Molecular Orbital Study of a Cobalt Reversible Oxygen Carrier

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Abstract: MO-LCAO calculations of ground-state electronic structure of Co(acacen), Co(acacen)NH_3, Co(acacen)O_2, and Co(acacen)(NH_3)O_2 have been carried out within the INDO-UHF approximation. The distribution of the unpaired electron obtained from these calculations is in good agreement with experimental spectroscopic data. The most important observations are related to the fact that the addition of an axial ligand, such as NH_3, shifts the spin density from the d_{yz} to d_{z^2} orbital; molecular O_2 interacts with such a spin density to produce an oxygenated compound where the coordinated O_2 resembles the dioxygen molecule more than the ionic O_2^- species.

Introduction

There is considerable interest in cobalt models of respiratory pigments which transport molecular oxygen in the biological systems.[1-3] A large variety of tetradentate Schiff base complexes of cobalt(II) undergo reversible binding of molecular oxygen, thus producing cycles of oxygenation-deoxygenation.

Despite the large amount of experimental and spectroscopic work on the latter complexes, the discussion of the electronic origin of cobalt reactivity with dioxygen has been always rather qualitative.[1,4,5] As a matter of fact the theoretical description of the ground and excited electronic states of square-planar and pentacoordinated cobalt(II) complexes with tetradentate Schiff bases have been based, up to now, on calculation models which are not particularly suitable for covalent metal complexes.[6,7] The molecular orbital approach would be more suitable for the analysis of the ground state electronic properties of this kind of molecules. However, the large number of atoms and the fact that low spin d^7 cobalt(II) complexes have open shell configurations introduces large computational difficulties for the application of the most sophisticated molecular orbital methods. At the same time the use of more simple empirical methods of the extended Hückel type[8] must be considered with great care, particularly because interelectronic repulsions, which are important in open shell configurations, are completely neglected.

We have carried out an INDO-UHF calculation[9,10] of the ground state of square, planar, pentacoordinated, and oxygenated species related to the complex Co(acacen), where acacenH_2 is the Schiff base obtained from the condensation of ethylenediamine with acetylacetone. This method of calculation, although semiempirical, has the great advantage of partly considering interelectronic repulsions and spin polarization effects. Moreover, this is the first example of the application of this calculation method to inorganic molecules of this type.

The Molecular Orbital Approach

The INDO-UHF[9,10] approximation requires the iterative solution of the matrix equations

$$F^\alpha C^\alpha = E^\alpha C^\alpha \quad F^\beta C^\beta = E^\beta C^\beta \tag{1}$$

where F is the Hartree-Fock matrix whose elements are defined as follows:

$$F_{ii}{}^\alpha = H_{ii} + \sum_{j\in A} R_{jj}(iijj) - R_{jj}{}^\alpha(ijij) + \sum_{B\neq A}\sum_{j\in B} R_{jj}(iijj) \quad i \in A \tag{2}$$

$$F_{ij}{}^\alpha = (2R_{ij} - R_{ij}{}^\alpha)(ijij) - R_{ij}{}^\alpha(iijj) \quad i,j \in A \tag{3}$$

$$F_{ij}{}^\alpha = H_{ij} - R_{ij}{}^\alpha(iijj) \quad i \in A, j \in B \tag{4}$$

In eq 2, 3, and 4 the symbols have their usual meaning. The matrices of total and spin density are defined as follows:

$$R = R^\alpha + R^\beta \quad \text{and} \quad D = R^\alpha - R^\beta \tag{5}$$

The evaluation of core integrals is based on the following assumptions:

$$H_{ii} = U_i + \sum_{B\neq A} Z_B\gamma_{AB} \quad i \in A \tag{6}$$

$$H_{ij} = S_{ij}\beta_{AB} \quad i \in A, j \in B \tag{7}$$

In eq 6 γ_{AB} is the mean value of the two-center coulomb integrals calculated according to Nishimoto and Mataga;[11] in eq 7 β_{AB} is the mean value of empirical atomic parameters according to Pople[9] and Clack.[12] The values of Oleari et al.[13] for U_i and two-electron monocentric integrals have been used. The monocentric exchange integrals have been calculated from Slater-Condon parameters.[14] As a matter of fact, the evaluation of basic integrals is slightly different from that originally proposed in the INDO approximation.[9] However, this fact does not seem to introduce any particular inconsistency. We have verified in the case of small organic molecules and radicals that our method gives satisfactory results. The INDO-UHF method has the advantage over other similar approximations of readily permitting the evaluation of spin density. However, the UHF method gives only eigenfunctions which are linear combinations of different spin states. In order to produce eigenfunctions with eigenvalues of S^2 not too far from the pure spin state value, we have used the "single annihilation operator" technique.[15]

The density matrices for the s state, after annihilation of the $s + 1$ component, are given by the following equations:

$$R'^\alpha = R^\alpha - (R^\alpha R^\beta R^\alpha - \tfrac{1}{2}R^\alpha R^\beta - \tfrac{1}{2}R^\beta R^\alpha)/x \tag{8}$$

$$R'^\beta = R^\beta - (R^\beta R^\alpha R^\beta - \tfrac{1}{2}R^\alpha R^\beta - \tfrac{1}{2}R^\alpha R^\beta)/x \tag{9}$$

where we have the following definition of x:

$$x = (s+1)(s+2) - \tfrac{1}{4}(N^\alpha - N^\beta) - \tfrac{1}{2}(N^\alpha + N^\beta) + \mathrm{tr}R^\alpha R^\beta \tag{10}$$

In this latter equation N^α and N^β are the number of electrons of different spin. The idempotency of the density matrices has been restored, before the annihilation procedure, by the following iterative relation:[16]

$$R_{i+1} = R_i{}^2(3I - 2R_i)$$

Molecular orbitals have been constructed on the basis of atomic orbitals of the type "single zed" Slater functions, with the exponents proposed by Clementi[17] for the first-row atoms

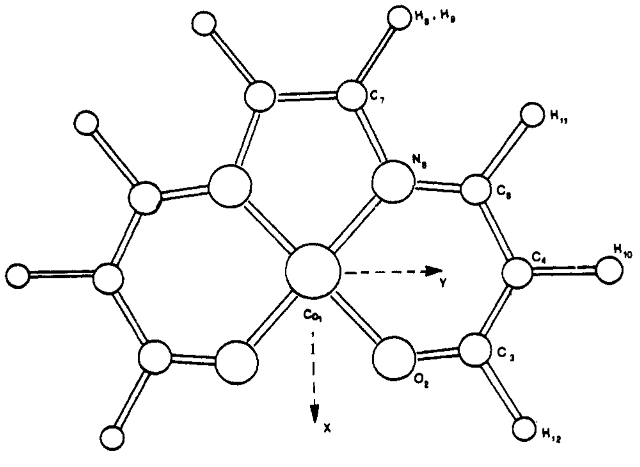

Figure 1. Numbering scheme of the atoms of Co(acacen).

and by Gouterman[18] for the first transition series. The calculation method reported in this paper, although semiempirical, has the advantage of requiring a relatively short computation time, which makes it suitable for the study of relatively large and complex molecules such as those in which we were interested. At the same time it is based on assumptions which are theoretically better established than those of other semiempirical methods of comparable computational difficulty.

Results

Orbital energies, electron densities, and spin densities have been calculated by the procedure described above in the case of square-planar Co(acacen), pentacoordinated Co(acacen)NH_3, and the two oxygen adducts Co(acacen)O_2 and Co(acacen)$NH_3(O_2)$. In order to reduce the computational effort, we have substituted the methyl group with hydrogen atoms, as reported in Figure 1.

Co(acacen). The symmetry of this complex has been approximated to C_{2v} although the x-ray analysis has shown that the CH_2-CH_2 bridge of the diamine is slightly distorted from planarity.[19] Sixty-seven valence orbitals have been considered, producing a molecular orbital arrangement where the 37 α electrons are described by $15a_1$, $5b_1$, $5a_2$, and $12b_2$ molecular orbitals and the 36 β electrons are described by $15a_1$, $5b_1$, $4a_2$, and $12b_2$ molecular orbitals. The d orbitals of the metal belong to a_1 (d_{z^2}, $d_{x^2-y^2}$), b_1 (d_{xz}), a_2 (d_{yz}), and b_2 (d_{xy}) irreducible representations, while the ligand orbitals belong to a_1 and b_2 (type σ_L) and b_1 and a_2 (type π_L) irreducible representations. Considering the monoelectronic energies we have evaluated the ionization potentials, which agree not too badly with the photoelectron spectrum of Co(acacen). The latter point has already been discussed in some detail in a preliminary communication.[20]

The main conclusions are that the first ionization potential involves the pseudoaromatic electronic system of the ligand, while ionizations involving d metal orbitals are at much higher energies (Figure 2). Such behavior is similar to that observed for Ni(acacen) and Cu(acacen).[21] The analysis of spin distribution shows that the spin density is highest in the d_{yz} orbital of the cobalt atom, being nearly zero in the ligand orbitals (Table I). This conclusion is in disagreement with that based on an extended Hückel-type[22] calculation. In this latter case the unpaired electron is not only localized in the d_{z^2} metal orbital, but also lies in the occupied level of higher energy, a conclusion which is completely in disagreement with the data of the photoelectron spectrum.

The rather unusual localization of the unpaired electron in an orbital of lower energy arises from the electronic repulsion terms which are considered in the INDO approximation, while they are completely neglected in the extended Hückel theory. It must be pointed out that in the case of open shells, as a d^7 low-spin cobalt(II) complex, the electron repulsion cannot be neglected. The localization of the maximum spin density in the d_{yz} orbital arises from the spin polarization process which differentiates the $4a_2$ (d_{yz} of the metal) molecular orbital of the spin α set from the equivalent $4a_2$ molecular orbital of the spin β set which is virtual. Molecular orbitals of energy lower than −15 eV are mainly composed of ligand orbitals and are coincident in the α and β sets. Molecular orbitals of irreducible representations a_1, b_1, and b_2 in the energy gap between −15 and −7 eV are split very little, thus producing a certain equivalence of the two density matrices. It is of interest to point out that a completely similar conclusion can be obtained when the problem is simplified by considering only the CoN_2O_2 atomic arrangement. In this simplified model the calculation has been carried out by using the CNDO Hamiltonian.[9] The two-center coulomb and nuclear attraction integrals have been calculated analytically and the empirical parameters β have been substituted by valence-state ionization energies. The open-shell system has been treated by the "restricted Hartree-Fock" method. The density matrix of the open shell has diagonal elements different from zero only for the a_2 symmetry

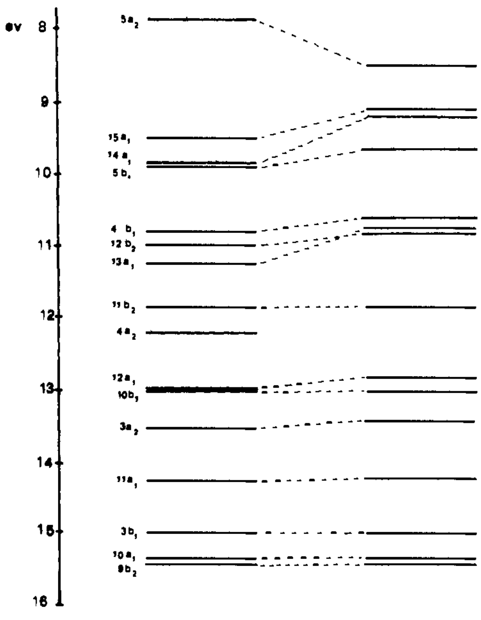

Figure 2. Monoelectronic energy levels (eV) above 16 eV for Co(acacen).

Table I. Spin Density Distribution in Co(acacen)[a]

	Orbitals			
Atom	*s*	*x*	*y*	*z*
1 Co[b]	0.0016	0.0008	0.0024	0.0045
2 O	−0.0008	−0.0042	−0.0007	0.0076
3 C	−0.0002	0.0000	−0.0002	−0.0022
4 C	0.0003	0.0001	0.0001	0.0049
5 C	−0.0002	0.0001	−0.0001	0.0005
6 N	−0.0018	−0.0036	−0.0020	0.0005
7 C	0.0000	−0.0004	0.0000	0.0000
8, 9 H	0.0001			
10 H	−0.0001			
11 H	−0,0009			
12 H	−0.0006			

[a] The numbering of the atoms is reported in Figure 1. [b] For Co, z^2 = 0.0006, xz = 0.0042, yz = 0.9683, $x^2 - y^2$ = 0.0004, xy = 0.0234.

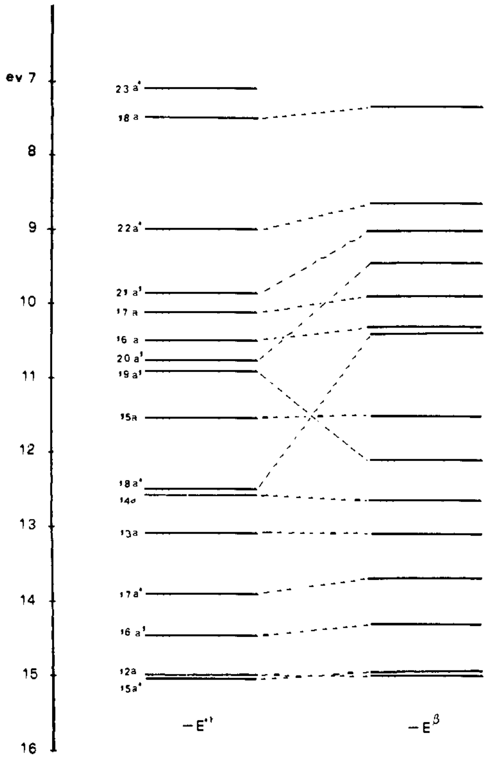

Figure 3. Monoelectronic energy levels (eV) above 16 eV for Co(acacen)NH_3.

block. The following values of diagonal elements have been calculated: 0.9661 (d_{yz}), 0.0437 (π_N), 0.0002 (π_O). They are not too far from the spin density values calculated considering the full set of valence orbitals (Table I). The localization of the unpaired electron in the d_{yz} metal orbital is in agreement with the results of EPR spectral analysis.

The exact assignment of the g values has been recently reported[23] from studies in nematic phase; this assignment is in agreement with that obtained in the case of Co(salen) from a single-crystal ESR investigation.[24] A very recent single crystal ESR investigation of Co(acacen) has been carried out.[25] Assuming that the unpaired electron is localized in the d_{yz} orbital, we have obtained, by the well-known first-order perturbation method,[26] the values of the ESR parameters reported in Table III.

Co(acacen)NH_3. It is well known that square-planar Co(II) complexes with tetradentate Schiff base add a ligand in an axial position, thus producing pentacoordinated compounds. Such a process is relevant for the reversible oxygenation reaction.[27] We have carried out our calculations on a molecule related to the well-characterized complex Co(acacen)-pyridine by substituting pyridine with ammonia. This would assume that substitution of pyridine with ammonia does not produce relevant quantitative changes in the electronic properties of the pentacoordinated complexes.

Such an assumption is supported by the fact that reversible oxygenation can be carried out in the presence of a series of different bases without evident differences in the enthalpy terms of the reversible addition reaction.[28] The point group symmetry of Co(acacen)NH_3 has been taken as C_s with the cobalt atom 0.2 Å above the ligand plane toward ammonia, in agreement with the known structure of Co(acacen)py.[29] In this symmetry the s, p_z, and d_{z^2} orbitals of the metal interact with π-type orbitals of the chelated ligand. This means that σ and π orbitals cannot be considered as separate. Seventy-four valence orbitals have been considered, producing a molecular orbital arrangement where 41 α electrons are described by 23 a′ and 18 a″ molecular orbitals and 40 β electrons by 22 a′ and 18 a″ molecular orbitals. The analysis of one-electron energy levels has shown (Figure 3) that the splitting produced by the spin polarization process is centered on the a′ irreducible representation to which belongs the d_{z^2} metal orbital where the maximum density of spin is localized (Table II).

Such a result is completely in agreement with the ESR data reported in the case of numerous pentacoordinated complexes derived from Co(acacen). We have analyzed in detail the effect of the electronic perturbation produced by the ammonia ligand along the axial direction. In order to do that, calculations have been carried out with the nitrogen atom of the ammonia molecule at 1.9, 2.2, and 2.5 Å, respectively, from the cobalt atom. In each case it has been observed that the total spin density localized on d cobalt orbitals is not increased with respect to that calculated in the case of Co(acacen). However, a larger localization in the d_{z^2} orbital of axial symmetry is observed. As a matter of fact an interesting observation is associated with the dependence of spin density on the cobalt-nitrogen distance. Decreasing the latter distance gives rise to two concomitant effects: a larger charge transfer from ammonia to cobalt and a larger spin transfer from the cobalt to the nitrogen atom (Table II). Both processes take place through a σ-type interaction. As a consequence the spin density in these complexes cannot be related to the strength of the donor properties of the axial ligand, but only to transfer and polarization mechanisms which are not related directly to donation from the axial base. From the calculated spin density on the 2s orbital of the ammonia nitrogen, we have evaluated the hyperfine coupling constant with the ^{14}N nucleus; at the three different distances the following values of A_{iso} have been obtained: 8.76, 4.97, 2.92 G.

The hyperfine coupling with ^{14}N in complexes of Co(acacen) with nitrogen donors has been observed only in the parallel resonance line and it is about 15 G; the couplings in the other two directions of the magnetic field are <1 G. Assuming that the dipolar contribution is very small, the value of A_{iso} for ^{14}N can be calculated to be about 5 G. In our calculations such a value would correspond to a cobalt-nitrogen distance of 2.2 Å, which is close to that observed in similar pentacoordinated complexes (e.g., Co(acacen)py[29]). Our results are also in agreement with the observed absence of any coupling with the nitrogen atoms of the chelating ligand which lie in the xy plane. In fact, from the spin density distribution reported in Tables I and II we can safely say that such a coupling must be always less than 1 G. Finally the increase of spin density localized in the 4s cobalt orbital on going from aquare-planar geometry to pentacoordination (Tables I and II) is worth mentioning. For a distance of 2.2 Å between cobalt and ammonia a spin density as high as 0.022 is calculated. We have been able to reproduce quite nicely the observed ESR parameters of Co(acacen)py (see Table III). In the fitting of ESR data of the related square-planar complex Co(acacen), similar values of the P and K constants have been used, with the only exception of the Fermi constant k, which was taken equal to 0.1. Such a decrease of the Fermi constant, together with the value of A_{iso} (^{59}Co) for the free ion,[30] would produce[31] a calculated spin density of 0.03-0.04 on the 4s cobalt orbital, in rather good agreement with our calculated value of about 0.02 (Table II).

Oxygen Adducts. The addition of an oxygen molecule to the pentacoordinated cobalt complexes has been interpreted mainly as a charge-transfer process.[4] However, a different approach can also be considered by assuming that the addition reaction can be interpreted mainly as a spin coupling between two interacting nonzero spin systems. Of course this latter model is considered as approximate because a certain amount of charge transfer takes place in the same time. It is known[32] that in the case of the collision of two nonzero spin systems (S_a and S_b), all the spin states between $S_a + S_b$ and $|S_a - S_b|$ can be reached; however, the state of higher multiplicity cannot

Table II. Spin Density Distribution in Co(acacen)NH_3[a]

	Orbitals								
Atom	s	x	y	z	z^2	xz	yz	x^2-y^2	xy
1 Co	0.0106	0.0012	0.0012	0.0175	0.8890	0.0026	0.0004	0.0005	0.0221
	0.0217	0.0014	0.0014	0.0102	0.9254	0.0028	0.0002	0.0005	0.0231
	0.0230	0.0023	0.0022	0.0038	0.9464	0.0033	0.0002	0.0006	0.0367
2 O	−0.0005	−0.0014	−0.0003	0.0093					
	−0.0009	−0.0010	−0.0003	0.0020					
	−0.0014	−0.0043	−0.0010	0.0015					
3 C	0.0002	0.0000	−0.0001	−0.0010					
	0.0003	0.0000	0.0000	−0.0009					
	0.0002	0.0000	−0.0001	−0.0012					
4 C	0.0004	0.0000	0.0001	0.0033					
	0.0000	0.0000	0.0001	0.0006					
	0.0006	0.0000	0.0001	0.0020					
5 C	0.0004	0.0001	0.0003	0.0024					
	0.0004	0.0001	0.0002	0.0000					
	0.0003	0.0001	0.0001	−0.0002					
6 N	−0.0012	−0.0023	−0.0013	−0.0011					
	−0.0014	−0.0021	−0.0012	−0.0002					
	−0.0026	−0.0043	−0.0026	−0.0008					
7 C	0.0003	0.0000	−0.0001	0.0000					
	0.0004	−0.0001	−0.0001	0.0000					
	0.0004	−0.0005	−0.0001	0.0000					
8 H	0.0000								
	0.0001								
	0.0002								
9 H	0.0002								
	0.0000								
	−0.0001								
10 H	−0.0001								
	0.0000								
	0.0000								
11 H	−0.0004								
	0.0002								
	−0.0008								
12 H	0.0001								
	0.0003								
	−0.0002								
13 N	0.0231	0.0010	0.0010	0.0016					
	0.0132	0.0007	0.0007	−0.0002					
	0.0086	0.0008	0.0008	−0.0016					
14, 15 H	0.0016								
	0.0019								
	0.0008								
16 H	0.0051								
	0.0020								
	0.0008								

[a] The numbering of the atoms is reported in Figure 1. For each atom the first, second, and third entry refers, respectively, to the CoN_{ax} distance equal to 1.9, 2.2, and 2.5 Å. The atoms 13, 14, 15, and 16 form the ammonia molecule.

Table III. ESR Parameters for Co(acacen) and Co(acacen)py[a]

	g_{zz}	g_{xx}	g_{yy}	A_{zz}, cm^{-1}	
Co(acacen)	2.04 (2.01)	3.17 (3.16)	2.00 (1.93)	−55.0 (35.9)	
Co(acacen)py	2.00 (2.012)	2.55 (2.435)	2.28 (2.225)	101.8 (92.3)	
	A_{xx}	A_{yy}	P, cm^{-1}	k[b]	K[b]
Co(acacen)	106.0 (115.8)	−25.0 (37.5)	0.0200	0.1	1.0
Co(acacen)py	65.7 (56.2)	24.3 (12.5)	0.0160	−0.15	1.0

[a] The experimental values in parentheses are taken for Co(acacen) from ref 35 and for Co(acacen)py from ref 23. [b] k is the Fermi constant and K is the Stevens constant.

participate in bond formation between the two interacting systems, while in the case of the state of lower multiplicity we have a concomitant charge transfer into the region of bonding. Such a transfer is directly related to the orbital overlap of the two fragments in which the spin density is localized. Such an interaction, which can be considered an antiferromagnetic type interaction, can be measured by the S^2 operator. When this eigenvalue is far from the theoretical value corresponding to the pure spin state of lower multiplicity, we are in a situation in which the coupling between the two fragments is very weak, corresponding to a very weak bonding interaction. We have thus applied this kind of calculation in the case of two complexes, Co(acacen)(NH_3)O_2 and Co(acacen)O_2, where the oxygen molecule interacts in a bent way with the cobalt atom. The Co-O and O-O distances have been taken as 1.86 and 1.26 Å, respectively, while the Co-O-O angle has been taken as 126°.[33,34]

The results reported in Table IV support the localization of the maximum spin density in the orbitals of the dioxygen. The original $\pi_g{}^z$ molecular orbitals of dioxygen strongly σ-interact with d_{z^2} orbital of cobalt and very weakly, in a pseudo π type of bonding, with the d_{xz} orbital; the $\pi_g{}^y$ molecular orbital displays only a π-type interaction with the d_{yz} orbital of cobalt. Our calculations give a value of 0.7641 for the eigenvalue of the S^2 operator, in agreement with a strong bonding interaction between the cobalt atom and the oxygen molecule. Magnetic coupling takes place between the unpaired electron originally localized on the d_{z^2} orbital of the cobalt atom and the $\pi_g{}^z$ orbital of dioxygen. In this mechanism the higher spin density of the oxygen adduct remains on the $\pi_g{}^y$ orbital of dioxygen. A very weak spin density (−0.086) also remains on the d_{z^2} cobalt orbital, corresponding to the very low coupling experimentally observed in all these oxygen adducts of cobalt complexes.[4,5] Such a mechanism of spin coupling gives rise to a relatively weak charge transfer of about 0.3 electron from cobalt to dioxygen.

When the related dioxygen adduct Co(acacen)O_2 is considered, we have a completely different situation, which could explain the necessity of a donor base in the axial position to produce this kind of bonding between cobalt and dioxygen. Following our approach of magnetic exchange between two interacting systems, we must assume that the spin density of

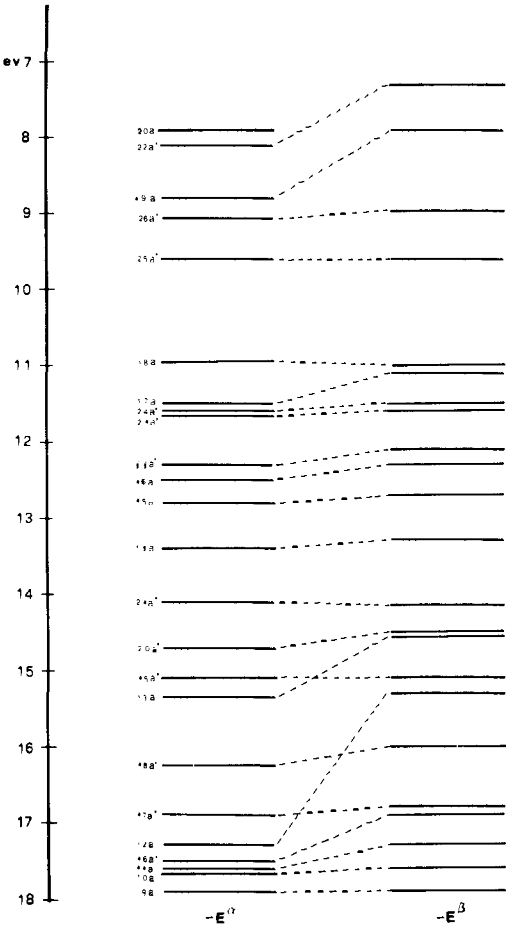

Figure 4. Monoelectronic energy levels (eV) above 18 eV for Co(acacen)$(NH_3)O_2$.

dioxygen interacts with the d_{yz} orbital of cobalt, where we have shown the higher spin density in the initial complex Co(acacen) to be localized. Assuming a bent bonding of dioxygen, we have only a very weak interaction of π type, corresponding to a weak spin coupling and a negligible charge transfer in the bonding region (Table V). Our self-consistent calculation produces an eigenvalue of S^2 of 1.1296, which is a value rather far from the theoretical doublet value. A total spin density of 1.36 electrons is localized on the oxygen moiety, while a spin density of −0.397 is on the d_{z^2} orbital of cobalt. In brief such a situation corresponds to a very weak bonding interaction between the cobalt atom and the dioxygen molecule.

Table IV. Spin Density Distribution in Co(acacen)$(NH_3)O_2$[a]

Atom	Orbitals *s*	*x*	*y*	*z*
1 Co[b]	−0.0028	−0.0007	−0.0009	−0.0041
2 O	0.0001	0.0023	0.0004	−0.0004
3 C	−0.0001	−0.0001	−0.0001	−0.0004
4 C	0.0000	0.0000	0.0000	0.0001
5 C	−0.0001	−0.0001	0.0000	−0.0007
6 N	0.0010	0.0026	0.0016	0.0014
7 C	0.0000	0.0001	0.0000	0.0000
8 H	0.0000			
9 H	0.0003			
10 H	−0.0001			
11 H	0.0004			
12 H	0.0002			
13 N	−0.0013	0.0000	0.0000	0.0012
14, H	−0.0002			
15				
16 H	−0.0004			
17 O	0.0110	0.0067	0.3794	0.0428
18 O	0.0078	−0.0025	0.6106	0.0197

[a] The numbering of the atoms is reported in Figure 1. The atoms 13, 14, 15, and 16 form the ammonia molecule. The atom 17 O is bonded to the cobalt atom. [b] For Co, $z^2 = -0.0816$, $xz = 0.0005$, $yz = 0.0050$, $x^2 - y^2 = -0.0001$, and $xy = -0.0060$.

Table V. Spin Density Distribution in Co(acacen)O_2[a]

Atom	Orbitals *s*	*x*	*y*	*z*
1 Co[b]	−0.0105	−0.0016	−0.0015	−0.0094
2 O	0.0008	0.0043	0.0009	0.0052
3 C	−0.0004	−0.0002	−0.0003	−0.0028
4 C	0.0001	0.0002	0.0001	0.0031
5 C	−0.0004	−0.0003	−0.0002	−0.0030
6 N	0.0029	0.0063	0.0037	0.0104
7 C	−0.0001	0.0002	0.0004	0.0000
8 H	0.0001			
9 H	0.0010			
10 H	−0.0003			
11 H	0.0012			
12 H	0.0004			
13 O	0.0070	0.0708	0.3881	0.1727
14 O	0.0060	0.0169	0.5975	0.1034

[a] The numbering of the atoms is reported in Figure 1. The atom 13 O is bonded to the cobalt atom. [b] For Co, $z^2 = -0.3971$, $xz = 0.0033$, $yz = 0.0079$, $x^2 - y^2 = -0.0002$, $xy = -0.0191$.

Discussion and Conclusion

The result of our calculation are generally in agreement with a series of experimental ESR and PES spectra, thus supporting the main assumption of our molecular orbital approach. In square-planar complexes the unpaired electron is localized mainly in the d_{yz} cobalt orbital. This result is in disagreement with what was previously proposed on the basis of the ligand field analysis of ESR spectra on powders or in nematic phase.[23,35] In previous papers the unpaired electron has been preferentially assigned to the d_{z^2} cobalt orbital. The best assignment of *g* values is related to the investigation in nematic phase; the first-order perturbation analysis of Hoffman et al.[23] has produced the following calculated values (observed values in parentheses): $g_{zz} = 2.00$ (2.01), $g_{xx} = 2.93$ (2.928), $g_{yy} = 2.005$ (1.934), $A_{zz} = 60.7$ (32.8), $A_{xx} = 81.5$ (100.3), $A_{yy} = 47.0$ (32.5), assuming the values $P = 0.0150$ cm^{-1}, $k = 0.1$, and $K = 1$. These latter values do not reproduce too well some of the *A* values together with the observed experimental trend $g_{xx} > g_{zz} > g_{yy}$. Moreover, in order to maintain the unpaired electron in the d_{z^2} orbital a rather low value is required for the coefficient $c = \sqrt{3}\xi/E(yz \rightarrow z^2)$. Assuming the well-known value of 0.4–0.5 kK for the spin-orbit coupling for divalent cobalt, the energy of the transition $E(yz \rightarrow z^2)$ would be higher than 400 kK, a rather unacceptable value. When the unpaired electron is localized in the d_{yz} orbital of cobalt, we not only obtain better agreement with the experimental ESR data, but also one finds that reasonable energies for the electronic transitions can be assumed in the fitting procedure. As a matter of fact, we have preferred to compare our calculation with experimental data obtained from spectra of powders than from spectra in nematic phase. From the x-ray investigation[19] we know that the molecule Co(acacen) is nearly planar in the crystal, while we may presume some weak solvation of the axial coordination position in the nematic phase. To support the latter assumption we have the experimental lowering of g_{xx} from 3.16 to 2.928 on going from the powder to the nematic phase. This is an expected trend when the coordination goes from square-planar geometry to a very weak pentacoordination, and it could explain the need of Hoffman et al. to use such a high-energy transition. The localization of the unpaired electron in the d_{yz} cobalt orbital is not unexpected; in fact, a single-crystal ESR investigation of the related Co(salen) complex has clearly shown that the unpaired electron is contained in the d_{yz} cobalt orbital.[24] Our molecular orbital approach has also indicated that this electronic situation already originates in the square-planar CoN_2O_2 chromophore; the other part of the tetradentate ligand exerts little influence on the relative position of the energy levels of the metal orbitals.

Very recently Dedieu and Veillard[36] have reported on an "ab initio" calculation on Co(acacen) and related pentacoordinated and oxygenated complexes with four different axial bases. In the square-planar complex they have only considered two electron configurations for the ground state, namely those in which the unpaired electron is located in d_{z^2} and $d_{x^2-y^2}$ cobalt orbitals. Obviously they have observed that the lower energy must be assigned to the $d^1{}_{z^2}$ electron configuration. In fact, ligand field calculations[5,6] have already shown that the $d^1{}_{x^2-y^2}$ electron configuration is largely destabilized. It is worth trying to extend this kind of calculation to other configurations, particularly those with the unpaired electron in the d_{yz} cobalt orbital.

In pentacoordinated complexes we have found, as have other authors,[4,23] a large localization of the spin density of the unpaired electron into the d_{z^2} cobalt orbital. We have also observed some electron transfer from the nitrogen atom of the axial base to the cobalt atom. Both phenomena are dependent on the cobalt–nitrogen distance in the axial direction. In the meantime we have pointed out for the first time two observations: the presence of the axial base does not increase the spin density on the metal, which was already high in the original square-planar complex, but it only localizes the spin density into the d_{z^2} cobalt atom orbital; moreover the spin distribution is not related to the electron transfer from the base to the cobalt atom. The latter process parallels the donor strength of the base, while the effect on the spin density distribution is related to polarization and exchange mechanisms which are not dependent on the strength of the base. In conclusion, the effect of the donor base is twofold: to shift the localization of the unpaired electron from the d_{yz} to the d_{z^2} metal orbital and to increase the nucleophilicity of the cobalt atom. The first effect can easily explain the radical reactivity of the cobalt atom, e.g., the easy reaction with oxygen,[37] the radical reaction with alkyl halides,[38] the easy reaction with nitric oxide,[39] and the lack of reaction with carbon monoxide.[40]

The second effect (together with the first) could explain the observed difficulty in achieving hexacoordination at room temperature, a process corresponding to the addition of one more donor base in the trans axial position.[28] However, this could also be due to the weak rigidity of the tetradentate ligand. With more rigid ligands such as phthalocyanines or porphyrins, hexacoordination can be easily reached.[41,42] Previously the only important effect of the addition of a base was related to a larger localization of the unpaired electron in the d_{z^2} orbital on going from square planar to pentacoordination. It appears that our conclusion is more attractive, because it implies a complete special redistribution of the spin density. The interaction of pentacoordinated cobalt complexes with dioxygen does not involve in our calculation a large charge transfer from cobalt to dioxygen, but only a spin-pairing process which produces a large spin density on the oxygen moiety. These results do not agree with previous interpretations in terms of a cobalt oxidation to produce the O_2^- species by a complete transfer of an unpaired electron localized on the cobalt atom[1,43] in the five-coordinate complex.

The decrease of hyperfine coupling A_{iso} with the ^{59}Co nucleus[1] and the observed O-O bond distance[34] of 1.26 Å, which fits well with 1.28 Å of KO_2,[44] were the main experimental support for an O_2^- description. This proposal was also in good agreement with a similar characterization of oxygen chemiadsorbed on metal oxide surfaces (e.g., MgO, TiO_2)[45] as an O_2^- species. However, we have shown that in our approach the lowering of A_{iso} with ^{59}Co can be explained as well by assuming rather strong magnetic interaction of two paramagnetic fragments (e.g., the cobalt atom and the dioxygen molecule), without invoking a delocalization of the cobalt unpaired electron into the dioxygen moiety. Moreover, the observed O-O distance of 1.26 Å does not agree with the value of 1.34 Å, which has been evaluated recently by measurements[46] and by very refined calculations[47] for the gaseous O_2^- species. It is possible that the value of 1.28 Å, observed in the ionic structure of KO_2, must be related to perturbations such as a strong electrostatic polarization in the lattice structure which can not be present in the completely different crystalline packing of the molecular adducts of cobalt complexes. Therefore the observed value of 1.26 Å could be in better agreement with a charge transfer of about 0.3 electron, which is the amount calculated in our molecular orbital approach. In conclusion, our description of the dioxygen moiety bound to cobalt still has a certain character of the initial dioxygen molecule.

In very recent work another description of the bonding has been suggested by using a qualitative molecular orbital approach.[48] The dioxygen bound to cobalt was claimed not to be O_2^- but considered very similar to singlet oxygen on the grounds of some recent experimental studies on O_2, CO, and CH_3NC adducts of the pentacoordinate Co(II) Schiff base complex, Co(salMeDPT). This view was consistent with experimental spectroscopic evidence available at the time but is inconsistent with the results from our molecular orbital calculation. For singlet oxygen, bonding the very low A_{iso} with ^{59}Co found in the dioxygen complex would require a large participation of a p metal orbital, although in a very qualitative picture. It has been shown that the CO adduct does not form.[49] The basic conclusion of Tovrog and Drago that O_2^- is not a correct formulation of the adduct thus rests on the CH_3NC adduct, which behaves as expected for their argument. Interestingly our results are not in contrast with those reached by Dedieu and Veillard in their "ab initio" calculations of the oxygen adducts.[36] In fact, we have the same symmetry of the dioxygen orbital in which the unpaired electron is localized.

The tendency to form dimers, which would support the localization of a negative charge on the terminal oxygen atom, can be explained by assuming an internal excitation to produce a true O_2^- species, which then very quickly dimerizes. To support this view some very recent kinetic studies[50] have shown in the reaction of dimerization the necessity of the preliminary formation of an activated oxygen adduct. Moreover, the observed O-O distance in one dimer, which is 1.339 ± 0.006 Å[51] (in very good agreement with the value of 1.34 Å calculated for the gaseous O_2^-), fits very well with this hypothesis. Of course the problem of the direct evaluation of the real charge density in these oxygen complexes is still open, and more sophisticated spectroscopic work would be necessary in order to settle this important point.

Finally, we have shown that in the absence of a base in the axial position we are in a very unfavorable situation for the magnetic exchange with the dioxygen molecule, which interacts in a bent way with the cobalt atom. This would support the lack of reactivity with dioxygen of the square-planar or weakly pentacoordinated cobalt complexes. It should be expected that, when the unknown $d_{yz} \rightarrow d_{z^2}$ promotion energy barrier is exceeded by an appropriate interaction with external sources of energy, even the square-planar complex could react with dioxygen.

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Localized Molecular Orbital Studies of Chemical Reactions. Deformation, Rearrangement, and Spin Polarization of Bonds Involved in Radical Reactions

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Abstract: Energy-localized molecular orbitals (LMO) generated from UHF-INDO wave functions have been used for the studies of the mechanism of abstraction and addition reactions of doublet radicals. The UHF wave functions for reacting systems have been interpreted in terms of the LMO mapping and the intermolecular configuration interaction. The deformation, rearrangement, and spin polarization of bonds developing with the progress of reaction can most conveniently be visualized in these terms. The whole aspects of the reactions are pictorially demonstrated by tracing the movements of the LMO charge centroids. It is concluded that both reactions appear to proceed by a three-stage mechanism which involves the successive β- and α-spin electron transfers and the concomitant spin polarization associated with particular LMO's. A possible relationship of the proposed mechanism with orbital crossing is discussed.

The formation of chemical bonds has recently been analyzed by several authors[1-3] from a rigorous quantum-mechanical viewpoint. Practically, however, rigorous treatments are not only too tedious to be manageable in general cases, but are often liable to complicate a simple and vivid picture of chemical reactions commonly used by the chemist. Thus, it seems of practical value to seek convenient procedures which could give us chemically meaningful visualization and interpretation of chemical reactions, with the concept of an electron pair bond preserved. Efforts along this line would indeed be