, and ψ_3

$$\psi_1 + \psi_2 = 2a + b \qquad \psi_1 - \psi_2 = b + 2c$$
$$\psi_3 = a - b + c$$

but ψ_3, the weakly occupied orbital, has somewhat more O_2 character than Fe character, which means the system is shifted toward high Fe $3d_{yz}$ occupancy and away from a pure ozone-like system. Thus, the system also resembles $(3d_{yz})^2$ to $1\pi_g{}^a$ donation, as if $1\pi_g{}^a$ were an empty acceptor orbital on the O_2 ligand.

The σ bond (Figure 3a) bears a close semblence to a localized version of the Co–O_2 σ bond (sum of parts b and c of Figure 5). It can most simply be described as a sp^2 hybrid on O_2 donating a small fraction of its electrons to the hybrid on the Fe. Again the strong mixing of $1\pi_u$ and $3\sigma_g$ with $1\pi_g$ and the retention of the electron pair by the O_2 preclude a simple spin-coupling view. Important contributions to the orbital asymmetry observed in the Mössbauer spectrum but neglected in most previous calculations arise from an expansion of d_{yz} toward the O_2 and contraction of d_{xz} away from the O_2. Although the $3d_{xz}$ orbital mixes with some of the O orbitals, it contributes little to the net Fe–O_2 bond, which arises mainly from the use of $3d_z$. This description can accommodate all of the experimental results.

We can get an overall picture of the situation from Figure 6, which shows four extreme situations: Fe^{2+} ($S = 0$)–$O_2{}^0$ ($S = 0$) would be $(1\pi_g{}^s)^2(1\pi_g{}^a)^0$, Fe^{3+} ($S = {}^1/_2$)–$O_2{}^-$ ($S = {}^1/_2$) would be $(1\pi_g{}^s)^2(1\pi_g{}^a)^1$, and Fe^{2+} ($S = 1$)–$O_2{}^0$ ($S = 1$) would be $(1\pi_g{}^s)^1(1\pi_g{}^a)^1$. We have plotted in Figure 6 the results of population analysis of our calculation and that of other calculations. Our result and most other results are close to the line joining the two spin possibilities for a $Fe^{2+}O_2{}^0$ charge distribution. Our calculation suggests contribution from all three resonance structures, but the simplest description results from viewing the bond as an O_2 with a $(1\pi_g{}^s)^2(1\pi_g{}^a)^0$ configuration ($^1\Delta_g$) forming a σ bond by donation from the $1\pi_g{}^s$ orbital and a contributing π bond by accepting electron density from Fe $3d_{yz}$ into $1\pi_g{}^a$. If one views the system as Fe^{3+}–$O_2{}^-$, then one must add strong π donation from $O_2{}^-$ to Fe. Similarly, if one views the systems as ozone-like, Fe^{2+} ($S = 1$)–$O_2{}^0$ ($S = 1$), then one must add strong σ donation from the Fe to the O_2 in addition to π donation from O_2 to Fe.

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Registry No. Iron porphyrin, 15213-42-0; cobalt porphyrin, 15612-49-4.