Binding of Dioxygen to Metal Complexes. The Oxygen Adduct of Co(acacen)

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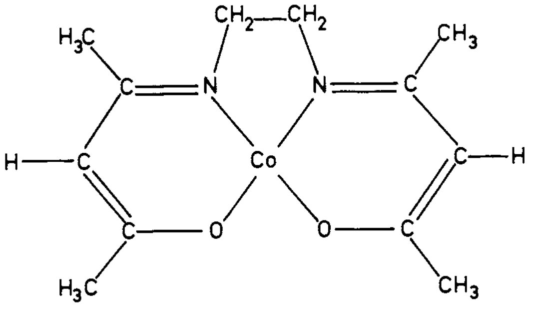
Abstract: Ab initio LCAO-MO-SCF calculations are reported for the oxygen adducts Co(acacen)LO$_2$ (with L a fifth axial ligand chosen for its σ and π donor or acceptor properties, L = none, H$_2$O, CO, CN$^-$, and imidazole). For the bent structure of the CoO$_2$ unit, the ground state corresponds to the electronic configuration $(\pi_g{}^a)^2(\pi_g{}^b)^1$ of the charge-transfer Co^{III}-O$_2{}^-$ type, in agreement with the metal to ligand charge transfer postulated previously on the basis of the EPR spectrum ($\pi_g{}^a$ and $\pi_g{}^b$ denote the dioxygen π_g antibonding orbitals, respectively, symmetrical and antisymmetrical with respect to the CoO$_2$ plane). The Co-O$_2$ bonding may be described essentially in terms of the interaction between the Co 3d$_{z^2}$ orbital and the $\pi_g{}^a$ orbital of dioxygen. The bent structure is found to be slightly more stable than the linear one (by 4-26 kcal/mol depending on the fifth ligand L) but much more stable than the perpendicular one (the Griffith's structure) (by 46-82 kcal/mol depending on the fifth ligand). These preferences are rationalized in terms of the main metal-ligand interactions. The perpendicular structure has a ground-state configuration $(\pi_g{}^b)^2(d_{z^2})^1$ or $(\pi_g{}^b)^2(\pi_g{}^a)^1$ (depending on the fifth ligand) with the $\pi_g{}^b$ orbital of dioxygen now more stable (in terms of orbital energies) than $\pi_g{}^a$. This destabilization of $\pi_g{}^a$ (compared to $\pi_g{}^b$) in the perpendicular structure is a consequence of a stronger dπ-pπ back-bonding. The destabilization of the perpendicular structure compared to the bent or linear structures appears as a consequence of a four-electron destabilizing interaction 3dπ-1π_u. A relationship is found between the calculated enthalpies of oxygenation, the σ donor ability of the fifth ligand, and the ease of oxidation of Co(II) to Co(III) (on the basis of Koopmans' theorem). Calculations for the system with one less electron, namely [Co(acacen)LO$_2$]$^+$, lead to the prediction that for an iron(II) porphyrin the perpendicular structure would be less stable than the bent one by 50 kcal/mol or more.

Synthetic oxygen carriers have attracted the interest of chemists for their possible relationship to the natural oxygen carriers such as hemoglobin and myoglobin. A number of reviews deal with the structure, binding, and reactivity of the dioxygen complexes.[1-6,17] Until recently attempts to prepare dioxygen complexes of Fe(II) have been rather elusive (see ref 7 and references therein) mostly as a consequence of the rapid irreversible autoxidation of Fe(II) to Fe(III). This was especially true of the attempts to isolate a solid dioxygen complex, a requisite to the x-ray crystallographic analysis (cf. below). The situation has been more favorable for synthetic oxygen carriers of Co(II), with the complexes of Co(II) known to interact reversibly with molecular oxygen for a long time.[1] Interest in the synthetic oxygen carriers of cobalt has been stimulated by the finding that coboglobin, the analogue of hemoglobin with cobalt in the place of iron, exhibits also reversible oxygen binding.[8]



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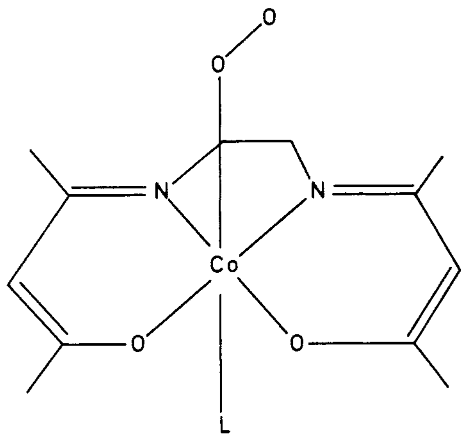

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One of the most studied oxygen carriers of Co(II) is the Co(acacen) complex **1** which binds reversibly dioxygen according to

$$\mathrm{Co(acacen)} + \mathrm{L} + \mathrm{O_2} \rightleftharpoons \mathrm{Co(acacen)LO_2}$$

to give the monomeric oxygen adduct **2**[9] (with L a coordinating base). The Co(acacen) complex is the simplest one among a large series of Schiff base complexes which bind molecular oxygen. Both this complex and the corresponding oxygen adduct are low-spin complexes with $S = \frac{1}{2}$.[9,10] On the basis of the EPR spectra, the unpaired electron appears associated with the 3d$_{z^2}$ orbital in the complex,[10,11] but with the oxygen molecular orbital 1π_g in the oxygen adduct.[10] It has been inferred that the oxygen adduct should be formulated as Co(III)-O$_2{}^-$ rather than Co(II)-O$_2$ complex.[10] EPR studies of a large number of oxygenated Co(II) complexes (including the cobalt porphyrin systems and vitamin B$_{12r}$) have led to a similar formulation.[8,12] Recent arguments against this Co(III)-O$_2{}^-$ formulation[13] have been dismissed.[14] Additional evidence for this formulation has been provided by x-ray photoelectron spectroscopic studies[15,16] and by the analysis of the infrared spectrum.[9] Furthermore, in the related molecule Co(bzacen)(py)O$_2$, the O-O bond length has been found equal to 1.26 Å,[19] a value which is close to the one of 1.28 Å for the superoxide ion O$_2{}^-$ in KO$_2$.[20]

Still there are a number of unanswered questions in connection either with the ease of oxygenation of the Co(II) Schiff-base complexes or with the structure of the dioxygen adducts, for instance (i) the relationship between the nature of the axial and equatorial ligands and the ease of oxygenation, and (ii) the structure, both electronic and geometric, of the Co-O$_2$ unit. Many authors have tried to relate the ease of oxygenation with the nature of the axial ligand, in other words to find if there is some trans effect.[9,10,21,22] An unsolved question is the nature of the axial interaction, whether it results of σ, π, or steric factors? According to Stynes et al. the π donor properties of the axial ligand (such as dimethylformamide, imidazole (Im), and MeIm) play the dominant role in oxygen binding to cobalt;[22] good π donors will strengthen the Co-O_2 bond by *increasing* the electron density available on the cobalt atom for back-bonding to dioxygen. However, according to Walker,[23] a *decrease* in electron density on the cobalt atom produced by back-bonding *from* Co *to* the axial ligand would favor the Co^{III}-O_2^- form of the Co-O_2 bond. Weschler et al.[24] and Carter et al.[21] have pointed out that σ donor effect, with strong σ donors, may play an important role, as well as the steric effects (steric effect occurs probably when the axial ligand is a piperidine molecule[21,22]). Chang and Traylor have suggested that, for the iron porphyrins, the large π basicity of imidazole reinforces the iron to dioxygen back-bonding.[25] However, a dioxygen adduct of the protoheme IX has been shown to exist with an axial ligand (the *tert*-butylamine molecule) of σ-donor character only.[26] With respect to the cis effect, two factors appear important:[21,27-29] (i) the nature of the atoms coordinated to cobalt, i.e., their electronegativity and π-withdrawal properties; and (ii) the delocalization of the π-electron density from the metal over the equatorial ligand.

The structure of the metal-dioxygen unit in the oxygen carriers has a long history.[30-35] Different structural models have been proposed for dioxygen binding, including a linear M-O-O unit **3**,[30] an end-on angular bond **4**,[31-34] and a sideways perpendicular structure **5**.[35] Synthetic oxygen carriers of Fe(II) (in the "picket fence" porphyrin) and of 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°.[7,19,36-38] However, there are a number of experimental data which do not fit with a bent structure and which have been interpreted by postulating a perpendicular structure either for the equilibrium geometry or for a transition state.[39-41] The ESR spectrum of Co(bzacen)(py)O_2 in solution has been interpreted on the basis of a complex containing magnetically equivalent oxygen atoms, a result which is consistent either with a triangular structure **5**, or with a rapid flipping of the O-O group between two bent positions as in **6**, with the sideways structure representing probably a transition state[39] (however, the frozen solution ESR spectrum indicates an asymmetric O_2^- group[12e]). It has been emphasized that the sideways, perpendicular structure corresponds to a formal coordination number of seven for the metal (when the complex is five coordinate in the absence of the dioxygen ligand), a sterically unfavorable situation[7,42,43] (as a consequence of the fact that the Griffith model produces an unfavorably short N-O distance of less than 2.60 Å in oxyhemoglobin[46]).

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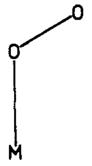

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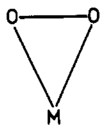

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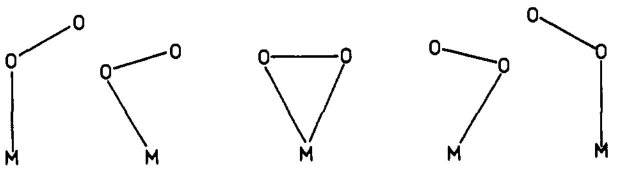

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Previous theoretical work on oxygen carriers has been centered on the oxygenated ferroporphyrin. Zerner et al. carried out extended Hückel calculations for the oxyferroporphine molecule with the linear and perpendicular structures **3** and **5** (with a water molecule as the sixth ligand).[47] They concluded that the linear geometry should be unstable since the $1\pi_g$ orbitals of dioxygen were found below the normally occupied $e_g(d\pi)$ and $b_{2g}(d_{xy})$ orbitals of iron (this would result in a formal structure Fe^{IV}-O_2^{2-} corresponding to an oxidative addition model[48]). They found the oxyferroporphine to be diamagnetic in the perpendicular structure, the degeneracy of the $1\pi_g$ orbital of dioxygen being lifted with the $1\pi_g(xy)$ orbital parallel to the porphyrin plane doubly occupied (the $1\pi_g(z)$ orbital perpendicular to the porphyrin plane mixes heavily with the metal $3d_{xz}$ orbital, an indication of $d\pi$-$p\pi^*$ back-bonding). A similar calculation has been carried out by Loew et al. for the bent structure with an imidazole molecule as the sixth ligand.[18] Extended Hückel calculations by Halton intended for the oxygen adducts of iron and cobalt porphyrins were restricted to the valence orbitals of the iron, oxygen, and nitrogen atoms (nitrogen of the pyrrole groups).[50,51] Heitler-London calculations have been reported for the Fe-O_2 unit in the perpendicular structure.[52] Ab initio GVB and CI calculations have been reported for the FeO_2 unit but the porphyrin was not included explicitly.[53] A semiempirical SCCC-MO calculation has been reported for the dimer μ-superoxo-bis(pentaamminecobalt(III)) cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$.[54] We report here ab initio LCAO-MO-SCF calculations for the oxygen adducts of Co(acacen). Our first goal was to assess the relative stability of the three possible structures for the Co-O_2 unit together with investigating the effect of the fifth axial ligand on the ease of oxygenation.

Calculations

LCAO-MO-SCF calculations have been carried out for the systems Co(acacen), Co(acacen)L (with L = none, H_2O, CO, CN^-, and imidazole), and Co(acacen)LO_2. In order to simplify slightly the calculations, the acacen ligand considered in the calculations differs from **1** by replacing the four methyl groups with hydrogen atoms and the ethylenediamine bridge N-CH_2-CH_2-N with two N-H groups. We believe that such a simplification should not alter significantly the results. In what follows we use the word acacen for this simplified ligand. The fifth ligands L were chosen for their variety of σ- and π-electron donor or acceptor abilities, H_2O being a mderate σ donor and CN^- a good σ donor and CO a poor σ donor and a good π acceptor. Imidazole is a moderate σ donor but its π-electron donor or acceptor character is the matter of some controversy[22,55]. Furthermore the imidazole ligand has some obvious biological significance. The case L = none corresponds to a five-coordinate oxygenated complex but it will be most useful to consider it as one extremity in the scale of σ donors (namely as a very poor σ donor).

For the Co(acacen) system we used the experimental geometry[56] which corresponds to a planar acacen ligand. The choice of axis is the one of Figure 1. The C-H and N-H bond lengths were taken equal to 1.09 and 1.00 Å. The Co(acacen) system has the C_{2v} symmetry. In the systems Co(acacen)L and Co(acacen)LO_2, the acacen ligand has been kept planar with the Co atom in the corresponding plane. This is probably a reasonable assumption in the case of six coordination since in the complex Co(bzacen)(py)(O_2) the Co atom is in the plane of the acacen ligand[19] (in Co(acacen)(py)(O_2) the acacen ligand is slightly folded[36]). This assumption may be more questionable in the case of five coordination since in the complexes Co(acacen)(CH_3)[57] and Co(acacen)(NO)[58] the acacen

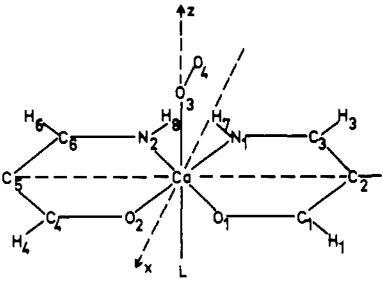

Figure 1. The Co(acacen)LO_2 molecule.

ligand is slightly bent with the Co atom respectively at 0.12 and 0.19 Å above the plane defined by the atoms $N_1N_2O_1O_2$. In the five-coordinate cobalt(II) porphyrin, Co(1-Me-Im)(OEP), the Co atom is 0.16 Å out of the mean plane of the porphyrin toward the imidazole ligand.[59] We have used experimental geometries for the fifth ligands L.[60] For the CN^- and CO ligands we assumed a linear coordination; this is indeed the case for CO in $Fe(C_{22}H_{22}N_4)(NH_2NH_2)(CO)$[63] and Ru(TPP)(EtOH)(CO).[64,68] We use the following Co-L bond lengths: (i) for L = H_2O, Co-O = 2.25 Å on the basis of the values 2.22 Å in Co^{III}(acacen)(H_2O)(vinyl)[71] and 2.23 Å in Co^{II}(bisacetylacetone)$(H_2O)_2$;[72] (ii) for L = imidazole, Co-N = 2.10 Å on the basis of experimental Co-N(sp^2) bond lengths;[19,35,59,73] (iii) for L = CN^-, Co-C = 1.96 Å on the basis of the value in the hexacarboxylic acid obtained by degradation of vitamin B_{12}[73f] (the Co-C bond lengths in $Co(C_{16}N_4H_{32})(CN)_2$ are 1.91 and 1.93 Å[65]); (iiii) for computational reasons we have used for L = CO the same Co-C bond length of 1.96 Å used for L = CN^-.[74] In the oxygen adducts Co(acacen)LO_2 with a bent structure, we have used for the Co-O_2 moiety the experimental geometry of Rodley and Robinson for Co(bzacen)(py)O_2[19] (namely Co-O_3 = 1.86 Å, O_3-O_4 = 1.26 Å, $\angle CoO_3O_4$ = 126°). The dioxygen ligand is in the $x0z$ plane (Figure 1) (which is a symmetry plane for the Co(acacen) system) as found in Co(acacen)(py)O_2.[36] The ligands H_2O and imidazole are in the $y0z$ plane, namely the plane of the ligand is perpendicular to the plane CoO_3O_4. This is indeed the case in the molecules Co(bzacen)(py)O_2[19] and Co(acacen)(py)O_2[36] with the pyridine plane perpendicular to the plane of the CoO_2 moiety.[76] With these assumptions the dioxygen adducts Co(acacen)LO_2 belong to the point group C_s, the plane $x0z$ being the symmetry plane (except for L = Im). For the linear and perpendicular structures of the cobalt-dioxygen unit, we kept the same Co-O_3 and O_3-O_4 bond lengths (namely 1.86 and 1.26 Å), with the Co-O_4 bond length also equal to 1.86 Å in the perpendicular structure. We have also carried some additional calculations for a bent structure with a CoO_3O_4 angle of 153° (namely the average value between the above angle of 126 and 180°) for L = none, H_2O, CN^-, and CO.[77]

Calculations have been carried out with a Gaussian basis set (10,6,4/7,3/3) contracted to [4,3,2/2,1/1] (minimal set except for the 3d functions of Co which are split). The (10,6,4) basis for the Co atom is built from a (9,5,3) basis optimized for Co^{2+} [78] incremented with one s function of exponent 0.20, one p function of exponent 0.25, and one d function of exponent 0.20 (these exponents are chosen so as to give a maximum of radial density about at midlength of the Co-ligand bonds).[79] The (7,3) basis set for first-row atoms is the one of ref 80 and the (3) basis set for H atoms is taken from ref 81. The open-shell treatment was based on the restricted Hartree-Fock formalism with two hamiltonians[82] using the system of programs ASTERIX.[83] Since we are at the SCF level, significant results can be obtained only by comparing systems with the same number of unpaired electrons, in order to keep the correlation error roughly constant.[84]

Table I. SCF Energies (in au) for Different Electronic Configurations of the Co(acacen) Complex

Electronic configuration	
$d_{xz}{}^2d_{yz}{}^2d_{z^2}{}^2d_{x^2-y^2}{}^1$	−1864.465
$d_{yz}{}^2d_{z^2}{}^2d_{x^2-y^2}{}^2d_{xz}{}^1$	−1864.519
$d_{xz}{}^2d_{z^2}{}^2d_{x^2-y^2}{}^2d_{yz}{}^1$	−1864.527
$d_{xz}{}^2d_{yz}{}^2d_{x^2-y^2}{}^2d_{z^2}{}^1$	−1864.548

Table II. The Energy Levels of Co(acacen)L (Closed Shells Only)

Orbital energy, au, L =					
None	CO	H_2O	Im	CN^-	Nature[a]
−0.342	−0.343	−0.325	−0.319	−0.185	$\pi_3 - \pi_3'$
−0.366	−0.361	−0.349	−0.341	−0.189	$\pi_3 + \pi_3'$
−0.479	−0.477	−0.456	−0.445	−0.296	d_{xz}, $\pi_2 + \pi_2'$
−0.514	−0.516	−0.498	−0.492	−0.364	$\pi_2 - \pi_2'$
−0.539	−0.535	−0.512	−0.500	−0.345	d_{yz}, $\pi_1 - \pi_1'$
−0.586	−0.581	−0.535	−0.557	−0.409	$\pi_2 + \pi_2'$, d_{xz}
−0.600	−0.591	−0.581	−0.577	−0.456	$\pi_1 + \pi_1'$
−0.615	−0.611	−0.593	−0.584	−0.456	$\pi_1 - \pi_1'$, d_{yx}

[a] The largest component is given first.

Discussion

The Systems Co(acacen) and Co(acacen)L. The systems Co(acacen) and Co(acacen)L are low-spin (S = ½) complexes of Co(II)d^7 as shown by magnetic measurements and EPR spectra.[9,10] The EPR spectra also indicate that the unpaired electron occupies the d_{z^2} orbital.[9-11] Then the ground state configuration may be written formally as $d_{xz}{}^2d_{yz}{}^2d_{x^2-y^2}{}^2d_{z^2}{}^1$ (with our choice of axis) (no particular significance is attached to the order of filled orbitals throughout). The same ground state configuration has been assigned to a large number of Co(II) Schiff base complexes[85-101] independently of four or five coordination (namely the presence or the absence of a fifth ligand L). However, different configurations have been proposed for the ground state of planar, four-coordinate Co(II) complexes with the unpaired electron either in the d_{yz} orbital (with a ground state configuration $d_{xz}{}^2d_{x^2-y^2}{}^2d_{z^2}{}^2d_{yz}{}^1$)[102-106] or in the $d_{x^2-y^2}$ orbital (with the present choice of axis, then with a ground state configuration $d_{xz}{}^2d_{yz}{}^2d_{z^2}{}^2d_{x^2-y^2}{}^1$).[85,88,100,107,108] The confusion is exemplified for the Co(salen) complex for which all three electronic configurations have been reported for the ground state[85,88-90,105-107] (however, see also ref 91 for the ambiguities in postulating orbital ground states from the spectral data). Since Co(salen) is a $N_2O_2Co(II)$ complex like Co(acacen), we have carried out SCF calculations for different electronic configurations of the Co(II) atom in order to find out the ground state configuration. The results are reported in Table I and indicate a ground state configuration $d_{xz}{}^2d_{yz}{}^2d_{x^2-y^2}{}^2d_{z^2}{}^1$ for the isolated planar molecule. There is a qualitative agreement between the theoretical values from Table I for the energies of the d-d transitions (excitation energies of 4600, 6400, and 18000 cm^{-1}) and the presence of absorption bands in the near-infrared region for related systems.[90,98,108]

We discuss briefly the ground state wave function for the complex Co(acacen) of C_{2v} symmetry. The energy levels of Co(acacen) are reported in Table II. The corresponding molecular orbitals may be considered as built through the interaction of the metal and ligand orbitals.[109] The symmetry properties of the orbitals for the cobalt atom and the acacen ligand are given in Table III. We have sketched in Figure 2 the

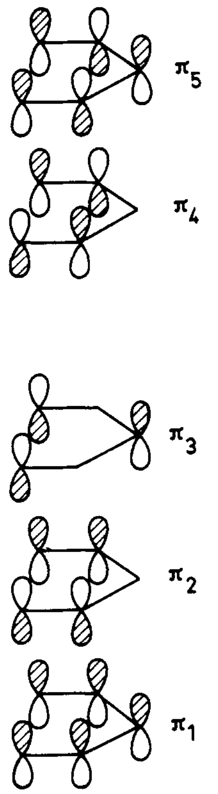

Figure 2. The π orbitals for one-half $[HN(CH)_3O]^-$ of the acacen ligand (the orbitals π_1 to π_3 are occupied).

Table III. The Symmetry Properties of the Cobalt, acacen, and Dioxygen Orbitals (within the C_{2v} and C_s Molecular Point Groups)[a]

	A′		A″	
	A_1	B_2	B_1	A_2
Co	$3d_{x^2-y^2}$ $3d_{z^2}$	$3d_{xz}$	$3d_{xy}$	$3d_{yz}$
acacen (π)		$\pi_i + \pi_i'$		$\pi_i - \pi_i'$
O_2		$3\sigma_g$		
		$\pi_u{}^a$		$\pi_u{}^b$
		$\pi_g{}^a$		$\pi_g{}^b$

[a] The notation $\pi_i \pm \pi_i'$ stands for the symmetrical and unsymmetrical combinations of the π_i orbital on each half of the acacen ligand.

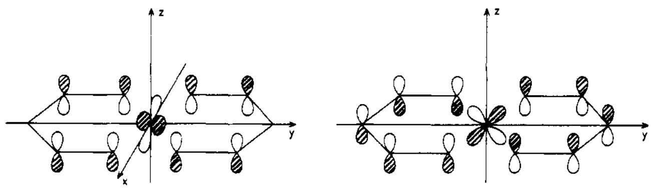

Figure 3. The antibonding combination between $(\pi_2 + \pi_2')$ and $3d_{xz}$ (left) and the bonding combination between $(\pi_1 - \pi_1')$ and $3d_{yz}$ (right).

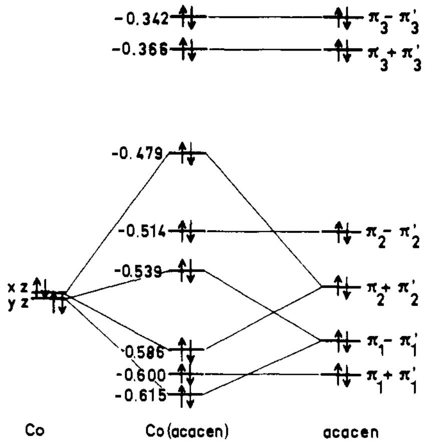

Figure 4. Interaction diagram between the acacen π orbitals and the cobalt $3d_{xz}$ and $3d_{yz}$ orbitals.

π molecular orbitals for one-half of the acacen ligand, namely the system $[HN(CH)_3O]^-$, as given from an independent SCF calculation. Examination of the wave function for Co(acacen) shows essentially two main interactions between the ligand π orbitals and the orbitals $3d_{xz}$ and $3d_{yz}$ of the metal: (i) an interaction between the $3d_{xz}$ orbital and the $\pi_2 + \pi_2'$ acacen orbital as shown in Figure 3 for the antibonding combination; (ii) an interaction between the $3d_{yz}$ orbital and the $\pi_1 - \pi_1'$ acacen orbital as shown in Figure 3 for the bonding combination (we denote $\pi_i \pm \pi_i'$ the symmetrical and antisymmetrical combinations of the π_i orbitals on each half of the acacen ligand). The corresponding interaction diagram for the ligand π orbitals and the metal $3d_{xz}$ and $3d_{yz}$ orbitals is shown in Figure 4. The wave function does not show any interaction between $3d_{xz}$ or $3d_{yz}$ and the empty ligand orbitals $\pi_4 + \pi_4'$ or $\pi_5 - \pi_5'$. This points to the absence of a back-bonding interaction $d\pi(Co) \rightarrow \pi^*$(acacen). We feel that the interactions between the σ orbitals of the equatorial ligand and the metal $3d_{xy}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ orbitals do not deserve any special discussion.

Energy levels based on an INDO calculation have been reported previously for the Co(acacen) complex in relationship with the photoelectron (PE) spectrum.[110] This paper contains several inconsistencies and errors. It is claimed that "all the discussions on the EPR spectrum of Co(acacen) have concluded that the unpaired electron is localized on the d orbitals of cobalt. Therefore from both PE and EPR results it is concluded that the molecular orbital mainly composed of 3d metal orbital and containing the unpaired electron is lower in energy than other molecular orbitals localized on the ligand", the only evidence from the PE spectrum being the fact that the PE spectra of Ni(acacen) and Cu(acacen) were previously interpreted by the same authors by "assuming that the first ionized electrons arise from a molecular orbital localized on the ligand".[111] Furthermore ionization energies are evaluated according to Koopmans' theorem although it is well known that this theorem cannot be used for transition metal complexes and organometallics as shown by previous work both at the ab initio level[113-116] and at the INDO level.[117] Finally it is concluded that the unpaired electron is in the d_{yz} orbital of the Co atom ($4a_2$ orbital with an orbital energy of 12.21 eV according to Tablel of ref 110). Not only is this at variance with our results which place the unpaired electron in the d_{z^2} orbital, but there are according to Figure 2 of ref 110 eight "doubly occupied" molecular orbitals with orbital energies higher than the $4a_2$ orbital. Usually the ground state from SCF calculations is obtained by filling the α and β space orbitals in the order of increasing orbital energies. Although such a situation where the open-shell orbital has a lower orbital energy than a number of closed-shell orbitals cannot be ruled out,[111] further justification would be needed. Furthermore this calculation yields four doubly occupied MO's and one singly occupied MO within the a_2 irreducible representation. Since this representation (Table III) includes only the $3d_{yz}$ orbital of Co and the $(\pi_i - \pi_i')$ orbitals of the acacen ligand (of which only three are doubly occupied for the free ligand) there should be at most four doubly occupied orbitals within this representation (or three doubly occupied and one singly occupied).

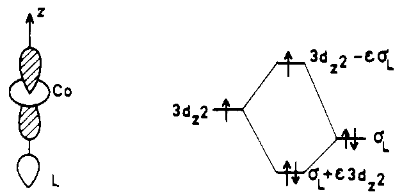

Figure 5. The antibonding combination between the $3d_{z^2}$ orbital of Co and the σ lone pair on the fifth ligand (left) and the destabilization of the $3d_{z^2}$ orbital (right).

Table IV. Orbital Energy ϵ (in au) and Molecular Orbital Expansion for the $3d_{z^2}$ Orbital in Co(acacen)L

L	ϵ	LCAO coefficients[a,b]
None	−0.574	$0.94d_{z^2}{}^1 + 0.14d_{z^2}{}^2 - 0.14(3s)_{Co} + 0.18(4s)_{Co}$
CO	−0.536	$0.95d_{z^2}{}^1 + 0.10d_{z^2}{}^2 - 0.26(2s)_{C_7} - 0.11z_{C_7} - 0.09(3s)_{Co} + 0.14(4s)_{Co}$
H_2O	−0.533	$0.95d_{z^2}{}^1 + 0.12d_{z^2}{}^2 - 0.11(2s)_{O_5} - 0.09z_{O_5} - 0.12(3s)_{Co} + 0.15(4s)_{Co}$
Im	−0.507	$0.95d_{z^2}{}^1 + 0.11d_{z^2}{}^2 - 0.15(2s)_{N_3} - 0.14z_{N_3} - 0.10(3s)_{Co} + 0.14(4s)_{Co}$
CN^-	−0.299	$0.93d_{z^2}{}^1 + 0.10d_{z^2}{}^2 - 0.27(2s)_{C_7} - 0.16z_{C_7} - 0.06(3s)_{Co} + 0.11(4s)_{Co}$

[a] Only the most significant terms in the expansion are reported. [b] The notation d^1 and d^2 refers to the split d functions; C_7, O_5, and N_3 designates the atom of the fifth ligand L which is coordinated to the metal.

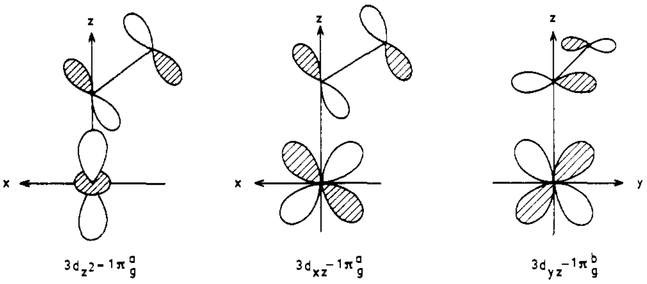

Figure 6. The main metal 3d–dioxygen $1\pi_g$ interactions in the bent structure.

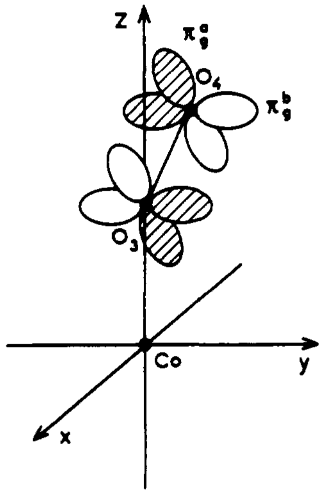

Figure 7. The orbitals $\pi_g{}^a$ and $\pi_g{}^b$ of the dioxygen ligand in the dioxygen adduct.

We limit our discussion of the wave function and energy levels for the five-coordinate Co(acacen)L systems to one specific feature, namely the influence of the fifth ligand L on the orbital energy of the $3d_{z^2}$ orbital. We have reported in Table IV the corresponding orbital energy and molecular orbital expansion. The $3d_{z^2}$ orbital is destabilized by an antibonding interaction with the lone pair of the fifth ligand as represented in Figure 5. This destabilization increases in the series L = none, CO, H_2O, Im, CN^- and may be taken as a measure of the σ-donor ability of the fifth ligand.

The System Co(acacen)LO₂. The Bent Structure. We have reported in Table V the SCF energies for the Co(acacen)LO_2 system with four different structures (linear, bent with a CoOO angle of 126°, bent with a CoOO angle of 153°, and perpendicular). We discuss first the electronic structure of the dioxygen adduct in the bent structure ($\theta = 126°$).

We shall analyze the bonding in the dioxygen adduct in terms of the interactions between the orbitals of the Co(acacen)L system and the orbitals of the dioxygen ligand. It turns out that the bonding, for the bent structure, may be understood on the basis of a small number of interactions which are represented in Figure 6, namely the ones between the $3d_{z^2}$, $3d_{xz}$ and $3d_{yz}$ orbitals of cobalt and the $1\pi_g$ and $1\bar{\pi}_g$ degenerate orbitals of dioxygen.[118] These π_g and $\bar{\pi}_g$ orbitals which are degenerate for the molecule O_2 are no longer equivalent in the complex with a bent structure. We distinguish them through the use of the labels $\pi_g{}^a$ and $\pi_g{}^b$ ($\pi_g{}^a$ is made of $2p_x$ and $2p_z$ orbitals of the oxygen atoms and is symmetrical with respect to the $x0z$ plane, $\pi_g{}^b$ is made of $2p_y$ orbitals and is antisymmetrical with respect to $x0z$, Figure 7).[120] In the limit one may think of the Co–O_2 system as a system of three electrons (namely the unpaired electron from cobalt and the two unpaired electrons from dioxygen) in three orbitals (the $3d_{z^2}$ orbital of Co and the $\pi_g{}^a$ and $\pi_g{}^b$ orbitals of dioxygen). We have emphasized previously[122] that this results in four possible electronic configurations for the low-spin ($S = 1/2$) ground state of the dioxygen adduct depending on the relative occupancy of the three orbitals d_{z^2}, $\pi_g{}^a$, and $\pi_g{}^b$. These four configurations may be classified with respect to both their symmetry properties and the formal oxidation number of the Co atom. For the C_s group which is the molecular point group for L = none, H_2O, CO, and CN^-, three configurations belong to the symmetrical representation A′, namely $(\pi_g{}^a)^2(d_{z^2})^1$ (denoted S_1), $(\pi_g{}^b)^2(d_{z^2})^1$ (denoted S_2), and $(\pi_g{}^b)^2(\pi_g{}^a)^1$ (denoted S_3), while the configuration $(\pi_g{}^a)^2(\pi_g{}^b)^1$ (denoted A) belongs to the antisymmetrical representation A″. The configurations S_1 and S_2 correspond to a formal oxidation number of II for Co while A and S_3 correspond to a charge transfer configuration Co^{III}–O_2^- (we have ruled out on intuitive grounds the configurations $(3d_{z^2})^2(\pi_g)^1$ which correspond to the opposite charge-transfer configuration Co^I–O_2^+, since they should be energetically unfavorable).

According to the results of Table V, the A configuration $(\pi_g{}^a)^2(\pi_g{}^b)^1$ is the ground state configuration for the bent structure with $\theta = 126°$ whatever the fifth ligand L.[123,124] This ground state configuration follows from the fact that the bonding may be described essentially in terms of the interaction of Figure 6 between the Co $3d_{z^2}$ orbital and the dioxygen $\pi_g{}^a$ orbital. This interaction stabilizes $\pi_g{}^a$ and destabilizes $3d_{z^2}$ as shown in Figure 8, then filling the molecular orbitals of Figure 8 in the order of increasing energy leads to a ground state configuration $(\pi_g{}^a)^2(\pi_g{}^b)^1$ of the Co^{III}–O_2^- type,[125] thus providing a rationale for the metal to ligand charge transfer postulated previously on the basis of the EPR spectrum. An interaction diagram similar to the one of Figure 8 has been proposed previously on a qualitative basis for the oxygen adduct of cobalt(II) and iron(II) porphyrins.[69] Examination of the wave function shows that the other interactions of Figure 6 are rather unimportant (the interaction $3d_{yz} - 1\pi_g{}^b$ would be a back-bonding interaction of the dπ–pπ type and is probably unfavorable on the basis of the Co^{III}–O_2^- ground state configuration). The degree of the interaction between $3d_{z^2}$ and $\pi_g{}^a$ decreases along the series L = none, H_2O, Im, and CN^-

Table V. Energy Values (in au) for the Four Possible Electronic Configurations ($S = \frac{1}{2}$) and the Three Geometric Structures of Co(acacen)LO$_2$ (Underlined Values Correspond to the Ground State for Each Geometric Structure)

		Geometric structure			
			Bent		
Fifth ligand L	Electronic configuration	Linear	$\theta = 153°$	$\theta = 126°$	Perpendicular
None	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	−2013.583	−2013.608	$\underline{-2013.635}$	−2013.508
	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	−2013.584	−2013.593	−2013.611	−2013.497
	$(\pi_g{}^a)^2(d_{z^2})^1$	$\underline{-2013.628}$	$\underline{-2013.627}$	−2013.630	−2013.521
	$(\pi_g{}^b)^2(d_{z^2})^1$	$\underline{-2013.627}$	−2013.625	−2013.619	$\underline{-2013.561}$
H$_2$O	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	−2089.360	$\underline{-2089.380}$	$\underline{-2089.406}$	−2089.274
	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	−2089.359	−2089.370	−2089.388	$\underline{-2089.275}$
	$(\pi_g{}^a)^2(d_{z^2})^1$	$\underline{-2089.377}$	−2089.378	−2089.382	−2089.270
	$(\pi_g{}^b)^2(d_{z^2})^1$	$\underline{-2089.376}$	−2089.377	−2089.373	*a*
CN$^-$	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	$\underline{-2105.703}$	$\underline{-2105.715}$	$\underline{-2105.735}$	−2105.619
	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	$\underline{-2105.701}$	−2105.709	−2105.720	$\underline{-2105.621}$
	$(\pi_g{}^a)^2(d_{z^2})^1$	−2105.620	−2105.621	−2105.626	−2105.517
	$(\pi_g{}^b)^2(d_{z^2})^1$	−2105.619	*a*	*a*	−2105.578
CO	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	−2125.958	$\underline{-2125.974}$	$\underline{-2126.004}$	−2125.873
	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	−2125.956	−2125.964	−2125.982	$\underline{-2125.877}$
	$(\pi_g{}^a)^2(d_{z^2})^1$	$\underline{-2125.962}$	−2125.963	−2125.967	−2125.860
	$(\pi_g{}^b)^2(d_{z^2})^1$	$\underline{-2125.962}$	*a*	−2125.961	*a*

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

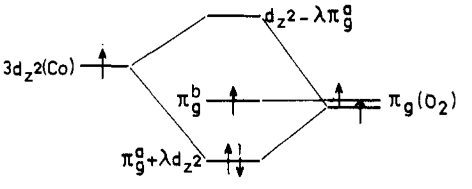

Figure 8. Simplified interaction diagram and the ground state configuration for the bent structure of the adduct Co(acacen)LO$_2$.

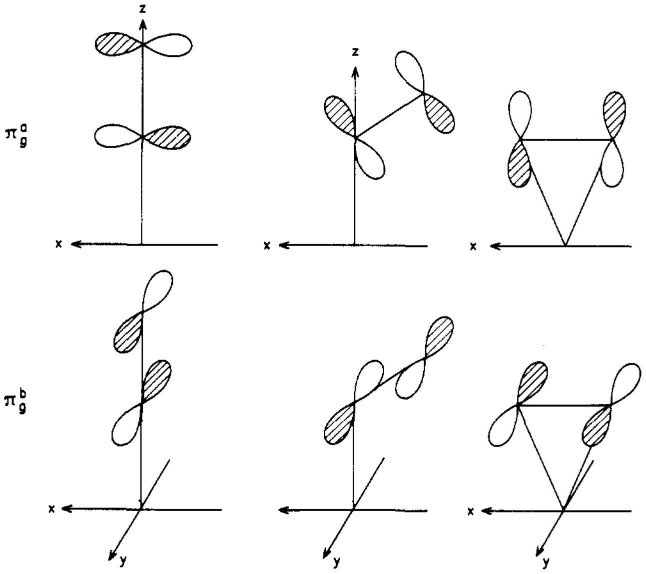

Figure 9. The orbitals $\pi_g{}^a$ and $\pi_g{}^b$ of the dioxygen ligand for the three structures linear, bent, and perpendicular.

as a consequence of the destabilization of 3d$_{z^2}$ with the σ donor ability of the fifth ligand.[13]

From Table V one may see that the relative stability of the Co^{III}-O$_2$$^-$ configurations (A and S$_3$) compared to the Co^{II}-O$_2$ configurations (S$_1$ and S$_2$) increases along the series L = none, H$_2$O, CO, and CN$^-$, id est with the σ-donor ability of the fifth ligand L. This is easily understood on the basis of the destabilization of the 3d$_{z^2}$ orbital with an increasing donor ability of the fifth ligand, the 3d$_{z^2}$ orbital being occupied only in the configuration S$_1$ and S$_2$.

Comparison of the results of Table V for $\theta = 126$ and 153° shows that the structure with $\theta = 126°$ is favored (we have not attempted to locate the minimum of the energy as a function of θ). The ground state configuration for $\theta = 153°$ is the A configuration for L = H$_2$O, CO, and CN$^-$ but the S$_1$ configuration for L = none. Since this situation for $\theta = 153°$ is somewhat intermediate between the cases $\theta = 126$ and 180° (linear structure, cf. below), this will be easily understood once the linear structure has been considered.

There is enough experimental evidence that the dioxygen adduct of Co(acacen) is a low-spin ($S = \frac{1}{2}$) system.[9,10] However, we have also carried out some SCF calculations for the high-spin ($S = \frac{3}{2}$) configuration $(\pi_g{}^a)^1(\pi_g{}^b)^1(d_{z^2})^1$ for L = none and CN$^-$. The results are reported in Table VI. Comparison with the SCF energies of Table V for the low-spin systems would yield for the bent structure the high-spin configuration as the most stable one in the absence of fifth ligand but with a change to the low-spin configuration in the case of a high-field ligand such as CN$^-$ (again as a consequence of the strong destabilization of the 3d$_{z^2}$ orbital). Since the error due to the correlation energy probably favors the high-spin configuration, not much significance should be attached to the fact that the calculation yields a high-spin configuration as the ground state for L = none.

Table VI. Energy (in au) of the High-Spin ($S = \frac{3}{2}$) Configuration $(\pi_g{}^a)^1(\pi_g{}^b)^1(d_{z^2})^1$ for the Three Geometric Structures of Co(acacen)LO$_2$ (L = none or CN$^-$)

	Geometric structure		
Fifth ligand	Linear	Bent ($\theta = 126°$)	Perpendicular
None	−2013.699	−2013.691	−2013.614
CN$^-$	−2105.693	−2105.685	−2105.624

The Linear Structure. In the linear structure the orbitals $\pi_g{}^a$ and $\pi_g{}^b$ (Figure 9) are nearly degenerate (they would be degenerate for L = none, CO, or CN$^-$ if the equatorial ligand would be of D_{4h} symmetry instead of C_{2v}). Their near degeneracy is evidenced from the nearly equal energies associated

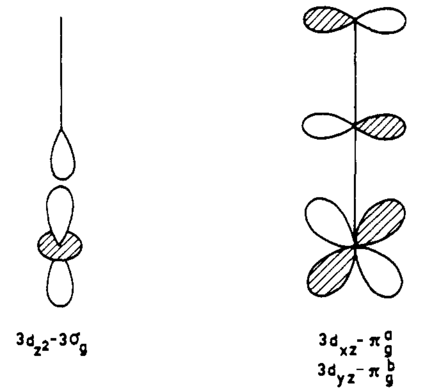

Figure 10. The metal-dioxygen interactions in the linear structure.

Table VII. Relative Stabilities (in kcal/mol) 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

in Table V with electronic configurations which differ only by interchanging $\pi_g{}^a$ and $\pi_g{}^b$ (like the configurations $(\pi_g{}^a)^2(\pi_g{}^b)^1$ and $(\pi_g{}^b)^2(\pi_g{}^a)^1$, or $(\pi_g{}^a)^2(d_{z^2})^1$ and $(\pi_g{}^b)^2(d_{z^2})^1$). The ground state configuration is $(\pi_g{}^a)^2(d_{z^2})^1$ (or the near-degenerate configuration $(\pi_g{}^b)^2(d_{z^2})^1$) for L = none, H_2O, and CO, namely for poor σ donors, but changes to $(\pi_g{}^a)^2(\pi_g{}^b)^1$ (or the near degenerate one $(\pi_g{}^b)^2(\pi_g{}^a)^1$) for a good σ donor. Again this change may be rationalized on the basis that a good σ donor raises the energy of the $3d_{z^2}$ orbital. One may ask for the reasons of the difference in the ground state configurations for the bent and the linear structures (with L = none, H_2O, and CO). Bonding in the linear structure may be described in terms of the interactions $3d_{z^2}$–$3\sigma_g$, $3d_{xz}$–$\pi_g{}^a$, and $3d_{yz}$–$\pi_g{}^b$ of Figure 10. The interaction $3d_{z^2}$–$3\sigma_g$ destabilizes the $3d_{z^2}$ orbital but probably less than the $3d_{z^2}$–$1\pi_g{}^a$ interaction in the bent structure[126] since the $1\pi_g$ orbital is well above the $3\sigma_g$ orbital in the oxygen molecule[127,128] (Figure 11). Then the orbital $3d_{z^2}$ is expected to be more stable in the linear structure than in the bent one. $\pi_g{}^a$ and $\pi_g{}^b$ are destabilized in the linear structure through an antibonding interaction with $3d_{xz}$ and $3d_{yz}$, whereas $\pi_g{}^a$ was stabilized in the bent structure (Figure 8). Then on going from the bent to the linear structure, $\pi_g{}^a$ should be destabilized, $\pi_g{}^b$ being weakly destabilized, whereas $3d_{z^2}$ should be stabilized. This gives some tentative clue to the change in the ground state configuration which certainly depends on a subtle balance of effects (the importance of the interelectronic repulsion in determining the ground state configuration cannot be minimized; this factor should favor the $(\pi_g{}^a)^2(d_{z^2})^1$ configuration over the $(\pi_g{}^a)^2(\pi_g{}^b)^1$ one since the latter has three electrons in the same region of space).

We have reported in Table VII the relative energies of the three structures as a function of the fifth ligand L. The linear structure comes rather close to the bent one for L = none, the difference in stability being only 4 kcal/mol for a five-coordinate adduct but increasing to 18–26 kcal/mol for a six-coordinate adduct. We have previously interpreted[126] on the basis of the main interaction of the σ type the slight preference for the bent structure. We have already mentioned that, for the interactions of Figure 11, the energy denominator will favor the bent structure since the $1\pi_g$ orbital of the oxygen molecule is well above the $3\sigma_g$ orbital. Furthermore, on the basis of the ground-state electronic configurations $(\pi_g{}^a)^2(\pi_g{}^b)^1$ and $(\pi_g{}^a)^2(d_{z^2})^1$ respectively for the bent and linear structures (as found in the case of weak or moderate σ donors L = none, H_2O, and CO), the interaction of Figure 11 for the bent structure is stabilizing for two electrons whereas the one for the linear structure is stabilizing for two electrons but destabilizing for a third one. Thus the bent structure is expected to be slightly favored over the linear one, in agreement with the SCF results of Table V. The destabilization of the linear structure increases from L = none to L = H_2O or CO (Table VII), i.e., when the σ-donor character of the fifth ligand increases. This is a consequence of the destabilization of the $3d_{z^2}$ orbital which is occupied in the linear structure but empty in the bent one (Figure 11). This destabilization should reach a maximum for L = CN^-, but then the linear structure prefers to adopt the $(\pi_g{}^a)^2(\pi_g{}^b)^1$ configuration rather than the $(\pi_g{}^a)^2(d_{z^2})^1$ configuration which becomes energetically unfavorable.

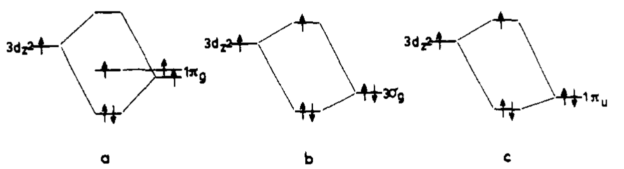

Figure 11. Simplified interaction diagrams (σ-type interactions only) for the three structures: (a) bent; (b) linear; (c) perpendicular.

The Perpendicular Structure. On the basis of the interactions of the σ type of Figure 11 (with the $3d_{z^2}$–$1\pi_u$ interaction 7 for the perpendicular structure), a comparable stability is expected for the linear and perpendicular structures, since both the overlap term and the energy denominator are comparable (the $3\sigma_g$ and $1\pi_u$ orbitals are near degenerate in the oxygen molecule) and in both cases the interaction is stabilizing for two electrons and destabilizing for a third one (we consider the electronic configuration $(\pi_g)^2(d_{z^2})^1$ which corresponds to the ground state for L = none with $\pi = \pi_g{}^a$ for the linear structure and $\pi = \pi_g{}^b$ for the perpendicular one). However, an essential feature in the perpendicular structure is the relative importance, compared to the linear and bent cases, of the interactions of the type dπ–pπ. There are two important interactions of this type, the $3d_{xz}$–$1\pi_g{}^a$ interaction and the $3d_{yz}$–$1\pi_u{}^b$ interaction (Figure 12). Evidence for these interactions comes from the analysis of the wave functions and we have reported in Tables VIII and IX the LCAO expansions for the corresponding molecular orbitals. It is obvious on the basis of overlap consideration that the interaction $3d_{xz}$–$1\pi_g{}^a$ should be much smaller in the linear structure (Figure 10) than in the perpendicular one (Figure 12) as may be seen from Table VIII. These dπ–pπ interactions are represented in Figure 13 with the following implications: (i) $\pi_g{}^a$ is destabilized with respect to $\pi_g{}^b$ and this gives the clue to the ground state configuration $(\pi_g{}^b)^2(d_{z^2})^1$ or $(\pi_g{}^b)^2(\pi_g{}^a)^1$ for the perpendicular structure: (ii) the $3d_{yz}$–$1\pi_u{}^b$ interaction is a four-electron destabilizing interaction which represents the main factor for the large destabilization of the perpendicular structure (Table VII).

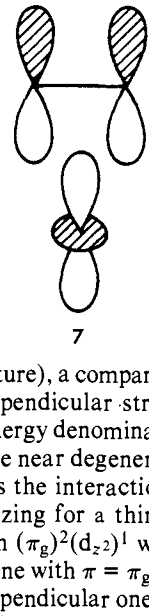

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Table VIII. The $3d_{xz}$–$\pi_g{}^a$ Interaction for Co(acacen)O_2

Geometric structure	Electronic configuration	Molecular orbital	LCAO expansion[a,b]
Perpendicular	$(\pi_g{}^a)^2(d_{z^2})^1$	$\pi_g{}^a - d_{xz}$	$-0.43zO_3 + 0.43zO_4 - 0.45d_{xz}{}^1 - 0.06d_{xz}{}^2$
		$d_{xz} + \pi_g{}^a$	$-0.56d_{xz}{}^1 - 0.09d_{xz}{}^2 + 0.44zO_3 - 0.41zO_4$
	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	$\pi_g{}^a$	$-0.62zO_3 + 0.74zO_4 - 0.12d_{xz}{}^1 + 0.07d_{xz}{}^2$
		d_{xz}	$-0.74d_{xz}{}^1 - 0.06d_{xz}{}^2 - 0.10zO_3 - 0.32zO_4$
Linear	$(\pi_g{}^a)^2(d_{z^2})^1$	$\pi_g{}^a$	$0.68xO_3 - 0.63xO_4 - 0.14d_{xz}{}^1 - 0.02d_{xz}{}^2$
		d_{xz}	$0.66d_{xz}{}^1 + 0.10d_{xz}{}^2 - 0.19xO_3 + 0.15xO_4$
	$(\pi_g{}^a)^2(\pi_g{}^b)^1$	$\pi_g{}^a$	$0.78xO_3 - 0.75xO_4 + 0.10d_{xz}{}^1 + 0.07d_{xz}{}^2$
		d_{xz}	$-0.92d_{xz}{}^1 - 0.10d_{xz}{}^2 - 0.09xO_3 - 0.02xO_4$

[a] Only the most significant terms in the expansion are reported. [b] The notation d^1 and d^2 refers to the split d functions.

Table IX. The $3d_{yz}$–$\pi_u{}^b$ Interaction for Co(acacen)LO_2 in the Perpendicular Structure

Fifth ligand	Electronic configuration (ground state)	Molecular orbital	LCAO expansion[a]
None	$(\pi_g{}^b)^2(d_{z^2})^1$	$\pi_u{}^b$	$-0.49yO_3 - 0.49yO_4 - 0.19d_{yz}{}^1 - 0.03d_{yz}{}^2$
		d_{yz}	$-0.69d_{yz}{}^1 - 0.11d_{yz}{}^2 + 0.25yO_3 + 0.29yO_4$
H_2O	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	$\pi_u{}^b$	$+0.35yO_3 + 0.37yO_4 - 0.38d_{yz}{}^1 - 0.02d_{yz}{}^2$
		d_{yz}	$+0.76d_{yz}{}^1 + 0.10d_{yz}{}^2 + 0.13yO_3 + 0.13yO_4$
CN^-	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	$\pi_u{}^b$	$-0.42yO_3 - 0.44yO_4 + 0.47d_{yz}{}^1 + 0.03d_{yz}{}^2$
		d_{yz}	$+0.81d_{yz}{}^1 + 0.10d_{yz}{}^2 + 0.21yO_3 + 0.21yO_4$
CO	$(\pi_g{}^b)^2(\pi_g{}^a)^1$	$\pi_u{}^b$	$+0.42yO_3 + 0.43yO_4 - 0.38d_{yz}{}^1 - 0.01d_{yz}{}^2$
		d_{yz}	$+0.82d_{yz}{}^1 + 0.09d_{yz}{}^2 + 0.14yO_3 + 0.15yO_4$

[a] Only the most significant terms in the expansion are reported. ($\pi_u{}^b$ represents the bonding combination for L = none and the antibonding combination for L = H_2O, CO, and CN^-.)

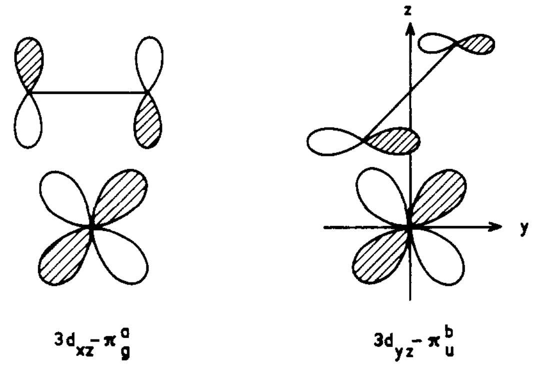

Figure 12. The $d\pi$–$p\pi$ type interactions $3d_{xz}$–$\pi_g{}^a$ and $3d_{yz}$–$\pi_u{}^b$ in the perpendicular structure.

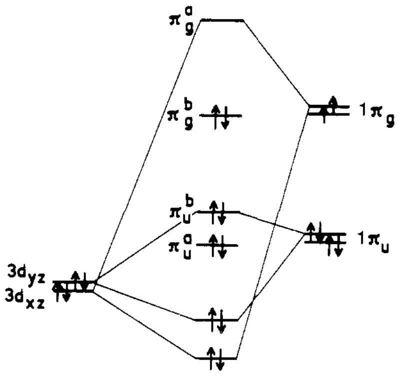

Figure 13. $d\pi$–$p\pi$ interaction diagram in the perpendicular structure.

The Population Analysis. We have reported in Tables X and XI the gross atomic populations and some orbital populations (limited to the orbitals of cobalt and oxygen) as given by the population analysis[130] for the ground state wave function of the bent structure. Although these numbers have senso strictu no physical meaning, they provide some additional evidence for the above analysis of the bonding.

There is a marked difference in the results from the population analysis according to the nature of the ground state configuration either of the type Co^{II}-O_2 (configurations S_1 and S_2) or of the type $Co^{III}O_2{}^-$ (configurations S_3 and A). The difference is felt not so much on the charge of the Co atom, in the range 25.70 to 25.83 for the charge-transfer configurations vs. a charge of 25.94 for the Co^{II}-O_2 configurations, but rather far away from the formal oxidation numbers of 2 and 3. The difference appears mostly at the level of the dioxygen ligand with a formal negative charge between 0.44 and 0.64 for the Co^{III}-$O_2{}^-$ configurations but with a formal charge close to zero for the configurations Co^{II}-O_2. It is found that much of the electron drift to the oxygen ligand comes from the acacen ligand which behaves in some way like an electron tank (the total charge of the acacen ligand varies between 74.77 and 75.12). A sizable fraction of the formal charge on the dioxygen ligand is found on the distal oxygen atom O_4, a factor which certainly plays a role in the formation of 2:1 complexes and in the process of metal oxidation through a proton attachment to the terminal oxygen.[7] In the bent structure the charge on the terminal oxygen atom increases with the σ-donor ability of the fifth ligand.

The absence of $d\pi$–$p\pi$ back-bonding from Co to dioxygen in the bent structure is shown by the values, close to two, found for the populations of the d_{xz} and d_{yz} orbitals (Table XI). The populations of the $3d_{z^2}$ and $4p_z$ orbitals increase with the σ-donor ability of the fifth ligand in the bent structure; the same trend is already apparent in the Co(acacen)L system.[131] The population of the $3d_{z^2}$ orbital decreases from a value of 1.00–1.14 in the Co(acacen)L system to a value of 0.52–0.67 in the oxygen adduct, a consequence of the electron transfer from cobalt to dioxygen.

The Enthalpies of Oxygenation and the Electronic Rearrangement upon Oxygenation. We have reported in Table XII

Table X. Gross Atomic Populations for the Ground State of Co(acacen)LO$_2$ (Linear and Bent Structures)

Geometry	Fifth ligand	Electronic configuration	Co	acacen	L	O$_3$	O$_4$	O$_3$ + O$_4$
Linear	None	$(\pi_g^a)^2(d_{z^2})^1$	25.94	75.08		8.03	7.94	15.97
	H$_2$O	$(\pi_g^a)^2(d_{z^2})^1$	25.94	75.12	9.93	8.03	7.95	15.98
	CN$^-$	$(\pi_g^a)^2(\pi_g^b)^1$	25.79	74.95	13.63	8.42	8.22	16.64
	CO	$(\pi_g^a)^2(d_{z^2})^1$	25.94	75.06	14.01	8.03	7.95	15.98
Bent	None	$(\pi_g^a)^2(\pi_g^b)^1$	25.75	74.80		8.29	8.15	16.44
	H$_2$O	$(\pi_g^a)^2(\pi_g^b)^1$	25.70	74.90	9.90	8.34	8.16	16.50
	CN$^-$	$(\pi_g^a)^2(\pi_g^b)^1$	25.83	74.95	13.64	8.36	8.21	16.57
	CO	$(\pi_g^a)^2(\pi_g^b)^1$	25.82	74.77	13.94	8.32	8.15	16.47

Table XI. Orbital Populations for the Ground State of Co(acacen)LO$_2$ (Bent Structure)

Fifth ligand	Co									O$_3$				O$_4$			
	d$_{z^2}$	d$_{xz}$	d$_{yz}$	d$_{x^2-y^2}$	d$_{xy}$	4s	4p$_x$	4p$_y$	4p$_z$	s	p$_x$	p$_y$	p$_z$	s	p$_x$	p$_y$	p$_z$
None	0.54	2.00	2.04	1.95	0.50	0.26	0.17	0.18	0.11	3.77	1.40	1.78	1.34	3.87	1.43	1.20	1.62
H$_2$O	0.52	2.00	2.04	1.95	0.48	0.25	0.16	0.17	0.14	3.77	1.43	1.74	1.40	3.87	1.43	1.24	1.64
CN$^-$	0.67	1.98	2.03	1.95	0.46	0.23	0.15	0.16	0.20	3.76	1.42	1.74	1.45	3.86	1.45	1.23	1.67
CO	0.63	1.98	2.03	1.95	0.51	0.22	0.17	0.18	0.13	3.76	1.41	1.76	1.38	3.87	1.43	1.21	1.64

Table XII. Calculated Enthalpies of Oxygenation ΔH (in kcal/mol)

L	Energy of Co(acacen)L, au	ΔH^a	$q(\text{Co})^b$	$\epsilon(3d_{z^2})^c$
None	−1864.548	+9	25.94	−0.574
H$_2$O	−1940.300	−3	25.93	−0.533
CO	−1976.890	−8	25.92	−0.536
Im	−2088.513	−12	25.90	−0.507
CN$^-$	−1956.550	−53	25.94	−0.299

[a] Calculated with respect to O$_2$($^1\Delta$) ($E = -149.1014$ au) (O$_2$($^3\Sigma$) is calculated to be 37 kcal/mol more stable than O$_1$($^1\Delta$) vs. an experimental stabilization of 23 kcal/mol[138]). [b] Charge of the Co atom in the Co(acacen)L system. [c] Orbital energy (in au) of the open-shell orbital (3d$_{z^2}$ orbital) in the Co(acacen)L system.

Table XIII. Population of the π Orbitals of Imidazole in Co(acacen)Im and Co(acacen)ImO$_2$

	Electronic configuration	
Co(acacen)Im		6.016
Co(acacen)ImO$_2$	S$_1$	6.006
	S$_2$	6.005
	S$_3$	6.003
	A	6.004

the calculated enthalpies of oxygenation. We do not put much significance on their absolute values but rather on their trend (to minimize the error due to the correlation energy, we have calculated the enthalpies of oxygenation with respect to O$_2$($^1\Delta$)). The enthalpy of oxygenation increases along the series L = none, H$_2$O, CO, Im, and CN$^-$, then roughly like the σ-donor ability of the fifth ligand. However, no relationship is found with the charge of the Co atom in the Co(acacen)L system (Table XII). A relationship does emerge with the orbital energy of the 3d$_{z^2}$ orbital (Table XII). Since the orbital energy is equal to the corresponding ionization potential according to Koopmans' theorem,[132,133] this points to a relationship between the ease of oxygenation and the ease of oxidation. Ibers postulated that "ligands which stabilize Co(III) relative to Co(II) would give systems with the highest affinity for oxygen".[22] Linear correlations have been found by Basolo et al. for cobalt chelates between the equilibrium constants for oxygen adduct formation and the ease of oxidation of Co(II) to Co(III) as measured by cyclic voltammetry.[21,134]

The role of axial ligands which are either π donor or π acceptor in the oxygenation reaction has been a matter of controversy.[22,23,25] For the CO ligand the population analysis does not show any π back-bonding; however, such a back-bonding would be rather unexpected on the basis of a formal oxidation number of III for the Co atom in the ground state configuration. π-donor ability has been postulated for the imidazole ligand.[22,25] We have reported in Table XIII the results of the population analysis for the imidazole ligand. This shows no significant donor or acceptor properties at the π level (the π orbitals are made of the p$_x$ basis functions with our choice of axis). On this basis, it appears that the imidazole ligand behaves as a pure σ donor. We cannot rule out the possibility that a more refined calculation would lead to a different conclusion (this might be the case for the π-acceptor property since a minimal basis set calculation may yield a poor description of the virtual orbitals). The absence of π donation from the imidazole ligand might be related to the choice of an unfavorable geometry. It is expected that π donation will occur from the π orbitals of imidazole to one (empty or half-filled) π^* orbital of dioxygen through the d$_\pi$ orbitals (d$_{xz}$ or d$_{yz}$) of cobalt. With our present choice of geometry (the imidazole ligand being in the $y0z$ plane), the π orbitals of imidazole interact with d$_{xz}$ which is filled and d$_{xz}$ interact with π_g^a which is also filled in the ground state, thus preventing electronic transfer from imidazole. However we feel that the lack of π transfer is not a mere consequence of the relative orientation of the two ligands dioxygen and imidazole. The S$_3$ configuration $(\pi_g^b)^2(\pi_g^a)^1$ does not show any π transfer from imidazole (Table XIII) although the half-filled orbital π_g^a could accommodate some π-electron transfer. Moreover it has been pointed out that a bent structure for a metal-diatomic unit represents an unfavorable situation for dπ–pπ back-bonding.[69,119] Although the situation might be more favorable with the dioxygen and imidazole ligands in the same plane, it is doubtful that the above conclusions would be changed. A strong argument is provided by the experimental structure of a "picket fence" porphyrin with the two possible orientations of the imidazole ligand, either coplanar or perpendicular to the dioxygen ligand.[42] Although a definite answer will probably require more accurate calculations, we believe that the π-electron donor or acceptor ability of the imidazole ligand has possibly been over emphasized.

Table XIV. The Change in the Atomic Charges upon Oxygenation of the Co(acacen) Molecule

Fifth ligand L	Co	acacen	L	O_2	ΣH[a]
None	−0.18	−0.26		+0.44	−0.14
H_2O	−0.23	−0.24	−0.03	+0.50	−0.15
CO	−0.10	−0.29	−0.08	+0.47	−0.14
Im	−0.14	−0.28	−0.07	+0.49	−0.14
CN^-	−0.11	−0.30	−0.16	+0.57	−0.16

[a] Sum over all hydrogen atoms of the acacen ligand.

Table XVI. Relative Stabilities (in kcal/mol) of the Bent, Linear, and Perpendicular Structures for $[Co(acacen)LO_2]^+$

Fifth ligand	Bent	Linear	Perpendicular
None	0	10	57
H_2O	0	9	64
CN^-	0	6	56
CO	0	8	67

It is somewhat difficult to discuss the influence of the equatorial ligand on the ease of oxygenation since we have kept the same equatorial ligand. A number of studies have shown that the oxygen uptake ability of a series of reconstituted hemoglobins increases in the order vinyl < hydrogen < ethyl for the side chains of the porphyrin ring.[28] We have reported in Table XIV the variations of the electronic charges of the metal and the ligands upon oxygenation. A large fraction (more than half) of the charge transferred to the dioxygen ligand comes from the equatorial ligand and about half of it from the hydrogen atoms of the acacen group. Then one may expect that a donor substituent on the equatorial ligand will increase the ease of oxygenation.

The System $[Co(acacen)LO_2]^+$. The "Co-O_2 unit" in the Co(acacen)LO_2 adduct has one electron more than the "Fe-O_2 unit" in oxyhemoglobin. Since interest in the Schiff-base complexes stems from the assumption that they may be regarded as possible models of hemoglobin and myoglobin, the effect of having one electron less, namely replacing Co(II)d^7 with Fe(II)d^6, should be investigated. This is relatively easy at the theoretical level. However, rather than considering a hypothetical compound Fe(acacen)LO_2, we preferred for obvious economical reasons to stay with the same system considered previously but with one electron less, namely we have repeated the SCF calculations for the system $[Co(acacen)LO_2]^+$. The possible configurations for the ground state are either $(\pi_g{}^a)^2$ or $(\pi_g{}^b)^2$.[135] The total energies for the three structures with L = none, H_2O, CO, and CN^- are reported in Table XV. The relative energies of the three structures are given in Table XVI. Since these are only model calculations for an hypothetical system, we stress only the main results from Tables XV and XVI. The ground state configuration is $(\pi_g{}^a)^2$ for the bent structure and $(\pi_g{}^b)^2$ for the perpendicular one. This was expected on the basis that $\pi_g{}^a$ is below $\pi_g{}^b$ for the bent structure of Co(acacen)LO_2 but above $\pi_g{}^b$ for the perpendicular one. The perpendicular structure is destabilized with respect to the bent one by 56–67 kcal/mol depending on the fifth ligand. These values are in the same range as the ones of 46–80 kcal/mol reported above for the Co(acacen)LO_2 systems. On this basis, we predict that the ground state configuration of an iron(II) porphyrin will be $(\pi_g{}^a)^2$ for the bent structure and $(\pi_g{}^b)^2$ for the perpendicular structure, the latter being less stable than the former by 50 kcal/mol or more.[136]

Conclusion

Through ab initio SCF calculations with a minimal basis set, we have given a rationale for the charge-transfer configuration Co^{III}-O_2^- proposed previously for a large class of oxygen adducts of Co(II) complexes on the basis of the EPR spectrum. Calculations for the three structures linear, bent, and perpendicular give the bent one as the most stable, in agreement with the crystallographic data for a number of oxygen adducts of Fe(II) and Co(II) complexes. However, an additional piece of information obtained from the calculations is the strong destabilization (by at least 50 kcal/mol) of the perpendicular structure proposed by Griffith over the bent and linear structures. This suggests that the EPR spectra of Co(bzacen)(py)O_2 (in solution) and of myoglobin, which were interpreted previously on the basis of a perpendicular structure, should be reinterpreted in a different way (possibly on the basis of a dynamic equilibrium for Co(bzacen)(py)O_2). The calculated enthalpies of oxygenation point to the stabilizing effect of the fifth ligand for the adduct (experimentally stable adduct formation is not possible in the absence of the fifth ligand[9]).[139] Furthermore they show a relationship between the ease of oxygenation, the σ-donor ability of the fifth ligand, and the ease of oxidation of Co(II) to Co(III). Calculation for the bent structure with imidazole as the fifth ligand would indicate that the π-electron donor or acceptor ability of the imidazole ligand has possibly been overemphasized. Finally, calculations for the system with one less electron, namely $[Co(acacen)LO_2]^+$ with the Co-O_2 unit now isoelectronic to the Fe-O_2 unit in oxyhemoglobin, indicate that the perpendicular structure of the Fe-O_2 unit should be less stable than the bent one by 50 kcal/mol or more for an iron(II) porphyrin.

The limitations of this work are obvious. We have used a minimal basis set (except for the d functions of the metal) at the SCF level together with fixed geometries (either experimental or assumed geometries). However, we feel that further refinements at the theoretical level, such as the use of larger basis sets or limited geometry optimization, should not affect seriously our qualitative conclusions.

Table XV. Energy Values (in au) for the Two 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	Electronic configuration	Geometric structure: Linear	Geometric structure: Bent (θ = 126°)	Geometric structure: Perpendicular
None	$(\pi_g{}^a)^2$	−2013.300	−2013.316	−2013.190
	$(\pi_g{}^b)^2$	−2013.300	−2013.283	−2013.209
H_2O	$(\pi_g{}^a)^2$	−2089.098	−2089.112	−2088.993
	$(\pi_g{}^b)^2$	−2089.098	−2089.080	−2089.009
CN^-	$(\pi_g{}^a)^2$	−2105.564	−2105.573	−2105.460
	$(\pi_g{}^b)^2$	−2105.563	−2105.550	−2105.484
CO	$(\pi_g{}^a)^2$	−2125.689	−2125.702	−2125.580
	$(\pi_g{}^b)^2$	−2125.687	−2125.670	−2125.595

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(139) A referee has objected that these calculations have no bearing on reality (with respect to the ease of oxygenation) since only the case L = imidazole shows experimentally an appreciable tendancy to bind O_2 reversibly, and furthermore the Co(acacen) system does not even bind CO. Our calculation does indicate little binding of CO to Co(acacen) (the computed enthalpy being 1 kcal/mol, see Table 1 of ref 122). The aim of such calculations, which should be considered as model calculations, is not to compute the enthalpies of oxygenation to within a few kcal/mol, but rather to account for some general trends (such as the stabilizing effect of the fifth ligand for the adduct or the relationship between the ease of oxygenation and the ease of oxidation of the metal). Ligands such as CN^- or CO were not considered per se but rather respectively as a model for a good σ donor and poor π acceptor or a poor σ donor and good π acceptor.

Luminescence Quenching of the Tris(2,2′-bipyridine)ruthenium(II) and Tris(1,10-phenanthroline)ruthenium(II) Cations

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Abstract: Luminescence quenching of the tris(2,2′-bipyridine)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II) cations by over 20 metal complexes and ions is reported. Quenching is predominantly by diffusion, but a small contribution of static quenching is present for the anionic quenchers. Heavy atom and paramagnetic quenching are unimportant deactivation pathways, and all quenching appears to be by electron and energy transfer. A general method for estimating infinite dilution ion pairing and quenching constants from luminescence data is described. Infinite dilution bimolecular quenching constants, $k_2{}^0$'s, and ion pairing constants are reported. The Debye theory adequately describes the maximum permissible $k_2{}^0$'s, but may only predict variations of k_2 with ionic strength up to $I \sim 0.001$. Decay times and excited state energies are reported for both donors, and they are compared as sensitizers. Using these sensitizers the lowest excited triplet state of $Co(CN)_6{}^{3-}$ is estimated at ~ 18.4 kK $< E_t < \sim 20$ kK and for $Fe(CN)_6{}^{4-}$ it is suggested that $E_t < \sim 18.0$ kK.

Since its introduction as a photosensitizer,[1] the tris(2,2′-bipyridine)ruthenium(II) cation has proved revolutionary.[2-16] It functions as an energy and an excited-state electron-transfer agent in a variety of inorganic and organic systems. It forms the prototype of a class of sensitizers whose energies can almost continuously span the visible into the near infrared.[13] It has formed the basis of a chemical actinometer for high power lasers[14] and promises to be useful in solar energy conversion.[8] We present a comprehensive study of the quenching of $Ru(bipy)_3{}^{2+}$ and the related $Ru(phen)_3{}^{2+}$ [bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline] by transition metal complexes.

Experimental Section

The acetylacetonates from Alfa Inorganics were recrystallized from benzene. The Co(III) and Cr(III) complexes were assumed to be anhydrous. Microanalysis showed the Cu complex to be anhydrous and the Co(II) and Ni(II) complexes analyzed to be dihydrates.