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Electronic Aspects of Dioxygen Binding to Cobalt-Schiff-Base-Complexes:

An *ab initio* Calculation

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It is shown that there are four possible electronic configurations for the ground-state of the dioxygen complex of Co(acacen)L (with the fifth ligand L = none, H_2O, Imidazole, CN^- and CO). From *ab-initio* calculations with a minimal basis set, close energy values are indeed computed for these four configurations with the lowest one (ground state configuration) corresponding to a charge-transfer configuration Co(III)–O_2^-, in agreement with the results of ESR spectroscopy from the literature. The enthalpy of oxygenation is related to the σ-donor ability of the fifth ligand and to the ease of oxydation of Co(II) to Co(III).

Key word: Schiff base complexes of Co(II)

Co(acacen)L (acacen = N,N′-ethylenebis-(acetylacetoneiminato), L = axial ligand) is known to bind reversibly molecular oxygen [1]. ESR studies on Co(acacen)LO_2 and other related Schiff base complexes of Co(II) indicate that this binding is accompanied by an electron transfer from cobalt to oxygen [1–2]. We report here some preliminary results from *ab-initio* LCAO-MO-SCF calculations[1] for Co(acacen)LO_2[2] with L = none, H_2O, Imidazole (Im), CN^-, and CO (see Fig. 1 for L = Im). We have used the experimental geometries for Co(acacen) [3], H_2O [4], Im [5]. The O_1–O_2, Co–O_1 bond lengths and Co–O_1–O_2 angle, respectively 1.26 Å, 1.86 Å, and 126°, and the orientation of the dioxygen ligand (bissecting the N–Co–N angle) have been taken from Ref. [6] (see also Ref. [7]). The cobalt to axial ligand distances (respectively 2.25 Å, 2.10 Å, 1.96 Å, 1.96 Å for H_2O, Im, CN^-, and CO) correspond to average values from the literature. The interatomic distance in CN^- and CO was taken as 1.15 Å [4].

In the complex the degenerate π_g and $\bar{\pi}_g$ orbitals of the dioxygen molecule are split due to the lower symmetry around the O–O axis [8] and the Co(acacen)LO_2 complexes are experimentally known to have only one unpaired electron [1]. Assuming that this unpaired electron for the Co(acacen)L complex is in the $3d_{z^2}$

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[1] With a (10, 6, 4/7, 3/3) gaussian basis set contracted to a minimal set (except for the 3*d* functions which are split).

[2] The calculations have been carried out with an acacen ligand where the ethylene bridge N–CH_2–CH_2–N was replaced by two NH groups and the methyl substituents with H atoms.

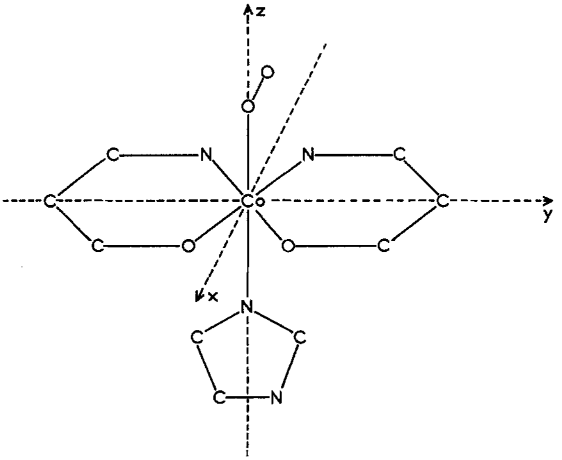

Fig. 1. The Co(acacen)ImO$_2$ molecule

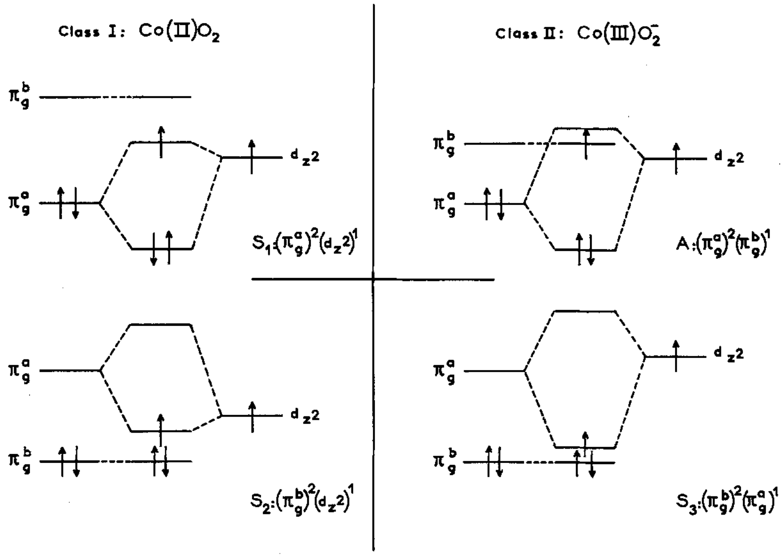

Fig. 2. Possible electronic configurations for a dioxygen adduct Co(acacen)LO$_2$

orbital[3] there are four possible electronic configurations for the ground state of the dioxygen adduct (Fig. 2). These four configurations of which three denoted S_1, S_2, and S_3 belong to the symmetric representation and one denoted A belongs to the antisymmetric one [the plane xOz which includes the dioxygen ligand being a

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[3] For the Co(acacen) complex the state with the configuration $(3d_{x^2-y^2})^2\ (3d_{z^2})^1$ is found at a lower energy than the state with the configuration $(3d_{x^2-y^2})^1\ (3d_{z^2})^1$ (−1864.548 a.u. *vs* −1864.465 a.u.). Since an axial ligand is expected to raise the energy of the $3d_{z^2}$ orbital, the same result would hold probably for the complexes Co(acacen)L. ESR experiments have shown that the unpaired electron is in the $3d_{z^2}$ orbital for Co(acacen) [8] and Co(acacen)L [1].

Table 1. Energy values (in a.u.) for the four possible configurations of Co(acacen)LO$_2$ and computed enthalpies (within brackets, in kcal/mole) for the oxygenation reaction[a]

L	S_1	S_2	S_3	A	$\varepsilon(3d_{z^2})$[b]	ΔH_L[c]
none	-2013.630 $(+12)$	-2013.619 $(+19)$	-2013.611 $(+24)$	-2013.635 $(+9)$	-0.574	–
H_2O	-2089.382 $(+12)$	-2089.373 $(+18)$	-2089.388 $(+8)$	-2089.406 (-3)	-0.533	-16
Im	-2237.589 $(+16)$	-2237.583 $(+19)$	-2237.615 (-1)	-2237.634 (-12)	-0.507	-17
CN^-	-2105.626 $(+16)$	–[d]	-2105.720 (-43)	-2105.735 (-53)	-0.299	-25
CO	-2125.967 $(+15)$	-2125.961 $(+19)$	-2125.982 $(+6)$	-2126.004 (-8)	-0.536	-1

[a] Computed with respect to O$_2$ $^1\Delta$ (the computed stabilization for O$_2$ $^3\Sigma$ with respect to O$_2$ $^1\Delta$ is 37 kcal/mole).

[b] Energy (in a.u.) of $3d_{z^2}$ orbital in Co(acacen)L.

[c] Computed enthalpy (in kcal/mole) of the reaction Co(acacen) + L → Co(acacen)L.

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

symmetry plane for L other than Im (Fig. 1)] correspond formally to the different possibilities regarding:

– the relative order of the π_g^a and π_g^b orbitals of the dioxygen ligand in the complex (π_g^a and π_g^b are related to the π_g and $\bar{\pi}_g$ orbitals of O$_2$, we denote π_g^b the one made from the $2py$ orbitals of the oxygen atoms; π_g^b is antisymmetrical with respect to the symmetry plane $x0z$);

– the relative location of the $3d_{z^2}$ orbital with respect to π_g^a and π_g^b;

– the relative magnitudes of Δ_1, the splitting between π_g^a and π_g^b, and Δ_2 the energy gap between the $3d_{z^2}$ and π_g^a orbitals after interaction. While the configurations S_1 and S_2 correspond to a formal oxydation number of II for Co, A, and S_3 correspond to a charge-transfer configuration Co(III)–O$_2^-$ (we have ruled out configurations $(3d_{z^2})^2(\pi_g)^1$ which would correspond to the opposite charge-transfer Co(I)–O$_2^+$).

We report in the Table 1 the computed energies for each configuration and different axial ligands. A first conclusion is that none of these configurations should be discarded *a priori* since they have comparable energy values. However the A configuration turns to be the most stable one in each case[4]. This is in agreement with the conclusion reached from ESR experiments on oxygen adducts of Co(II) complexes (acacen [1], salen [2], porphyrin [9–10], vitamin B$_{12r}$ [11]) that the unpaired electron is largely delocalized on the oxygen atoms and that these adducts should rather be formulated as Co(III)–O$_2^-$ complexes[5] (see also Ref. [12]). The relatives stabilities of A with respect to S_1 and of S_3 with respect

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[4] Since the three S configurations are close in energy, it may be that configuration interaction may stabilize the lowest S configuration more than the A configuration.

[5] This conclusion should not be affected by the possible effect of configuration interaction, since the lowest S state (except for L = none) is S_3 which corresponds also to a charge-transfer configuration Co(III)–O$_2^-$.

to S_2 (i.e. of the Co(III)O_2^- configuration with respect to the Co(II)O_2 one when keeping the same relative order for the π_g^a and π_g^b orbitals) increase along the series L = none, H_2O, Im, CN^-, hence with the σ-donor ability of the fifth ligand. This is easily rationalized on the basis of the change induced in the orbital energy of the $3d_{z^2}$ orbital as a function of the fifth ligand L in Co(acacen)L (Table 1). We have also reported in the Table 1 the computed enthalpies for the oxygenation reaction. These are also found to vary as both the σ-donor ability of the fifth ligand L and the energy of the $3d_{z^2}$ orbital along the same series. This supports the suggestion of Ibers [10] that "ligands which stabilize Co(III) relative to Co(II) would give systems with the highest affinity for oxygen". Such a correlation has indeed been reported recently by Basolo *et al.* [13] between the equilibrium constants for oxygen adduct formation and the ease of oxydation of Co(II) to Co(III). CO is found to behave as a weak σ donor. Comparatively to the other ligands L, CO shows only little binding with Co(acacen) (Table 1). This is in agreement with the experimental evidence for little if any binding of CO with Co-porphyrindimethyl ester and Coboglobin [14].

It has been suggested [15] that imidazoles have a greater enhancement on the oxygen carrier ability than pyridines through their π donor ability (π-bonding from the π occupied orbitals of the ligand to the appropriate orbitals d_{xz} or d_{yz} of Co). The results of a population analysis show no significant variation in the π-electron population of the imidazole ligand in Co(acacen)ImO_2 compared to Co(acacen)Im. There are three possible reasons for this lack of π-bonding. First there may be no π-interaction for imidazole (pyridine being considered as a π-electron acceptor [16] and imidazole as a better π-donor than pyridine). Next the chosen orientation of the imidazole ring with respect to dioxygen as in Fig. 1 might be inappropriate[6]. Then the π occupied orbitals of imidazole interact through the $3d_{xz}$ orbital only with the filled π_g^a orbital. With the ring in the $x0z$ plane instead of the $y0z$ plane, they would interact through the $3d_{yz}$ orbital with the half filled π_g^b orbital, hence leading to the possibility of π-electron transfer from the imidazole (however, we find no evidence of a π-electron transfer in the S_3 configuration which has an half-filled π_g^a orbital). The last reason may be the use of a minimal basis set which does not give an appropriate description of virtual orbitals, hence of the electron-acceptor properties.

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[6] However a recent cristallographic study of an Iron(II) porphyrin dioxygen complex [17] has shown that there are two types of coordinated dioxygen with the Fe–O–O plane either parallel or perpendicular to the trans axial imidazole plane.

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Note Added in Proof. Configuration interaction between the three *S* configurations does not change the above conclusions (A. Dedieu, to be published).