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End-on versus Side-on Coordination of Dioxygen Model *ab initio* Calculations for the Adducts of Co(acacen)

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From *ab initio* calculations, the ground state electronic configuration is found for the three possible structures (linear, bent or perpendicular) of the cobalt-dioxygen unit in the adducts Co(acacen) LO_2 (L= none, H_2O, CN^-, CO). The bent structure is energetically the most favourable, being slightly more stable than the linear one (by 4–26 kcal/mole depending on the fifth ligand L) but much more stable than the perpendicular one (by 46–82 kcal/mole). These results are rationalized in terms of the main metal-ligand interactions, with the bent structure stabilized by a $3d_{z^2}$-$1\pi_g^a$ interaction and the perpendicular structure destabilized by a four-electron destabilizing interaction $3d_{xz}$-$1\pi_g^a$.

Key words: Co(acacen), adducts of ~ – Dioxygen, coordination of ~

The structure of the iron-dioxygen unit in the oxygen carriers such as the molecules of hemoglobin and myoglobin has a long history [1–6]. Different structural models have been proposed for dioxygen binding, including a linear M–O–O unit *1* [1], an "end-on" angular bond *2* [2–5] or a sideways triangular structure *3* [6]. Synthetic oxygen carriers of Fe(II) (such as the "picket fence" porphyrin) and Co(II) (in a variety of complexes) have been structurally characterized as systems with M–O–O bent bonds, the corresponding angle being in the range 124°–155° [7–11]. However there is still the possibility that for a given complex the energy difference between the three structures *1*–*3* could be small, with the environmental factors influencing which of the forms is the more stable. ESR of cobalt oxygen carriers labeled with ^{17}O shows a complex containing magnetically equivalent oxygen atoms, a result which is consistent either with a triangular structure or with a rapid flipping of the O–O group

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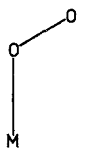

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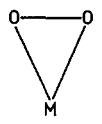

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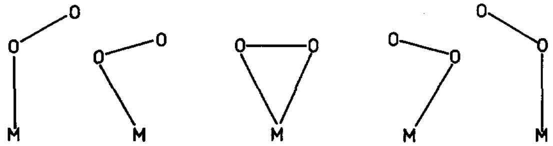
between two bent positions as in *4* [12], with the sideways structure representing probably a transition state. A recent report on the ESR spectra of oxycobaltmyoglobin and oxycobalthemoglobin proposed the perpendicular structure [13].



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We have previously calculated [14] the wavefunctions and the energies of the Co(acacen)LO$_2$ dioxygen adduct [with the fifth ligand L = none, H$_2$O, imidazole (Im), CN$^-$ and CO] for the bent structure *2* (we used for the Co–O–O angle the experimental value reported for the Co(bzacen) complex [8]). We present here the results of similar calculations for the three above structures *1*–*3*, using the same basis sets and geometries as in Ref. [14]. The Co–O$_1$ and O$_1$–O$_2$ bond lengths were kept respectively to 1.86 Å and 1.26 Å in the three structures, with the Co–O$_2$ bond length also equal to 1.86 Å in the perpendicular structure. The results for the bent structure correspond to the ones reported previously for L = none, H$_2$O, CN$^-$, and CO. Then the ground state configuration was of the type $(\pi_g^a)^2(\pi_g^b)^1$

Table 1. Energy values (in a.u.) for the four possible electronic configurations and the three geometric structures of Co(acacen)LO$_2$ (underlined values correspond to the ground state for each geometric structure)

Fifth ligand L	Electronic configuration	Geometric structure		
		Linear	Bent	Perpendicular
L = none	$(\pi_g^a)^2(\pi_g^b)^1$	−2013.583	$\underline{-2013.635}$	−2013.508
	$(\pi_g^b)^2(\pi_g^a)^1$	−2013.584	−2013.611	−2013.497
	$(\pi_g^a)^2(d_{z^2})^1$	$\underline{-2013.628}$	−2013.630	−2013.521
	$(\pi_g^b)^2(d_{z^2})^1$	−2013.627	−2013.619	$\underline{-2013.561}$
L = H$_2$O	$(\pi_g^a)^2(\pi_g^b)^1$	−2089.360	$\underline{-2089.406}$	−2089.274
	$(\pi_g^b)^2(\pi_g^a)^1$	−2089.359	−2089.388	$\underline{-2089.275}$
	$(\pi_g^a)^2(d_{z^2})^1$	$\underline{-2089.377}$	−2089.382	−2089.270
	$(\pi_g^b)^2(d_{z^2})^1$	−2089.376	−2089.373	[a]
L = CN$^-$	$(\pi_g^a)^2(\pi_g^b)^1$	$\underline{-2105.703}$	$\underline{-2105.735}$	−2105.619
	$(\pi_g^b)^2(\pi_g^a)^1$	−2105.701	−2105.720	$\underline{-2105.621}$
	$(\pi_g^a)^2(d_{z^2})^1$	−2105.620	−2105.626	−2105.517
	$(\pi_g^b)^2(d_{z^2})^1$	−2105.619	[a]	−2105.578
L = CO	$(\pi_g^a)^2(\pi_g^b)^1$	−2125.958	$\underline{-2126.004}$	−2125.873
	$(\pi_g^b)^2(\pi_g^a)^1$	−2125.956	−2125.982	$\underline{-2125.877}$
	$(\pi_g^a)^2(d_{z^2})^1$	$\underline{-2125.962}$	−2125.967	−2125.860
	$(\pi_g^b)^2(d_{z^2})^1$	$\underline{-2125.962}$	−2125.961	[a]

[a] No stationary value of the energy was achieved.

Table 2. Relative stabilities (in kcal/mole) of the bent, linear and perpendicular structures for Co(acacen) LO_2

L	Bent	Linear	Perpendicular
none	0	4	46
H_2O	0	18	82
CN^-	0	20	72
CO	0	26	80

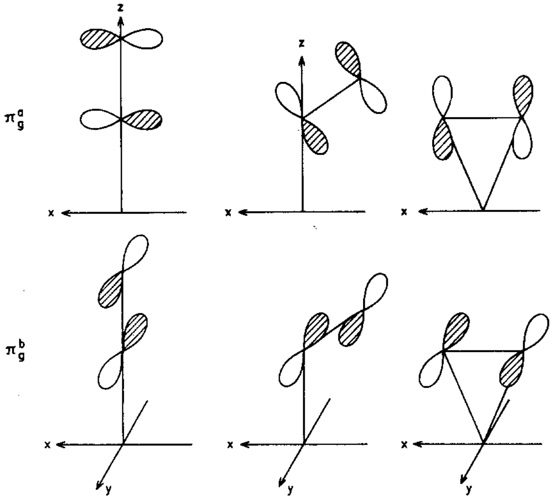
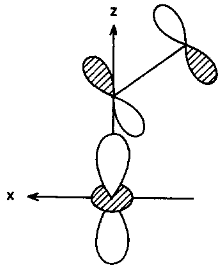


Fig. 1. The orbitals π_g^a and π_g^b of the dioxygen ligand for the three structures linear, bent and perpendicular

corresponding to a charge-transfer Co(III)–O_2^- configuration, in agreement with the conclusions from the ESR studies that the unpaired electron is largely delocalized on the oxygen atom [15, 16]. We have reported in Table 1 the computed energies for the electronic configurations discussed previously [14] and corresponding to the three structures for L = none, H_2O, CN^-, and CO. We have given in Table 2 the relative energies of the three structures as a function of the fifth ligand L.

We first discuss the electronic configuration of the ground state for each structure. The four possible electronic configurations are denoted $(\pi_g^a)^2(\pi_g^b)^1$, $(\pi_g^b)^2(\pi_g^a)^1$, $(\pi_g^a)^2(d_{z^2})^1$ and $(\pi_g^b)^2(d_{z^2})^1$, keeping for π_g^a and π_g^b our previous definition, namely π_g^b made from the $2p_y$ orbitals and π_g^a from a mixture of $2p_x$ and $2p_z$ orbitals, π_g^a and π_g^b are represented in Fig. 1 for the three structures. Since the molecule retains the C_s symmetry (with the x0z plane containing the dioxygen ligand being the plane of symmetry) the notation S_1, S_2, S_3, and A for the four electronic configurations remains appropriate. For the bent structure, the ground state electronic configuration was of the $(\pi_g^a)^2(\pi_g^b)^1$ type [14], a consequence of the fact that the bonding may be described essentially in terms of the interaction 5 between the metal $3d_{z^2}$ orbital and the ligand π_g^a orbital.



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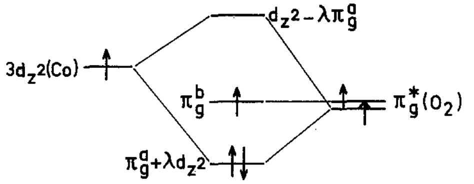
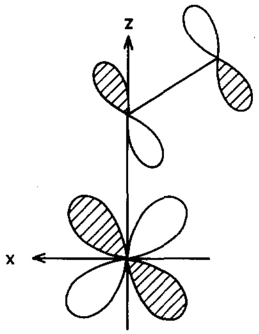


Fig. 2. Simplified interaction diagram and the ground state configuration $(\pi_g^a)^2(\pi_g^b)^1$ for the bent structure of the adduct Co(acacen)LO$_2$

This interaction stabilizes π_g^a and destabilizes $3d_{z^2}$ according to the diagram of Fig. 2 (a similar interaction diagram has been proposed on a qualitative basis for Co(II) and Fe(II) porphyrins [17]). Other interactions such as *6* and *7* between π_g^a or π_g^b and the $3d_{xz}$ or $3d_{yz}$ orbitals are found unimportant [18] (the interaction $3d_{xz}$-π_g^a would be of the $d\pi$-$p\pi$ type for linear coordination, the interaction $3d_{yz}$-π_g^b is a backbonding $d\pi$-$p\pi$ interaction which is probably unfavourable on the basis of the Co(III)–O_2^- configuration) (for a more detailed discussion of the interactions between a metal atom and a diatomic ligand in a linear or bent structure, we refer the reader to the work of Hoffmann *et al.* on the coordination of the nitrosyl ligand [19]).



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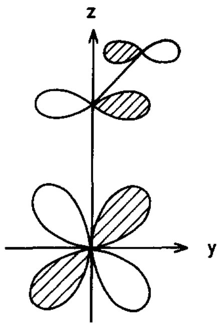

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In the linear structure, the orbitals π_g^a and π_g^b are nearly degenerate (they would be degenerate if the equatorial ligand would be of D_{4h} symmetry instead of C_s [6]). This near-degeneracy may be seen from the fact that the configurations obtained by interchanging π_g^a and π_g^b have nearly equal energies (Table 1). The ground-state

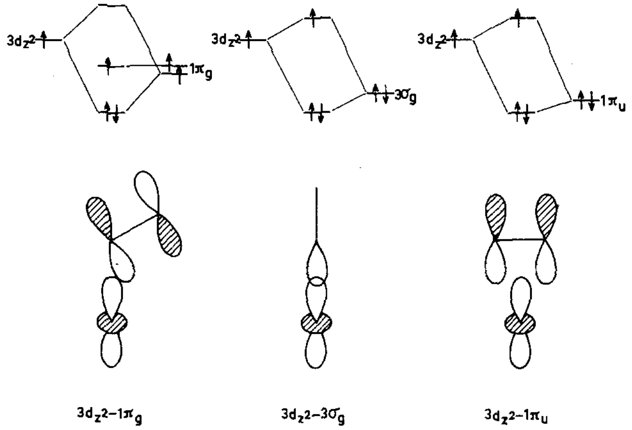

Fig. 3. Simplified interaction diagrams (σ-type interactions only) for the three structures

configuration is either $(\pi_g^a)^2(d_{z^2})^1$ when the fifth ligand is a poor σ-donor (L = none or CO) or $(\pi_g^a)^2(\pi_g^b)^1$ for a good σ-donor (L = CN$^-$). This is easily rationalized on the basis that a good σ-donor raises the energy of the $3d_{z^2}$ orbital [14]. When we turn to the perpendicular structure, the ground-state electronic configuration changes to either $(\pi_g^b)^2(d_{z^2})^1$ for L = none or $(\pi_g^b)^2(\pi_g^a)^1$ for L = CN$^-$ or CO. This points to the fact that although π_g^b and π_g^a are still nearly degenerate, π_g^b is below π_g^a for the perpendicular structure (whereas it was the opposite for the linear and bent structures).

We attempt now to rationalize the relative energies of the three structures in terms of the main metal-ligand interactions. We have considered in Fig. 3 the interactions which are of the σ-type, namely $3d_{z^2}$-$1\pi_g^a$ for the bent structure, $3d_{z^2}$-$3\sigma_g$ for the linear one and $3d_{z^2}$-$1\pi_u^a$ for the perpendicular one (the metal-ligand interactions for the perpendicular structure are similar to the metal-olefin interaction in the Chatt-Dewar scheme [20, 21]). According to perturbation theory, the degree of interaction between two orbitals depends both on their overlap and on the corresponding energy gap denominator [22]. In the bent and linear structures, the overlap terms for the interactions of Fig. 3 are probably comparable but the energy denominator should favor the bent structure since the $1\pi_g$ orbital of the oxygen molecule is well above the $3\sigma_g$ orbital. If we assume that the electronic configurations for the bent and linear structures are respectively $(\pi_g^a)^2(\pi_g^b)^1$ and $(\pi_g^a)^2(d_{z^2})^1$ (which is indeed the case for poor σ donors, L = none and CO of Table 1), then according to Fig. 3 the interaction is stabilizing for two electrons in the bent structure whereas it is stabilizing for two electrons and destabilizing for one electron in the linear structure. Thus the bent structure is expected to be slightly favored over the linear one, in agreement with the results of Table 2[1]. σ-donation by the fifth ligand will destabilize the $3d_{z^2}$ orbital and comparatively more the

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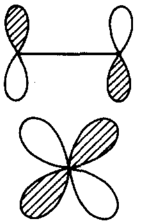
[1] However the situation is opposite for the high-spin state $(\pi_g^a)^1(\pi_g^b)^1(d_{z^2})^1$, with the linear structure slightly more stable than the bent one. This reversal may be understood on the basis of the interaction diagrams of Fig. 3 since one electron has to be promoted from π_g^a into $3d_{z^2}$ in the diagram for the bent structure, whereas for the linear structure only the relative populations of the nearly degenerate orbitals π_g^a and π_g^b are changed.

linear structure with the configuration $(\pi_g^a)^2(d_{z^2})^1$ than the bent one with the configuration $(\pi_g^a)^2(\pi_g^b)^1$. This results in a decrease in the relative stability of the linear structure from L = none to L = CO (Table 2). Introduction of a good σ-donor such as CN^- should make the linear structure more unfavourable, however this results in a change of the ground-state configuration from $(\pi_g^a)^2(d_{z^2})^1$ to $(\pi_g^a)^2(\pi_g^b)^1$.

We turn now to a comparison of the linear and perpendicular structures. Then both the overlap term and the energy denominator are comparable (the $3\sigma_g$ and $1\pi_u$ orbitals are nearly degenerate in the oxygen molecule). With the electronic configuration $(\pi_g)^2(d_{z^2})^1$ (which is the ground state configuration for L = none, with either $\pi_g = \pi_g^a$ for the linear structure or $\pi_g = \pi_g^b$ for the perpendicular one, Table 1), the interaction of Fig. 3 is stabilizing for two electrons and destabilizing for one electron in the two structures. Then, on the basis of the σ-type interaction, both structures should be of comparable stability. However, for a $(\pi_g^a)^2(d_{z^2})^1$ or $(\pi_g^a)^2(\pi_g^b)^1$ configuration, interaction of the $d\pi$-$p\pi$ type between π_g^a and $3d_{xz}$ such as *8* turns out to be quite important in the perpendicular structure and comparatively more important than the corresponding one *9* in the linear structure (the overlap term being larger in *8* than in *9*). Since this is a four-electron destabilizing interaction [23] the perpendicular structure should be destabilized with respect to the linear one. Furthermore, this destabilization of the π_g^a orbital results in π_g^b being more stable than π_g^a, with the ground state configuration being now $(\pi_g^b)^2(d_{z^2})^1$ rather than $(\pi_g^a)^2(d_{z^2})^1$ (case L = none) or $(\pi_g^b)^2(\pi_g^a)^1$ rather than $(\pi_g^a)^2(\pi_g^b)^1$ (case L = CN^-). Destabilization of the perpendicular structure in its ground state configuration $(\pi_g^b)^2(d_{z^2})^1$ or $(\pi_g^b)^2(\pi_g^a)^1$ with respect to the linear structure is explained in a similar way on the basis of a four-electron destabilizing interaction between the bonding orbital π_u^b and the metal orbital $3d_{yz}$.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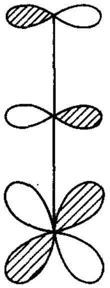
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Note Added in Proof: Calculations for the $[Co(acacen)LO_2]^+$ system with one electron less (hence with the metal-dioxygen unit isoelectronic to the iron(II)dioxygen moiety of hemoproteins) yield very similar results: the most stable structure is the bent one, with the linear and perpendicular structures respectively less stable by 6–10 kcal/mole and 56–67 kcal/mole depending on the fifth ligand.