Density Functional Theory Studies of the Binding of Molecular Oxygen with Schiff's Base Complexes of Cobalt[†]

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Gradient-corrected density functional theory calculations using the B3LYP hybrid functional have been performed on Co(acacen)(pyridine) and Co(salen)(pyridine) complexes and their adducts with molecular oxygen (acacen = 2,11-dihydroxy-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene, salen = 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene). Calculated optimized geometries and dioxygen binding energies show good agreement with experiment. The binding energy for Co(acacen)(pyridine) is calculated to be 53.5 kJ mol^{-1} (experiment = 63.1 kJ mol^{-1}), and the binding energy for Co(salen)(pyridine) is calculated to be 46.8 kJ mol^{-1} (experiment = 51.8 kJ mol^{-1}). The calculated O−O distances are in the range 1.28−1.29 Å, which compares to 1.26 Å from crystal structure data for Co(acacen)(pyridine)(O$_2$). Model complexes for Co(acacen)(pyridine) are also examined, and ligand substitution effects correlated with the computed Co−O distance. The calculated O−O vibrational frequency (1243 cm^{-1}) is slightly higher than typical experimental frequencies while the calculated Co−O frequency is 439 cm^{-1}. The effect of basis set variation on the computed binding energy in the model complexes was also examined, and it was found that a more flexible basis set was required when using standard effective core potentials for cobalt. In addition, the inclusion of basis set superposition error and the zero point correction were found to severely reduce the magnitude of the calculated binding energy.

Introduction

The discovery of cobalt-containing coordination complexes that are able to bind molecular oxygen reversibly was made by Werner over a century ago.[1] Since that time a wide range of other complexes have been found to have similar behavior. In particular, the study of Schiff's base compounds has been particularly popular due to the structural similarity of such compounds to biological systems. A Schiff's base can be thought of as the imine product of the condensation reaction of a primary amine with an aldehyde or ketone. For example, early work by Tsukami[2] showed that a color change is observed when oxygen is bubbled through a solution of Co(II)(salen) (salen = 1,6-bis-(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene, Figure 1a), which is indicative of oxygen binding to cobalt. The salen molecule is a quadridentate ligand coordinating to the central metal cation through the OH and N groups. A base frequently occupies one axial coordination site, and the dioxygen binds to the other. Chelating ligands of this class have been studied extensively to further understand the thermodynamics and kinetics of oxygen binding in these model systems. There have been a number of excellent reviews[3−5] in this area which address such issues as thermodynamic aspects,[6] theoretical studies,[7,8] and catalytic activity.[9,10]

There have been several notable theoretical studies on cobalt Schiff's base complexes and their interaction with dioxygen. Veillard and co-workers[11] performed single-point ab initio Hartree−Fock calculations on a variety of model cobalt complexes based on the acacen ligand (acacen = 2,11-dihydroxy-4,9-dimethyl-5,8-diaza-2,4,8,10-dodecatetraene, Figure 1b). They found that the bent dioxygen geometry was considerably more

stable than linear and perpendicular models and that the calculated spin (doublet) and charge distribution were consistent with experiment. Fantucci and Valenti[12] performed semiempirical INDO calculations on Co(acacen) models with and without ammonia and dioxygen. They found that on binding the ammonia base the spin density shifts from a predominantly d$_{yz}$ to a d$_{z^2}$ orbital, which is the correct orientation for binding dioxygen. The oxygenated complex is found to resemble O$_2$ rather than O$_2^-$. More recently, Valko and co-workers[13] performed a combined ESR, magnetic susceptibility, and quantum chemical study on copper and cobalt salen adducts with dioxygen. They found a large metal-to-ligand charge transfer combined with a spin−spin pairing process and a large spin density on dioxygen. The INDO/2 method is found to give a description which is consistent with previous studies whereas the QR-INDO/1 method fails to represent the spin pairing process correctly.

To investigate the electronic structure of substituted Co(II)-(acacen) complexes and the Co(II)(salen) complexes, this paper uses hybrid density functional methods, an approach which has been found to provide surprisingly good descriptions of the

(3) Basolo, F.; Hoffmann, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975,** *8,* 384.
(4) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981,** *39,* 295.
(5) Martell, A. E., Sawyer, D. T., Eds. *Oxygen complexes and oxygen activation by transition metals*; Plenum: New York and London, 1988.
(6) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984,** *84,* 137.
(7) Boča, R. *Coord. Chem. Rev.* **1983,** *50,* 1.
(8) Bytheway, I.; Hall, M. B. *Chem. Rev.* **1994,** *94,* 639.
(9) Drago, R. S. *Coord. Chem. Rev.* **1992,** *117,* 185.
(10) Bianchini, C.; Zoellner, R. W. *Adv. Inorg. Chem.* **1997,** *44,* 263.
(11) Dedieu, A.; Rohmer, M.-M.; Veillard, A. *J. Am. Chem. Soc.* **1976,** *98,* 5789.
(12) Fantucci, P.; Valenti, V. *J. Am. Chem. Soc.* **1976,** *98,* 3832.
(13) Valko, M.; Klement, R.; Pelikán, P.; Boča, R.; Dlhán, L.; Böttcher, A.; Elias, H.; Müller, L. *J. Phys. Chem.* **1995,** *99,* 137.

† LA-UR 98-5035.
(1) Werner, A.; Mylius, A. Z. *Z. Anorg. Allg. Chem.* **1898,** *16,* 245.
(2) Tsumaki, T. *Bull. Chem. Soc. Jpn.* **1938,** *13,* 252.

structural and thermochemical properties of transition metal compounds as compared to Hartree−Fock-based methods. Full geometry optimization was employed, and the optimized geometries were compared to experiment. The dioxygen binding energies are calculated for each model, and these values are correlated with the nature of the substituents on the ligand and with thermochemical data.

Theoretical Background

Calculations using density functional theory (DFT) are a rapidly growing choice for the study of many systems using first-principles approaches. They include electron correlation effects which are important for many chemical processes at a similar computational cost to calculations at the Hartree−Fock level of theory. Although the reliability of these methods for small organic molecules has been well established, studies of transition metal containing compounds are less well developed. In particular calculations on paramagnetic systems where a number of spin states are possible provide a particular challenge to the approach. A gradient-corrected density functional method was recently used in a study of structure and spectra of cytochrome P450 and its adducts with dioxygen.[14]

This work uses the B3LYP hybrid functional, which is a three-parameter hybrid functional which combines the gradient-corrected exchange functional of Becke and the correlation functional of Lee, Yang, and Parr[15,16] with Hartree−Fock exchange. This relatively new method has recently shown promising results, suggesting that it may be preferable to other commonly employed functionals.[17] Geometry optimizations were performed with the Berny analytical gradient method.[18] All calculations were performed with the *Gaussian94*[19] software.

As will be discussed in greater detail later, most of the calculations are of the all-electron type with the 6-311G all-electron basis set of Wachters and Hay[20,21] for cobalt with various additions. The 6-31G basis typically forms a starting point for basis set studies of ligands. The results using effective core potentials are also presented for model ligands where the starting point is the LANL2DZ basis set. In addition, selected results are presented at the Hartree−Fock level of theory with local exchange using the SVWN density functional, and gradient-corrected exchange with the BLYP density functional.

Experimental Structural Background

The Schiff's base cobalt complexes are able to form both 1:1 and 2:1 adducts with dioxygen. It is possible to influence which of these species form by varying such parameters as the polarity of the solvent, the steric nature of ligand substituents, and temperature. Although early work suggested that the Co(salen) complex formed a 1:1 adduct,[22] more recent work has suggested that a 2:1 complex is more likely.[23] If four methyl
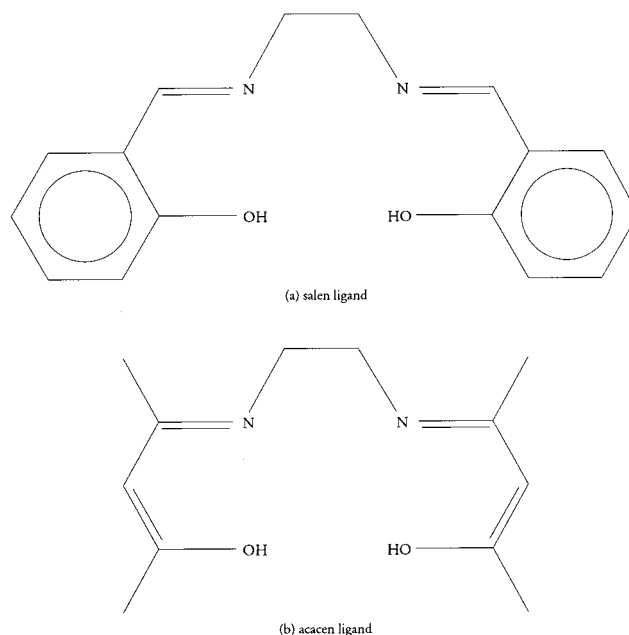

Figure 1. Schiff's base ligands.

substituents are added to the ethylene bridge, this is sufficient to form exclusively the 1:1 complex.[23] It has recently been shown that one method that appears to be successful in suppressing 2:1 complex formation is to use a pentadentate Schiff's base type ligand.[24] In these studies we focus on models for the 1:1 adduct.

The Co(acacen) complex shows roughly four times the affinity for oxygen as Co(salen) complex.[22] This is thought to be due to the aromatic ligand reducing the charge density on cobalt available for donation to oxygen.

There have been a number of crystallographic studies on cobalt Schiff's base complexes that provide useful data which can be used to construct starting models.

It is often difficult to crystallize samples of sufficient quality for high-resolution X-ray diffraction studies. This is frequently due to the low thermal stability of the complexes formed. However, it has been found that it is easier to make more stable complexes if bulky substituents are incorporated in the ligand structure, which increases their solubility. The additional problem of disorder in the structure has also made structure determinations difficult.

Brückner and co-workers performed a single-crystal X-ray study of Co(acacen) with benzene. They determined the average Co−O and Co−N bond distances to be 1.85(1) and 1.87(1) Å, respectively, and located all the heavy atoms in the complex.[25] Calligaris and co-workers attempted to solve the structure of the same complex with pyridine replacing benzene and with molecular oxygen coordinated.[26] However, due to the poor quality of the single crystals in the study, only a limited set of structural parameters were obtained. The important results of this study are that the pyridine molecule is found to be oriented such that the plane of the ring bisects the N−Co−O angle in the plane of the ligand and that the oxygen molecule is

(14) Harris, D.; Loew, G.; Waskell, L. *J. Am. Chem. Soc.* **1998**, *120*, 4308.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(17) Zygmunt, S. A.; Mueller, R. M.; Curtiss, L. A.; Iton, L. E. *J. Mol. Struct. (THEOCHEM)* **1998**, *430*, 9.

(18) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheesman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong. M. W.; Andreas, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian Inc.: Pittsburgh, PA, 1995.

(20) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(21) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(22) Tauzher, G.; Amiconi, G.; Antonini, E.; Brunori, M.; Costa, G. *Nature* **1973**, *241*, 222.

(23) Chen, D.; Martell, A. E. *Inorg. Chem.* **1987**, *26*, 1026.

(24) Rybak-Akimova, E. V.; Otto, W.; Deardorf, P.; Roesnet, R.; Busch, D. H. *Inorg. Chem.* **1997**, *36*, 2746.

(25) Brückner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1968**, *2*, 386.

(26) Calligaris, M.; Nardin, G.; Randaccio, L.; Tauzher, G. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 419.

approximately parallel to the normal to the pyridine ring. They also give the Co—O$_2$ bond length to be 1.95(5) Å and the Co—N(pyridine) distance to be 2.15(4) Å. One further crystallographic study has also been performed on the related compound *N*,*N'*-ethylenebis(benzoylacetoniminato)cobalt(II)-(pyridine)O$_2$ by Rodley and Robinson.[27] This complex replaces two of the methyl groups of the acacen ligand with phenyl groups. This earlier study shows the same relative orientation for pyridine and oxygen with respect to the chelating ligand and also gives several useful structural parameters: ∠O—Co—O = 126(2)°, O—O = 1.26(4) Å, ∠N(pyridine)—Co—O = 177(3)°, Co—O = 1.86 Å, Co—N(pyridine) = 2.02 Å.

Calligaris and co-workers[28] solved the structure of Co(II)-(salen) with pyridine coordinated. Surprisingly, in the light of adsorption measurements, the crystal structure features a 1:1 complex with the following structural data: Co—N(pyridine) = 2.10(2) Å, Co—O(salen) = 1.90(1) Å, Co—N(salen) = 1.90(1) Å. The ethylene bridge is eclipsed due to symmetry. In an earlier study,[29] the same workers determined the structure of the dioxygen addition product of the same ligand with dimethylformamide replacing pyridine. In this case, the 2:1 complex is found.

A large number of other crystallographic studies have also been performed with more bulky substituents on the basic salen core structure and also changes in the axial base.[30-36] The structures are qualitatively similar to those detailed above. O—O distances in the range 1.25(2)—1.35(1) Å are observed. Surprisingly these values do not appear to be correlated to the nature of the substituents on the conjugated ring system. However, the base strength of the molecule bound axially opposite to dioxygen does appear to have a more direct influence on the dioxygen bond length.[36]
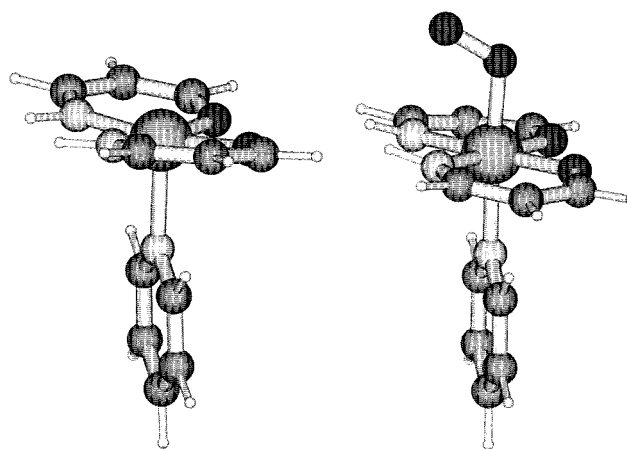
Results and Discussion

Calculations on Simple Models for Co(acacen) and Co-(acacen)(O$_2$). A. Geometries. Although it is known that Schiff's base ligands have a strong tendency to form 2:1 adducts with dioxygen, our calculations will focus on the much simpler 1:1 adducts.

The first set of calculations performed were based on the simplified model in which the methyl groups are replaced with hydrogens and second the ethylene bridge between the two nitrogens is removed (Figure 2). This model was previously used in the semiempirical calculations of Fantucci and Valenti.[12]

Full geometry optimizations using the B3LYP hybrid functional were performed on the model system with O$_2$ (denoted *adduct*) and without O$_2$ (denoted *complex*). while retaining the symmetry of the C_s point group. The following basis sets were chosen for the calculations: 6-311G (Co), 6-31+G* (dioxygen), and 6-31G on the remaining atoms.

The initial geometry of the acacen ligand was taken from the crystal structure of Brückner and co-workers[25] as detailed

(27) Rodley, G. A.; Robinson, W. T. *Nature* **1972**, *235*, 438.
(28) Calligaris, M.; Minichelli, D.; Nardin, G.; Randaccio, L. *J. Chem. Soc. A* **1970**, 2411.
(29) Calligaris, M.; Nardin, G.; Randaccio, L.; Ripamonti, A. *J. Chem. Soc. A* **1970**, 1069.
(30) Avdeef, A.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 1432.
(31) Avdeef, A.; Schaefer, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5153.
(32) Gall, R. S.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 2758.
(33) Gall, R. S.; Rogers, J. F.; Schaefer, W. P.; Christoph, G. G. *J. Am. Chem. Soc.* **1976**, *98*, 5135.
(34) Jameson, G. B.; Robinson, W. T.; Rodley, G. A. *J. Chem. Soc., Dalton* **1978**, 191.
(35) Huie, B. T.; Leyden, R. M.; Schaefer, W. P. *Inorg. Chem.* **1979**, *18*, 125.
(36) Schaefer, W. P.; Huie, B. T.; Kurilla, M. G.; Ealick, S. E. *Inorg. Chem.* **1980**, *19*, 340.

(a) model for Co(acacen)(pyridine) complex   (b) model for Co(acacen)(pyridine)(O$_2$) adduct

Figure 2. Models for Co(acacen)(pyridine) and Co(acacen)(pyridine)-(O$_2$).

Table 1. Summary of Optimized Geometries (Bond Lengths and Angles[a]) for the Simple Model for Co(acacen)(pyridine) and Co(acacen)(pyridine)(O$_2$)

	Co—O$_{ac}$[b]	Co—N$_{ac}$	Co—N$_{pyr}$[c]	Co—O$_2$	O—O	Co—O—O
complex	1.91	1.92	2.17			
expt[d]	1.85(1)	1.87(1)				
adduct	1.91	1.92	2.08	1.92	1.28	117
expt[e]			2.15(4)[e]	1.95(5)[e]		

[a] Bond lengths in angstroms, bond angles in degrees. [b] Subscript ac refers to an atom which is part of the acacen ligand. [c] Subscript pyr refers to an atom which is part of the pyridine molecule. [d] Taken from the crystal structure of Co(acacen)(benzene).[25] [e] Taken from the crystal structure of Co(acacen)(pyr)(O$_2$).[26]

above. Pyridine was added as the axial base with the initial Co—N(pyridine) distance set to 2.1 Å. For the dioxygen adduct, the Co—O and O—O bond lengths were set to 1.90 and 1.30 Å, respectively. The O—Co—O bond angle was set to 120°. The relative orientation of the ligands was chosen such that the pyridine bisected the O—Co—N angle, whereas the dioxygen orientation bisected the N—Co—N angle. The two models are illustrated in Figure 2.

Convergence of the SCF wave function initially proved difficult, so the following procedure was adopted. The SCF wave function was first converged using a minimal basis set (STO-3G) at the (unrestricted) Hartree—Fock level of theory. This wave function was then used as a guess for an analogous calculation at the B3LYP level of theory. The basis set was then progressively advanced from STO-3G to 3-21G to the final full basis set projecting the previous solution onto the larger basis set to form the guess.

For the Co(acacen)(pyridine), both the doublet and quartet spin states were considered.

A summary of the geometric data for the optimized complex and adduct in the doublet spin state is given in Table 1. It can be seen from the table that the calculated cobalt—acacen bond lengths are overestimated compared to the crystal structure. In the case of the adduct, the cobalt—pyridine bond distance is underestimated by our calculations. However, the Co—O bond length and Co—O—O bond angle are within the range expected for other coordination compounds of this class.

Comparing the energies of the two optimized complexes, the doublet was found to be lie slightly lower in energy (ca. 5.4 kJ mol^{-1}) than the quartet. This result is in agreement with ESR
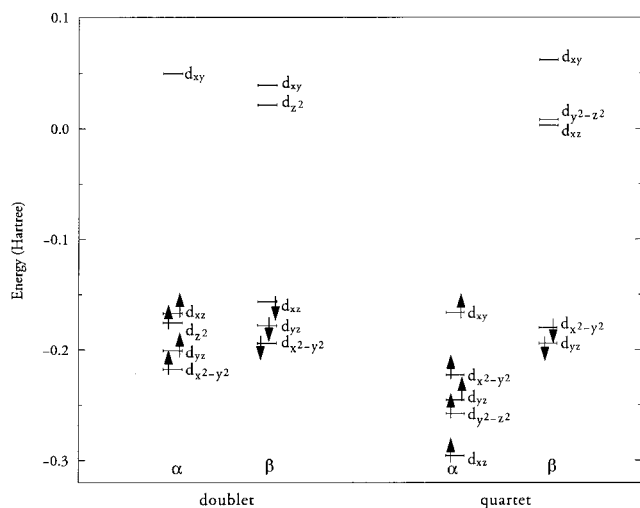
Figure 3. Quantitative molecular orbital diagram for the Co(acacen)-(pyridine) model in the doublet and quartet states.
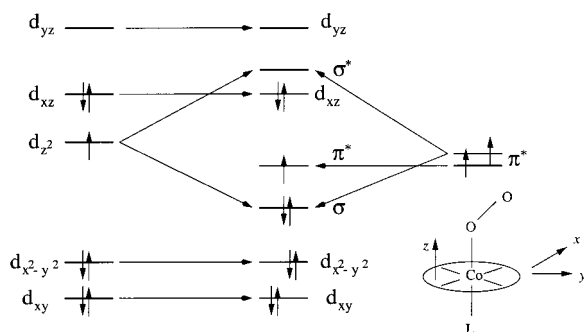

Figure 4. Schematic energy level diagram for Co(II)−dioxygen Schiff's base complexes based on an analysis of the orbital energies from density functional theory calculations.

measurements which have shown the ground state to be a doublet state. For the adduct, the quartet state was dissociative. A quantitative molecular orbital diagram for the doublet and quartet states is given in Figure 3. Only the highest energy molecular orbitals containing metal character of α and β spin for the unrestricted B3LYP calculation are shown; other orbitals are omitted for clarity. The single unpaired electron in the complex resides in a molecular orbital of primarily d_{z^2} character, which is consistent with ESR measurements. The quartet state is formed from the doublet from the excitation $d_{xz} \rightarrow d_{xy}$. An analysis of the electron density plot for this orbital shows that the pyridine nitrogen polarizes the d orbital such that there is an increased electron density in the direction of the vacant coordination site of the cobalt ion.

A qualitative molecular orbital diagram for the adduct is shown in Figure 4.

σ bonding and antibonding orbitals are formed from the combination of the cobalt $3d_{z^2}$ orbital and one set of oxygen π* antibonding orbitals, whereas π-bonding and antibonding orbitals arise from overlap of the Co $3d_{yz}$ orbital and the other set of oxygen π* antibonding orbitals. The orbital ordering is such that the unpaired electron resides in an orbital of predominantly oxygen π* character. This result is consistent with ESR studies on these systems that show the unpaired electron to be on the oxygen.[4] The nature of the σ bonding orbital provides information on the extent of charge transfer in the complex.[8,37] If the σ orbital has predominantly oxygen π character and little Co character, then the complex can be viewed as $Co^{3+}-O_2^-$ with a dative bond. Contributions from the lower

Table 2. Fitted Charges and Calculated Spin Densities for the Optimized Geometries of the Simple Model for Co(acacen)(pyridine) and Co(acacen)(pyridine)(O₂)

	$q(Co)$	$q(N_{ac})$	$q(O_{ac})$	$q(N_{pyr})$	$q(O_1)^a$	$q(O_2)^a$
complex	1.25	−0.91	−0.67	−0.38		
adduct	1.85	−1.01	−0.76	−0.52	−0.26	−0.26

	$\rho_s(Co)$	$\rho_s(N_{ac})$	$\rho_s(O_{ac})$	$\rho_s(N_{pyr})$	$\rho_s(O_1)^a$	$\rho_s(O_2)^a$
complex	1.02	−0.01	0.00	0.06		
adduct	−0.21	0.00	0.01	−0.01	0.66	0.54

a The numbering is such that Co−O₁−O₂ is the bonding sequence.

energy σ and π bonding orbitals on oxygen can also lead to a rehybridization. The other possibility is that the Co−O₂ σ orbital has significant contributions from both cobalt atomic orbitals and oxygen π orbitals, in which case a $Co^{2+}-O_2$ bond is formed. If the interaction between the orbitals is strong, a true covalent bond is formed, whereas if it is weaker the bond can be described as spin coupled. The use of configuration interaction calculations has been used to distinguish between these various possibilities for a simple porphyrin model.[8]

Charges were fit to the calculated electrostatic potential of the optimized geometries using the CHelpG scheme.[38] A radius of 1.90 Å is used for cobalt, which is the approximate value for the Co−O covalent bond length in this system. A similar method for deriving CHelpG charges was used recently for a study on iron complexes.[39] The results are given in Table 2. It can be seen that the introduction of dioxygen to the complex causes a shift in negative charge primarily from the transition metal center to the oxygen molecule which is consistent with previous models. The charge on each oxygen is approximately the same and represents a total charge transfer of one half-unit from the complex to dioxygen. It is interesting to note that if a much smaller value for the Co radius is used (such as the cobalt-(II) *ionic* radius, 0.65 Å), then no change in cobalt charge is observed on dioxygen binding. This is the same result obtained by Veillard and co-workers using a Mulliken population analysis.[11]

The calculated spin densities for complex and adduct are given in Table 2. The unpaired spin is entirely confined to the cobalt atom in the case of the complex in an orbital of approximately d_{z^2} character. With the formation of the adduct, the unpaired spin is transferred to the dioxygen moiety with only a small residual spin remaining on cobalt. This is consistent with the molecular orbital diagram in Figure 3. The small residual spin is similar to, though not as dramatic as, that observed by Valko and co-workers[13] in their semiempirical QR-INDO/1 calculations.

B. Dioxygen Binding Energies. The binding energy of dioxygen on the Co(acacen)(pyridine) complex can be calculated from the relation

$$\Delta E_{bind}^{opt} = E_{adduct}^{opt} - E_{complex}^{opt} - E_{O_2}^{opt} \quad (1)$$

where E_{adduct}^{opt}, $E_{complex}^{opt}$, and $E_{O_2}^{opt}$ are the energies of the geometry optimized structures of Co(acacen)(pyr)(O₂), Co(acacen)-(pyr), and molecular oxygen, respectively. Using this expression, a binding energy of 49.1 kJ mol⁻¹ is calculated for the model

(37) Hall, M. B. Bonding of dioxygen to transition metals. In *Oxygen complexes and oxygen activation by transition metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York and London, 1988.
(38) Breneman, C. M.; Wilberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
(39) Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565.

system compared with the experimental value as measured by Amiconi and co-workers[40] of 63.1 kJ mol^{-1}.

The binding energy corrected for basis set superposition error is given by the expression

$$\Delta E_{bind}^{bsse} = E_{adduct}^{opt} - E_{complex}^{opt} - E_{O_2}^{opt} - (\Delta E_{complex}^{bsse} + \Delta E_{O_2}^{bsse}) \tag{2}$$

where $\Delta E_{complex}^{bsse}$ and $\Delta E_{O_2}^{bsse}$ are defined as

$$\Delta E_{complex}^{bsse} = E_{complex,bsse}^{adduct} - E_{complex}^{adduct} \tag{3}$$

$$\Delta E_{O_2}^{bsse} = E_{O_2,bsse}^{adduct} - E_{O_2}^{adduct} \tag{4}$$

where $E_{complex}^{adduct}$ is the energy of the complex at the optimized geometry of the adduct with the dioxygen atoms removed, $E_{complex,bsse}^{adduct}$ is the energy of the same system but with orbitals centered on the position of the dioxygen atoms, and $E_{O_2}^{adduct}$ and $E_{O_2,bsse}^{adduct}$ are the analogous quantities for dioxygen.

The inclusion of the basis set superposition error (BSSE) is found to decrease the binding energy by approximately 33 kJ mol^{-1}. This BSSE correction represents an upper bound to the effects of basis set limitations. Nevertheless in the following sections we investigate the effects of basis set and of more realistic models for the Schiff's base ligands.

Additionally, calculations were performed to assess the contribution of zero-point energy and basis set superposition energy to the binding energy. The addition of the zero-point correction is found to reduce the binding energy to 39.5 kJ mol^{-1}.

C. Basis Set Variation and the Use of Effective Core Potentials. To further assess the effect of basis set choice on the calculations, the basis sets on the acacen ligand and the dioxygen were also varied.

To assess the variation of basis set and level of theory for the dioxygen ligand, calculations on O_2, O_2^-, and O_2^{2-} were carried out at the Hartree–Fock level of theory and also using three levels of density functionals (Table 3). Moving from the 6-31G* to the 6-31+G* basis, which includes diffuse functions to describe negative ions, results in very little difference in geometry for the neutral species and monoanion, but the calculated electron affinity increases markedly, in the latter basis by 70–130 kJ mol^{-1}. While at the Hartree–Fock level of theory the O_2^- anion is predicted to be unbound in both basis sets, all DFT methods predict the anion to be bound in agreement with experiment. The best agreement is achieved with the 6-31+G* basis set and the B3LYP functional (55 compared to 42.5 kJ mol^{-1} experimentally). Using this combination of basis set and level of theory, the vibrational frequencies of O_2 and O_2^- were computed. As can be seen in the table, the vibrational frequencies are slightly overestimated but are nonetheless reproduced to within 100 cm^{-1} of experiment.

Now basis set variations on the adduct will be considered. As in the previous section, all the calculations are single-point computations performed on the geometry-optimized structures as obtained in section A. The following basis sets were tried: Co (6-311G, 6-311+G, 6-311G*, and 6-311+G*) and O_2 (6-31G* and 6-31+G*), the remaining atoms being kept at the 6-31G level. It is found that the largest binding energy corresponds to the basis set initially chosen (that is, 6-311G on cobalt and 6-31+G* on O_2). Omitting the diffuse function on

(40) Amiconi, G.; Brunori, M.; Antonini, E.; Tauzher, G.; Costa, G. *Nature* **1970**, *228*, 549.

Table 3. Results of Calculations on Oxygen Species

method[a]	Hartree–Fock	SVWN	BLYP	B3LYP
	O_2 Bond Length (Å)[b]			
6-31G*	1.168	1.214	1.240	1.215
6-31+G*	1.169	1.214	1.241	1.215
	expt = 1.208 Å			
	O_2 Electron Affinity (kJ mol^{-1})[c]			
6-31G*	−141.7	−18.4	−76.1	−52.5
6-31+G*	−73.5	99.7	55.1	55.1
	expt = 42.5 kJ mol^{-1}			
	O_2 Vibrational Frequency (cm^{-1})			
6-31+G*				1647
	expt = 1550 cm^{-1}			
	O_2^- Bond Length (Å)[b]			
6-31G*	1.296	1.343	1.386	1.353
6-31+G*	1.298	1.338	1.385	1.351
	expt = 1.35 Å			
	O_2^- Vibrational Frequency (cm^{-1})			
6-31+G*				1175
	expt = 1130 cm^{-1}			
	O_2^{2-} Bond Length (Å)[b]			
6-31G*	1.529	1.576	1.683	1.618
6-31+G*	1.497	1.528	1.621	1.569
	(expt = 1.49 Å)[d]			

[a] Method of calculation: Density functional theory calculations (SVWN = Slater exchange with VWN correlation functional,[46] BLYP = Becke88 functional with Lee, Yang, and Parr correlation functional,[47,48] B3LYP as detailed earlier[15,16]), all calculations are unrestricted. [b] The optimized O–O bond length. [c] Positive values indicate stable O_2^-. [d] No gas-phase data available. For comparison, O–O in K[O_2] is 1.28 Å, O–O in Na$_2$[O_2] is 1.49 Å (solid state).

oxygen decreases the computed binding energy by 10.9 kJ mol^{-1}. Increasing the quality of the basis set on cobalt only has a small influence on the binding energy. In all cases, increasing the basis set on cobalt stabilizes the complex more than the adduct, and consequently the binding energy is reduced.

Calculations were also performed using effective core potentials (ECPs) on cobalt, which replace the inner electrons, and compared with the all-electron results from the previous section. Since ECPs are widely used in transition metal calculations, we were interested in comparing their performance with various basis sets using density functional theory. The basis set on dioxygen and ligands remains unchanged in this study, and the geometry remains fixed at the all-electron geometry. The starting point was the LANL2DZ basis set, as designated in *Gaussian94*,[19] which consists of 3s, 3p, and 2d functions to describe the "outer core" 3s and 3p electrons as well as the valence 3d, 4s, and 4p electrons. For all of these studies the same ligand basis sets were used, i.e., 6-31+G* on the O and 6-31G on the other atoms in the acacen ligand and on pyridine. LANL2DZ (unc. sp) consists of the same basis but uncontracting the initial Gaussian basis as five s and five p basis functions. 311G changes the d basis by using three contracted d functions, or 311, from the all-electron calculations of Wachters.[20] 311+G adds another d function, contracted 3111, as recommended by Hay[21] to describe d^n configurations. The 311G valence basis should correspond approximately to the previous 6-311G all-electron basis for cobalt, and similarly for 311+G and 6-311+G.

Using the LANL2DZ standard basis set for cobalt in the DFT calculation gives only a slight O_2 binding energy of −5.9 kJ mol^{-1}, while using the same basis with more flexibility in the s,p set gives −12.6 kJ mol^{-1}. Comparing the ECP results with the corresponding calculation using an all-electron basis set (given in parentheses), the binding energies are −52.7 (−49.1) kJ mol^{-1} and −38.1 (−20.5) kJ mol^{-1}, respectively, indicating

(a) original orientation from experiment

(b) reduced steric hindrance model

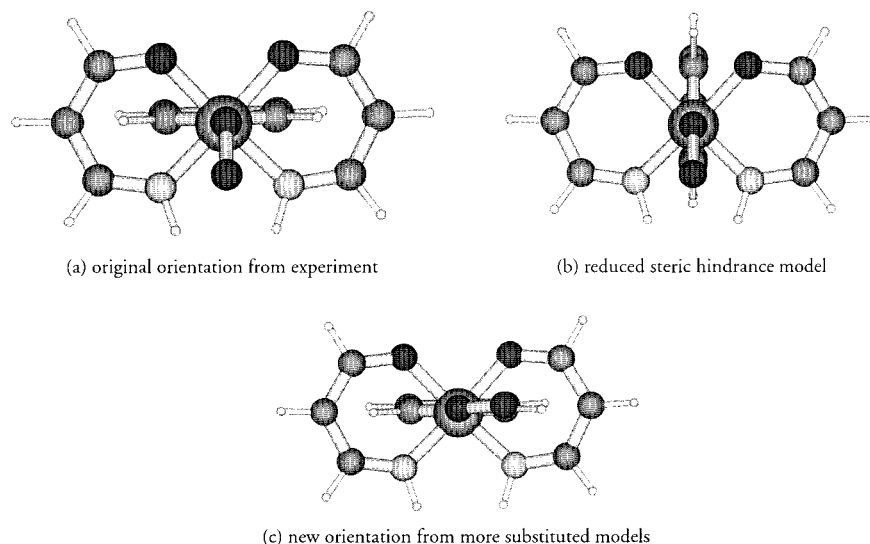
(c) new orientation from more substituted models

Figure 5. Different relative orientations for Co(acacen)(pyridine)(O₂).

Table 4. Summary of Calculations on Relative Ligand Orientations in Co(acacen)(pyridine)(O₂) Models

orientation	E_{rel}(adduct)^a (kJ mol^{-1})	E_{bind} (kJ mol^{-1})	Co–O (Å)	O–O (Å)	Co–O–O (deg)
a	+1.7	−49.1	1.92	1.28	117
b		−47.6	1.90	1.29	116
c	+18.0	−41.4	1.92	1.28	118

^{a} Where E_{rel} is the energy of the adduct relative to the most stable of the three orientations.

a 5–18 kJ mol^{-1} effect introduced by the ECP. One conclusion that emerges from this is that the original ECP basis sets developed for Hartree–Fock calculations require more flexibility to describe the cobalt s and p orbitals when doing DFT calculations.[41] The other result is that increasing the d basis set actually gives a smaller O₂ binding energy. This can be explained by noting that the extra functions in the larger basis set help the d^7 state of the Co(II) in the complex as compared to the d^6 state of the Co(III) in the O₂ adduct.

The remainder of the calculations in this work were performed using the original basis sets detailed in section A.

D. Vibrational Frequencies. The vibrational frequencies of dioxygen molecule adducts have been found to fall into three classes: 1160–1100 cm^{-1}, which are similar to those for superoxides; 740–880 cm^{-1}, which correspond to those for peroxides; and an intermediate range, 940–1010 cm^{-1}.[5] For example, oxyhemoglobin (1132 cm^{-1})[42] and oxymyoglobin (1103 cm^{-1})[43] have frequencies in the superoxide class. Their cobalt analogues also fall into the same range (1144 cm^{-1}).[44] The vibrational spectra of our Co(acacen)(pyridine)(O₂) adduct model was calculated and the O–O frequency found to be 1243 cm^{-1}, which is slightly higher than the range expected, but still between the values for the O₂ molecule and the O₂$^-$ ion in Table 3. Since, in the calculations on the dioxygen molecule and its corresponding anion, the vibrational frequencies are slightly overestimated, it is not surprising that a similar result is found here for the adduct. In contrast, the computed frequency for the Co–O bond stretch is 439 cm^{-1}, which is slightly lower than expected for cobalt in these class of complexes.[5]

(41) Russo, T. V.; Martin, R. L.; Hay, P. J. *J. Phys. Chem.* **1995**, *99*, 17085.
(42) Alben, J. O. *The Porphyrins* **1978**, *3*, 334.
(43) Maxwell, J. C.; Volpe, J. A.; Barlow, C. H.; Caughey, W. S. *Biochem. Biophys. Res. Commun.* **1974**, *58*, 166.
(44) Proniewicz, L. M.; Kincald, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 675.
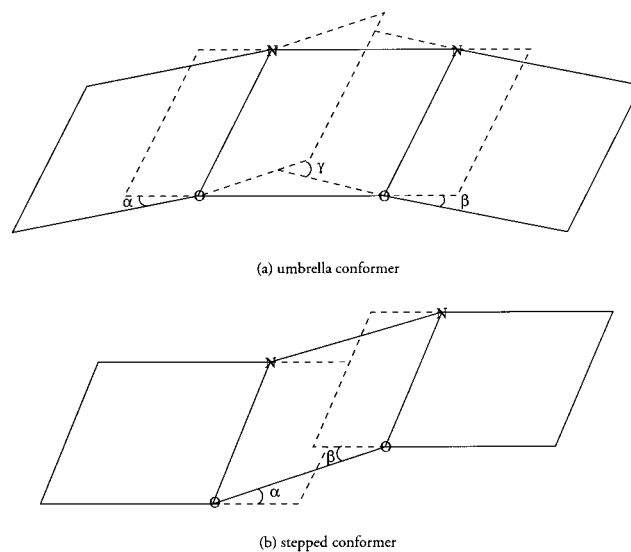

(a) umbrella conformer

(b) stepped conformer

Figure 6. Different conformers for Schiff's base ligands after Calligaris et al.[45]

Table 5. Summary of Geometrical and Thermochemical Data for Calculations on Co(acacen)(pyridine)(O₂) Models with an Ethylene Bridge Added

model	E_{bind}(adduct)^a (kJ mol^{-1})	Co–O (Å)	O–O (Å)	Co–O–O (deg)
orientation a				
without bridge	−13.8	1.92	1.28	117
with bridge: gauche	−10.7	1.92	1.29	118
orientation b				
without bridge	−11.4	1.90	1.29	116
with bridge: cis	−12.2	1.90	1.28	118
with bridge: gauche	−11.5	1.91	1.29	121
orientation c				
without bridge	−9.9	1.92	1.28	118
with bridge: gauche	−11.5	1.92	1.29	119

^{a} Where E_{bind} is defined as in eq 1.

Influences on O₂ Binding Energy to Co(II) Complexes. A. Relative Ligand Orientation. There are a number of possibilities regarding the relative orientation of the axial base, the Co(acacen) ligand system, and molecular oxygen in Schiff's base complexes in crystallographic studies in the literature.[26,27,30,32–36] In almost all cases, the axial base is found to

Table 6. Conformational Data from Calculations for Models of Co(acacen)(pyridine)(O$_2$) Complexes and Their Comparison with Experiment

structure	ψ_1 (deg)	d (Å)	conformer	α (deg)	β (deg)	γ (deg)	d_1 (Å)	d_2 (Å)	ψ_2 (deg)
acacen-model adduct									
ligand orientation a: gauche	44.1	0.0	umbrella	2.2	17.9	19.9	−0.23	0.37	2.0
ligand orientation b: gauche	41.5	0.0	stepped	6.2	14.5	8.8	−0.34	0.23	0.9
ligand orientation b: cis	0.0	0.0	umbrella	7.0	7.0	14.1	0.26	0.26	0.0
ligand orientation c: gauche	46.4	0.0	stepped	2.7	16.4	14.5	−0.31	0.33	2.1
CH$_3$O·Co(salen)(pyr): expt[a]	43.0	0.0	umbrella	4.0	15.5	17.0	−0.40	0.27	3.2
Cu(salen)CHCl$_3$: expt[b]	41.3	0.1	stepped	6.5	16.9	12.1	−0.44	0.12	2.7

[a] Reference 49. [b] Reference 50.

Table 7. Summary of Optimized Geometry and Binding Energy for Substituted Co(acacen)(pyridine)(O$_2$) Models

	E_{bind} (kJ mol^{-1})	Co−O (Å)	O−O (Å)	Co−O−O (deg)
H adduct	−49.1	1.92	1.28	117
Me adduct	−59.4	1.91	1.29	117
F adduct	−29.7	1.98	1.26	118

**Table 8.** Summary of Calculated Charges for the Optimized Geometry of Substituted Co(acacen)(pyridine)(O$_2$) Models

	$q(Co)$[a]	$q(N_{ac})$	$q(O_{ac})$	$q(N_{pyr})$	$q(O_1)$[b]	$q(O_2)$[b]
H complex	1.25	−0.91	−0.67	−0.38		
H adduct	1.85	−1.01	−0.76	−0.52	−0.26	−0.26
Me complex	1.14	−0.93	−0.68	−0.38		
Me adduct	1.64	−1.03	−0.76	−0.44	−0.27	−0.28
F complex	1.17	−0.99	−0.67	−0.39		
F adduct	1.36	−1.04	−0.70	−0.37	−0.16	−0.15

[a] Charges calculated using CHelpG scheme.[38] [b] The numbering is such that Co−O$_1$−O$_2$ is the bonding sequence.

approximately bisect the N−Co−O bond angle. One of the few exceptions is the structure of Co(salpeen)(O$_2$) (salpeen = 1,6-bis(2-hydroxyphenyl)-2,5-diaza-3-[2-(2-pyridyl)ethyl]-1,5-hexadiene), where the use of a five-coordinate Schiff's base imposes the constraint that the pyridyl group lie on the bisector of the N−Co−N bond angle.[34] However, the dioxygen orientation has often been difficult to determine due to disorder in the crystal structure. For example, Calligaris and co-workers[26] could not distinguish between the Co−O−O plane bisecting the N−Co−N angle or the O−Co−O angle in Co(acacen)(pyridine). Although the structure of Co(bzacen)(benzene)(O$_2$) (bzacen = 1,10-dihydroxy-1,10-diphenyl-3,8-dimethyl-4,7-diaza-1,3,7,9-decatetraene) shows the dioxygen bisecting the N−Co−N angle,[27] the majority of other crystal structures have the dioxygen lying in the same plane as the axial base and bisecting the N−Co−O angle. Since either of the two possible Co−O−O orientations allows good overlap between the π^* orbitals of molecular oxygen and the d orbitals on cobalt, it has been postulated that the driving force for the observed orientation is controlled by steric interactions either between the O$_2$ and atoms in the same molecule (for example, methyl substitution on the ethylene bridge[36]) or by intermolecular interactions in the crystal.[30]

To investigate the relative energetics of the various orientations, two further calculations corresponding to different orientations were performed on our simple Co(acacen) models. Figure 5 illustrates the orientations that were considered. Figure 5a represents the original orientation from the previous calculations. In the absence of other effects, it might be expected that the configuration with the least steric hindrance would be that with both the pyridine and dioxygen lying between the two halves of the acacen ligand as in Figure 5b. Finally we also consider the orientation obtained from crystal structures involving substituted salen ligands (Figure 5c).

The results of full geometry optimization calculations with these three cases are summarized in Table 4. As can be seen from the table, orientation b is calculated to have the lowest

(a) Co(acacen)(pyridine)(O$_2$)

(b) Co(salen)(pyridine)(O$_2$)
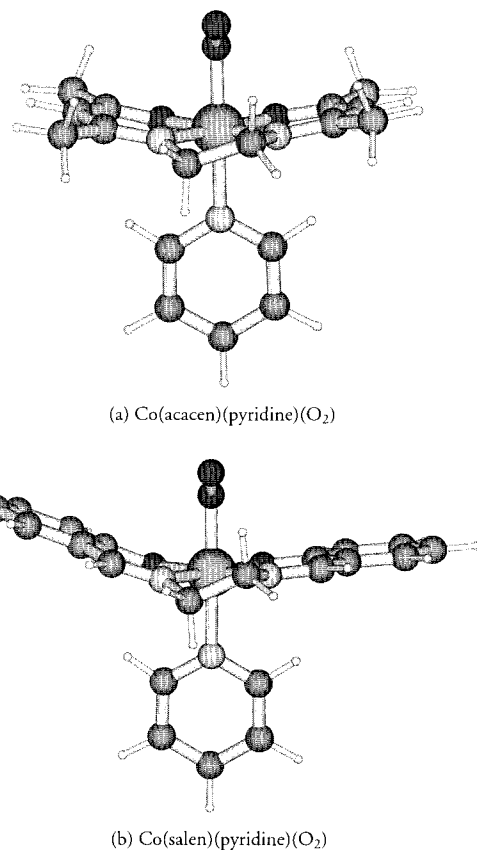
Figure 7. Calculated optimized structures for cobalt Schiff's base complexes.

energy, but it can be noted that it does have a lower binding energy for dioxygen than orientation a. Presumably the extra effects of intermolecular interactions in the solid state disfavor b over a. Orientation c is the least favorable of the set. It is likely that the additional steric effects that are present in the more substituted system favor this configuration in those cases.

As was seen in Figure 1, the actual structure of the acacen ligand has an ethylene bridge between the two nitrogen atoms. The conformation of the bridge is closely linked to the relative conformation of the two arms of the acacen ligand. Calligaris and co-workers[45] have quantified the various possible conformations. Two possible ligand conformations are identified for penta- and hexacoordinate complexes: the "umbrella" and "stepped" conformers as illustrated in Figure 6. The conformers can be described in terms of three angles. α and β are the angles between the two arms and the cobalt coordination plane, and γ

(45) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385.
(46) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(47) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3096.
(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

Table 9. Summary of Calculations (Bond Lengths and Angles[a]) on Co(acacen)(pyr) and Co(salen)(pyr) and Their Adducts with Dioxygen

	Co−O$_{ac}$	Co−N$_{ac}$	Co−N$_{pyr}$	Co−O$_2$	O−O	Co−O−O	E_{bind}
Co(acacen)(pyr)	1.91	1.93	2.17				
Co(salen)(pyr)	1.91	1.92	2.08				
expt[b]	1.85(1)	1.87(1)					
expt[b]	1.90(1)	1.90(1)	1.90(1)				
Co(acacen)(pyr)(O₂)	1.92	1.93	2.07	1.91	1.29	118	53.5
Co(salen)(pyr)(O₂)	1.91	1.92	2.08	1.91	1.28	119	46.8
expt[d]			2.15(4)[e]	1.95(5)[e]			
expt[e]			2.02	1.86	1.26(4)	126(2)	
expt[f]							63.1
expt[g]							51.8

[a] Distance in angstroms, angles in degrees, binding energy (E_{bind}) in kJ mol⁻¹. [b] Data taken from crystal structure of Co(acacen)(benzene).[25] [c] Data taken from crystal structure of Co(salen)(pyridine).[28] [d] Data taken from crystal structure of Co(acacen)(pyridine)(O₂).[26] [e] Data taken from crystal structure of Co(bzacen)(pyridine)(O₂).[27] [f] Data for Co(acacen)(pyr) + O₂ from Amiconi and co-workers.[40] [g] Data for Co(salen)(pyr) + O₂ from Amiconi and co-workers.[40]

Table 10. Conformational Data from Calculations for Models of Co(acacen)(pyridine)(O₂) and Co(salen)(pyridine)(O₂) Complexes and Their Comparison with Experiment

structure	ψ_1 (deg)	d (Å)	conformer	α (deg)	β (deg)	γ (deg)	d_1 (Å)	d_2 (Å)	ψ_2 (deg)
Co(acacen)									
complex	45.0	−0.2	umbrella	3.0	12.1	13.1	−0.24	0.37	3.4
adduct	32.6	0.0	umbrella	7.4	15.1	22.4	−0.07	0.37	0.8
Co(salen)									
complex	45.7	−0.2	umbrella	3.2	15.2	16.8	−0.28	0.36	3.8
complex: expt	0.0	−0.2	umbrella	14.4	14.4	28.8	0.05	0.05	0.0
adduct	46.1	0.0	umbrella	3.1	23.9	26.8	−0.19	0.41	1.8
CH₃O·Co(salen)(pyr): expt[a]	43.0	0.0	umbrella	4.0	15.5	17.0	−0.40	0.27	3.2
Cu(salen)CHCl₃: expt[b]	41.3	0.1	stepped	6.5	16.9	12.1	−0.44	0.12	2.7

[a] Reference 49. [b] Reference 50.

is the book angle between arms. In addition, the ethylene bridge can be described in terms of two distances d_1 and d_2 of the carbon atoms from the coordination plane and the CH₂−CH₂ torsion angle, ψ_1. In addition, the dihedral angle between the N−O−O−N series of atoms (ψ_2) measures the degree of distortion of the cobalt coordination plane from planarity. One additional distance, d, measures the distance of cobalt from the central plane. This work found that a symmetrical umbrella structure (that is, $\alpha = \beta$) leads to a cis conformation for the ethylene bridge, whereas a stepped conformation favors the "half-chair" gauche conformation (a symmetrical displacement of carbon atoms above and below the coordination plane). Any distortion from the symmetrical structure causes the gauche conformer to be observed.

It might be expected that the presence of the ethylene bridge in the acacen ligand would destabilize any structure with dioxygen in an orientation bisecting the N−Co−N bond angle due to steric repulstion between the bridge and dioxygen. To examine this possibility, the basic acacen models were modified to include the ethylene bridge and the calculations repeated. Calculations were performed with the bridge in the gauche conformation on ligand orientations a−c as defined in Figure 5; this necessarily requires breaking of the C_s space group symmetry used in the previous calculations. For comparison, a calculation was performed on the model with ligand conformation b and a cis bridge. A summary of the geometrical and thermochemical data for these calculations is given in Table 5. It can been that the expected trend is observed for ligand orientation a, but in the other two cases, a more favorable binding energy is observed. The most favorable change is for orientation c, where dioxygen lies approximately parallel to the bridge. In addition, comparing the total energies rather than the binding energies of the two ethylene bridge conformations for ligand orientation b, the gauche conformer is found to be more stable by ca. 12.5 kJ mol⁻¹ as would be expected from steric arguments.

The book angles and other structural data related to the relative conformation of the arms of the acacen ligand were calculated for the minimized structure, and the results are summarized in Table 6.

As has been noted previously, the lack of structural data makes a direct comparison with experiment difficult. Data are presented for two salen-type structures without dioxygen coordinated. The range of our calculated structural values is similar in magnitude to that observed in the experimental studies. We can note that the conformer with a cis conformation for the ethylene bridge produces a symmetrical umbrella structure. The most energetically stable structure prefers to adopt the stepped conformation however, although the reasons for this preference are not obvious on steric grounds. More book angle data will be examined later in this paper.

B. Substituent Effects. It has been postulated that the affinity that a given Schiff's base complex has for dioxygen is dependent on the available charge density on cobalt. For example, the Co-(acacen) complex has an oxygen affinity roughly four times greater than the analogous Co(salen) complex, the common explanation for which is that the presence of the extended conjugation system in the salen ligand reduces the charge density at oxygen and reduces the binding energy.

To test this hypothesis within our simple acacen model, two further calculations were performed with substituents placed at the carbons adjacent to N and O on the acacen ligand. We chose one electron-withdrawing substituent (F) and one electron-donating substituent (Me, as in the acacen ligand itself). The geometry and binding energy are given in Table 7. The calculated partial charges are given in Table 8. As can be seen from the results, the binding energies do indeed follow the

(49) Cesari, M.; Neri, C.; Pergo, G.; Perrotti, E.; Zazzetta, A. *J. Chem. Soc., Chem. Commun.* **1970**, 270.
(50) Gerloch, M.; Mabbs, F. E. *J. Chem. Soc. A* **1967**, 1598.

predicted trend, although the change in going from H to Me is somewhat less than expected. The Co−O bond length appears to correlate quite well with the computed binding energy as does the O−O bond length. However, the Co−O−O bond angle appears to be less sensitive to the substituents. These results are in contrast to a series of crystal structure determinations based on the Co(salen) system with a variety of substituents with differing electron-donating/withdrawing properties that failed to elucidate any obvious trends of the functional groups on the Co−O and O−O bond lengths.[30,32,33,35,36] From Table 8, it can be seen that the replacement of H by Me results in a reduction in charge on cobalt and has relatively little effect on the charges of the atoms of the acacen ligand. This trend is not seen for the fluorinated ligand though. It would be expected that the charge on cobalt would be increased by this substituent; it is slightly decreased compared to the parent complex. There is a slight increase in the negative charge on the acacen ligand, however. In each of the cases, when dioxygen binds to the complex, the charge on cobalt is increased as electron density shifts to the dioxygen molecule. This charge transfer appears to be greatest for H and least for F, due to the electron-withdrawing properties of fluorine.

Results on More Realistic Complexes: Co(acacen) and Co(salen). Although the use of model complexes allows more rapid computation and can be used to elucidate many of the structural trends in these complexes, the treatment of the full adducts and complexes for acacen and salen systems is now well within the bounds of current computational resources. The final calculations presented here are performed on the full acacen and salen complexes with no symmetry constraints imposed. The optimized structures are shown in Figure 7. A summary of the structural data is given in Tables 9 and 10. From the results presented in previous sections for acacen complexes, we recall that the introduction of an ethylene bridge reduces the dioxygen binding energy, whereas the addition of methyl substituents increases the binding energy. Since the full acacen ligand structure incorporates both of these structural characteristics, we would expect the computed binding energy to be a balance of these two factors. The computed binding energy for the full acacen model is 53.5 kJ mol^{-1}, which is slightly greater than for the model structure (49.1 kJ mol^{-1}). By comparison, the binding energy for the full salen model is 46.8 kJ mol^{-1}, which is consistent with the greater dioxygen affinity for the acacen complex.

It is interesting to note that both the minimized structures for the acacen and salen complexes are asymmetric (in that α ≠ β) umbrella structures; the source of this asymmetry is not obvious from simple steric arguments, but it would be expected that the presence of the ethylene bridge would have some effect. In both the acacen and salen systems, the book angles open significantly on binding of dioxygen.

Conclusion

In this paper we have presented the first studies of cobalt−dioxygen complexes of Schiff's base ligands in which the molecular geometries were fully optimized using accurate electronic structure techniques. Both model complexes have been examined where the effects of substituents were systematically varied as well as realistic complexes—Co(acacen) and Co-(salen)—along with their dioxygen adducts. The B3LYP functional provides an accurate description of the geometries and dioxygen binding energies of these complexes. The subtlety of conformational energetics is not well reproduced, however, with the current level of theory.