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Theoretical Investigation of the Ground and the Lowest Excited States of Co(SB) Complexes (SB = Schiff Base)

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RHF-plus-correlation calculations have been performed on the ground and the lowest excited states of the complex Co(foracim)$_2$, chosen as a model for Co(SB) complexes (SB = Schiff base). The wave functions thus obtained have been subjected to Mulliken population analysis and analyzed in terms of the orbitals of the separate constituent fragments. The ground state of the isolated complex corresponds to a quartet state of B_1 symmetry, split by the spin-orbit interactions into two Kramers doublets. Assignments are given for the various bands observed in the near-infrared and visible regions.

For a long time tetradentate Schiff base (SB) complexes of transition metals have attracted much interest in the field of coordination chemistry, from both theoretical and experimental points of view. In this context various complexes of Co(II) with planar tetradentate Schiff bases, like acacen, salen, and salophen, have been particularly studied because of their peculiar magnetic properties and spectroscopic characteristics and because of their capability of coordinating reversibly dioxygen.

Among the points of theoretical interest are the characterization of the particular effects related to the large numbers of electrons in these molecules, the analysis of the interaction between the d orbitals of the transition-metal atom and the delocalized π system of the organic ligand, and the prediction of their spectroscopic and magnetic properties. Despite all this, only few ligand field,[1-3] semiempirical,[4] or minimal basis Hartree-Fock[5] calculations have been performed on these systems in the last few years. The most relevant one is the ab initio calculation reported in ref 5, where however a small basis set is used and only a very limited investigation of the various electronic excited states is performed. This is essentially due to the technical difficulties associated with the number of electrons; note also that the electronic correlation energy is usually neglected, although essential in many cases to obtaining the correct energy spectrum.

Such complexes have also been the subject of a large number of experimental investigations concerning their electronic[1-3,6,7] and EPR[8-14] spectra and their magnetic properties.[15,16] However, many characteristics of this class of compounds have not been completely clarified.

The study of the electronic spectrum to identify the d-d transitions in the presence of a ligand field, for example, has encountered difficulties because several bands fall in the near-infrared region with a low intensity while a large part of the visible region is obscured by intense charge-transfer and intraligand ($\pi \rightarrow \pi^*$) transitions. This latter difficulty has been overcome by performing circular dicroism (CD) spectroscopy on optically active similar compounds like for example Co(acac(−)pn) (acacpn = *N,N'*-propane-diylbis(acetylacetone iminate),[2,3] and the results of the interpretation of the near-infrared visible, and CD spectra on this compound are reported in Table III.

As regards the investigation of their magnetic properties, a low-spin ($S = {}^1/_2$) character of these complexes is usually assumed, due to values of μ_{eff} ranging between 2.1 and 2.9 μ_B, which have been interpreted as arising from the presence of one unpaired electron and an apparently large orbital contribution. This is also confirmed by the EPR studies on Co(acacen) in different environments,[8-14] which, with some remaining uncertainties, seem to agree with a doublet spin ground state interacting with the magnetic moment of the ^{59}Co nucleus ($I = {}^7/_2$).

However, it has not been possible to clearly identify the electronic ground state of the Co(SB) complexes from the EPR data, and four possible ground state configurations have been proposed with the unpaired electron described respectively by the $3d_{x^2}$, $3d_{z^2-y^2}$, $3d_{xz}$, or $3d_{xy}$ orbitals (more recent solid-phase EPR studies seem to support the $3d_{xy}{}^1$ configuration[14]).

An accurate quantum-mechanical study of these complexes is therefore quite interesting in order to interpret those properties, like the electronic spectrum and the magnetic features, which are not yet fully understood.

As a first step in this direction, we present in this paper several results of accurate HF-plus-correlation calculations relative to the lowest electronic states of a molecule Co(OCHCHCHNH)$_2$ = Co(foracim)$_2$, chosen as the simplest but at the same time chemically significant model of such complexes. As shown in Figure 1, the (foracim)$_2$ ligand differs from a typical tetradentate SB, like acacen (*N,N'*-ethylenebis(acetylacetone iminate)), in that hydrogen atoms replace the four methyl groups and two iminic groups replace the ethylenediamine bridge. Such a simplified ligand, which has been used also in previous calculations,[5,17,18] is chemically significant, since it presents the main characteristics of the real ligands, while the relative positions and nature of its highest monoelectronic levels should give a realistic picture of the corresponding quantities in the complexes involving larger Schiff bases.

Following the lines of a previous article on a related compound,[18] the purpose of this paper is therefore to characterize at the level of an accurate HF-plus-correlation calculation the electronic and magnetic properties of the ground and a few excited states of the system and to analyze their wave functions in terms of the cor-

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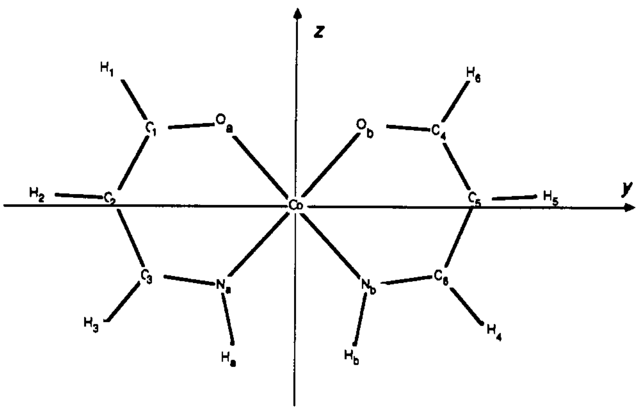

Figure 1. Geometry of the Co(foracim)$_2$ (foracim = formylacetaldehyde iminato = OCHCHCHNH) complex in the *zy* plane.

responding wave functions of the separate fragments.

In comparison with previous calculations on the same system we enlarge the basis set used in the HF calculations, include the lowest excited states of the complex, and evaluate the correlation energy. We think that such points are very important in order to resolve the energy spectrum, which exhibits a relevant number of states quite close in energy.

Computational Details

LCAO-MO-SCF calculations have been performed in the restricted Hartree-Fock (RHF) approximation to derive wave functions for various states of the Co(foracim)$_2$ molecule.

With regard to the geometry of the model complex, we have taken the experimental parameters of Co(acacen) in the solid phase as given in ref 19; they correspond to a planar slightly nonsymmetrical structure, but we have symmetrized them to obtain a C_{2v} molecular geometry, with the axes chosen as shown in Figure 1. The geometrical parameters that concern the hydrogen atoms not present in acacen have been derived from analogous organic molecules and are $R(\text{N-H}) = 1.02$ Å, $R(\text{C-H}) = 1.10$ Å, $\gamma(\text{HCN}) = 110°$, $\gamma(\text{NCH}) = 123°$, and $\gamma(\text{OCH}) = 118°$. Note that in the following calculations we have chosen the (*zy*) plane as the plane that contains the molecule and the *z* axis as the principal axis of symmetry (see Figure 1). Due to this fact, the d-orbital classification differs from the one usually encountered in crystal field theory, the difference consisting simply in exchanging the *x* and *z* coordinates in the d subscripts.

All the calculations have been carried out with a basis set of (14s,9p,6d/11s,6p/5s) spherical Gaussian functions contracted to (8s,4p,3d/4s,2p/2s) for Co, first-row atoms, and hydrogen, respectively. This basis set corresponds to the Huzinaga double-ζ one for hydrogen and the first-row atoms.[20] For cobalt we have used the (14s,9p,5d) basis contracted to (8s,4p,2d) of Watchers,[21] augmenting the p_z set with two diffuse functions ($\alpha_p = 0.24$ and 0.10) and the d set with one diffuse function ($\alpha_d = 0.1657$) and recontracting the d functions to (4,1,1) as suggested by Shim and Gingerich.[22] Altogether we have used 450 Hermite Gaussian functions contracted to 160 functions for describing the 101 electrons of our prototype molecule.

For evaluating the correlation energy, we have used a method proposed in previous papers[23-25] and applied successfully to several different molecular systems.[18,26-31] Such an approach is based on the separation of the correlation energy into a long-range part, due to the quasi-degeneracy among different independent-particle states and taken into account, if necessary, by using a small MCSCF expansion, and a short-range correlation energy, which can be evaluated by means of the numerical integration of a functional of the first-order HF density matrix. A theoretical justification of an approach like the present one has been recently given by Harris and Pratt[32] and Levy,[33] who proved the existence of a universal function of the first-order HF density matrix that gives the exact correlation energy. In a different context like that of solid-state physics, similar approachs based on the Hohenberg-Kohn theorem[34] are widely and successfully used.[35-37]

With respect to the standard CI method our technique presents two main advantages: (a) It is much less time consuming, since it requires only a numerical integration that can be performed very efficiently by integrating the difference between the functional for the molecule and that for an assembly of noninteracting atoms[38] and therefore seems particularly appropriate in the case of large systems, like the metallo-organic molecules of the type under consideration. (b) It assures the same level of accuracy in calculating the correlation energy of the various electronic states of interest, which is obviously very important for obtaining a correct excitation energy spectrum; see for example previous calculations on the electronic excited states of molecules like ethylene[27] and formaldehyde.[28] A detailed analysis of the accuracy of this method as applied to the ground state of various molecules, radicals, and crystalline systems can be found in ref 31.

Finally, we observe that since in our approach the correlation energy is evaluated separately, by using a specific technique, it is not necessary to include a correlation contribution via the unrestricted Hartree-Fock method, which, beside, causes a mixing of states having different spin symmetries.

Discussion

One purpose of this paper is to characterize, in an independent-particle model, the molecular orbital (MO) structure of the ground and the lowest excited states of the Co(foracim)$_2$.

As already stressed, the experimental data (in particular the EPR spectra) have led to controversial interpretations as concerns the nature of the ground state; it seems in fact that there is only one unpaired electron, but it is not clear if it should be assigned to the $3d_{x^2}$, $3d_{z^2-y^2}$, $3d_{xz}$, or $3d_{xy}$ orbitals (the only accepted conclusion is that the $3d_{yz}$ orbital, pointing toward the ligand donor atoms, is the highest in energy). Correspondingly, four possible ground-state configurations can be proposed, which correspond to single-determinant doublet states and which we formally write as

$$...(3d_{xz})^2,\ (3d_{xy})^2,\ (3d_{z^2-y^2})^2,\ (3d_{x^2})^1$$

$$...(3d_{xz})^2,\ (3d_{xy})^2,\ (3d_{x^2})^2,\ (3d_{z^2-y^2})^1$$

$$...(3d_{xz})^2,\ (3d_{x^2})^2,\ (3d_{z^2-y^2})^2,\ (3d_{xy})^1$$

$$...(3d_{xy})^2,\ (3d_{x^2})^2,\ (3d_{z^2-y^2})^2,\ (3d_{xz})^1$$

Beside these configurations, one can consider the promotions of one electron from the highest occupied orbitals to the unoccupied $3d_{yz}$ orbital to give quartet and doublet states with three open shells (i.e. singly occupied orbitals), etc. We have therefore

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Table I. Hartree–Fock (E_{HF}), Correlation (E_c), and Total (E_T) Energies, of Various States of Co(foracim)$_2$, Classified According to Their Spatial Symmetry, Their Spin Function (S), and Their Single-Particle Configuration[a]

sym	*n*	configuration	S	E_{HF}	E_c	E_T
A_1		$23a_1^2/3a_2^24a_2^1/5b_1^26b_1^1/18b_2^219b_2^1$	Q	−1871.52474	−3.78579	−1875.31053
	1	$22a_1^223a_1^1/4a_2^2/6b_1^2/18b_2^2$	D	−1871.49926	−3.79354	−1875.2927
	4	$23a_1^2/3a_2^24a_2^1/5b_1^26b_1^1/18b_2^219b_2^1$	A	−1871.41531	−3.79365	−1875.20895
	5	$23a_1^2/3a_2^24a_2^1/5b_1^26b_1^1/18b_2^219b_2^1$	B	−1871.41618	−3.78860	−1875.20478
	2	$23a_1^224a_1^1/3a_2^2/6b_1^2/18b_2^2$	D	−1871.17264		
	3	$23a_1^224a_1^1/4a_2^2/5b_1^2/18b_2^2$	D	−1871.15900		
A_2		$22a_1^223a_1^1/4a_2^2/5b_1^26b_1^1/18b_2^219b_2^1$	Q	−1871.52322	−3.78596	−1875.30918
	1	$23a_1^2/3a_2^24a_2^1/6b_1^2/18b_2^2$	D	−1871.48229	−3.79323	−1875.27551
		$21a_1^222a_1^123a_1^1/3a_2^24a_2^1/6b_1^2/19b_2^2$	Q	−1871.43105		
	4	$22a_1^223a_1^1/4a_2^2/5b_1^26b_1^1/18b_2^219b_2^1$	A	−1871.41443	−3.79407	−1875.20850
	5	$22a_1^223a_1^1/4a_2^2/5b_1^26b_1^1/18b_2^219b_2^1$	B	−1871.42617	−3.78912	−1875.21528
	2	$22a_1^2/4a_2^25a_2^1/6b_1^2/18b_2^2$	D	−1871.27470	−3.79157	−1875.06626
	3	$23a_1^2/4a_2^25a_2^1/5b_1^2/18b_2^2$	D	−1871.23236	−3.79202	−1875.02438
B_1		$22a_1^223a_1^1/3a_2^24a_2^1/6b_1^2/18b_2^219b_2^1$	Q	−1871.53249	−3.78632	−1875.31880
	1	$23a_1^2/4a_2^2/5b_1^26b_1^1/18b_2^2$	D	−1871.47605	−3.79328	−1875.26933
		$21a_1^222a_1^123a_1^1/4a_2^2/5b_1^26b_1^1/19b_2^2$	Q	−1871.42484		
	4	$22a_1^223a_1^1/3a_2^24a_2^1/6b_1^2/18b_2^219b_2^1$	A	−1871.42266	−3.79421	−1875.21686
	5	$22a_1^223a_1^1/3a_2^24a_2^1/6b_1^2/18b_2^219b_2^1$	B	−1871.43477	−3.78942	−1875.22419
	2	$22a_1^2/4a_2^2/6b_1^27b_1^1/18b_2^2$	D	−1871.29446	−3.79108	−1875.08554
	3	$23a_1^2/3a_2^2/6b_1^27b_1^1/18b_2^2$	D	−1871.26600	−3.79194	−1875.05793
B_2		$21a_1^222a_1^123a_1^1/4a_2^2/6b_1^2/18b_2^219b_2^1$	Q	−1871.52312	−3.78630	−1875.30942
		$22a_1^223a_1^1/3a_2^24a_2^1/5b_1^26b_1^1/19b_2^2$	Q	−1871.43813		
		$21a_1^222a_1^123a_1^1/4a_2^2/6b_1^2/18b_2^219b_2^1$	A	−1871.41380	−3.79398	−1875.20778
		$21a_1^222a_1^123a_1^1/4a_2^2/6b_1^2/18b_2^219b_2^1$	B	−1871.42517	−3.78905	−1875.21422
	1	$22a_1^2/4a_2^2/6b_1^2/18b_2^219b_2^1$	D	−1871.40007	−3.79422	−1875.19429
	3	$23a_1^2/3a_2^2/6b_1^2/18b_2^219b_2^1$	D	−1871.38884	−3.79391	−1875.18275
	2	$23a_1^2/4a_2^2/5b_1^2/18b_2^219b_2^1$	D	−1871.37600	−3.79393	−1875.17052
	4	$22a_1^223a_1^1/3a_2^24a_2^1/5b_1^26b_1^1/19b_2^2$	A	−1871.25567		
	5	$22a_1^223a_1^1/3a_2^24a_2^1/5b_1^26b_1^1/19b_2^2$	B	−1871.23007		

[a] The quartet, standard doublet, and nonstandard doublet states are indicated respectively by the symbols Q, D, and A/B as explained in the text. The numbers (*n*) in the second column define the coefficients c_i of Table II.

performed several RHF calculations relative to these possible electronic configurations, thus obtaining various states that have been classified according to their spatial and spin symmetries. Some of the results of such calculations are given in Table I.

Note that for each configuration with three different open shells (three singly occupied orbitals) there exist two distinct doublet states, corresponding to the two possible spin couplings of the three electrons and described by the following prototype spin functions (see pp 61 ff of ref 39):

$$\theta_A(1/2;\, 0) = \alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$$

$$\theta_B(1/2;\, 1) = [\beta\alpha\alpha - \alpha(\alpha\beta + \beta\alpha)/2]\sqrt{2/3}$$

In Table I such states are indicated respectively by the symbols A and B, while the corresponding quartet state is indicated by Q.

We observe that the RHF wave functions corresponding to the various configurations reported in Table I are orthogonal among themselves, either because of different symmetry or because of differences in their orbital occupation numbers, so that no problem of variational collapse can arise.

From the results of Table I we single out a few important points. (a) The most striking result of our calculations is the fact that the ground state of the molecule, in the RHF approximation, is represented by an open-shell wave function corresponding to a quartet of B_1 symmetry. (b) Three of the quartet states obtained via one-electron promotions from the lowest $^2A_1$ doublet state are lower in energy than the original $^2A_1$ state and lie almost degenerate ($\Delta E = 0.03$ eV) at an energy only a bit higher than that of the $^4B_1$ ground state (about 0.3 eV). (c) The lowest double state, the $^2A_1$ one, is a standard doublet that lies at about 0.7 eV above the group of quartets together with two other standard doublets; next in energy there is a group of six nonstandard doublets (2.0–2.5 eV over the ground state).

In order to check this ordering of states and to obtain more accurate transition energies, we have also calculated the correlation energy. Such a calculation has been performed in two steps.

First we have evaluated the short-range part of the correlation energy, by using the approach proposed in refs 23–25 for the RHF wave functions of Table I (the results of these calculations are reported in Table I together with the SCF energy values). We observe that the inclusion of the short-range part of the correlation energy does not alter the ordering of the states and also introduces relatively small changes in the values of the transition energies.

As a second step, in order to evaluate the long-range part of the correlation energy, we have calculated the interaction matrix elements among the RHF wave functions of the same spin and space symmetries, which are orthogonal among themselves, because of differences in their occupation numbers, but mutually interacting as eigenfunctions of different HF operators. We have performed these small CI calculations only for the doublet states, which are the most mutually interacting states. The energies, eigenvalues, and eigenvectors, obtained by diagonalizing the corresponding Hamiltonian matrices, are given in Table II. They show that the mixing among the lowest and the excited doublet states of each symmetry is negligible in the A_1 symmetry but appreciable in the A_2 and B_1 symmetries (where the first state is lowered by about 0.01 au) and quite relevant in the B_2 symmetry ($\Delta E = 0.044$ au).

From such results we can conclude that the lowest electronic state of the Co(foracim)$_2$ molecule is described in the independent-particle approximation by the open-shell configuration ($...22a_1^223a_1^1/...3a_2^24a_2^1/...6b_1^2/...18b_2^219b_2^1$) corresponding to a quartet state of B_1 symmetry.

The high multiplicity ($S = 3/2$) character of the ground state is a surprising result, apparently not in agreement with the magnetic and EPR data, although some experimental evidence seems to indicate the presence of low-lying quartet states.

We have still to consider, however, the effect of the relativistic components of the electronic Hamiltonian, whose contribution is known to be quite large for square-planar complexes of this type[40]

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Table II. Eigenvalues and Eigenvectors of the Hamiltonian Matrices, Constructed on the Basis of the HF Wave Functions of Table I[a]

sym	state	E	c_1	c_2	c_3	c_4	c_5
$^2A_1$	1	−1871.49934	+0.9998	−0.0126	−0.0106	−0.0090	+0.0041
	2	−1871.20097	+0.0160	+0.7708	+0.6353	−0.0405	+0.0181
	3	−1871.13017	+0.0002	−0.6360	+0.7717	+0.0007	+0.0003
	4	−1871.41564	+0.0091	+0.0296	+0.0236	+0.9916	+0.1233
	5	−1871.41626	+0.0055	+0.0179	+0.0142	+0.1225	+0.9922
$^2A_2$	1	−1871.49249	+0.9401	+0.0018	+0.0035	+0.3398	+0.0076
	2	−1871.28655	+0.0028	+0.9058	+0.4238	+0.0015	+0.0011
	3	−1871.22050	+0.0007	−0.4236	+0.9058	+0.0051	+0.0022
	4	−1871.40425	−0.3399	+0.0015	−0.0044	+0.9404	+0.0117
	5	−1871.42617	−0.0032	−0.0001	−0.0024	−0.0136	+0.9999
$^2B_1$	1	−1871.48657	+0.9266	−0.0184	−0.0333	+0.3734	+0.0157
	2	−1871.30845	+0.0226	+0.8675	+0.4959	+0.0380	+0.0120
	3	−1871.25156	+0.0092	−0.4970	+0.8671	+0.0293	+0.0119
	4	−1871.41256	−0.3748	−0.0051	−0.0304	+0.9261	+0.0154
	5	−1871.43480	−0.0129	−0.0041	−0.0151	−0.0223	+0.9995
$^2B_2$	1	−1871.44420	+0.6129	+0.5179	+0.5987	+0.0083	+0.0022
	2	−1871.37387	−0.7874	+0.3424	+0.5113	−0.0130	−0.0040
	3	−1871.34769	+0.0604	−0.7836	+0.6182	+0.0013	+0.0004
	4	−1871.25726	−0.0127	+0.0019	+0.0018	+0.9715	−0.2367
	5	−1871.22846	−0.0078	+0.0010	+0.0009	+0.2366	+0.9716

[a] The numbering of the coefficients c_i is defined in Table I.

(note also that the corresponding atomic states of cobalt exhibit an experimental splitting of about 600–800 cm^{-1}).

In order to estimate this effect, we have taken into account for simplicity only the one-electron part of the spin–orbit operator

$$H_{so} = (e^2/hc)^2\sum_{i}\sum_{A}(Z_A/r_{iA}^3)\vec{l}_{iA}\cdot\vec{S}_i$$

and we have performed a second-order quasi-degenerate perturbational calculation on the $^4B_1$ state using H_{so} as the perturbing Hamiltonian. In such a perturbational calculation the four spin components of the $^4B_1$ ground state are split by H_{so} in two groups of doubly degenerate states, the so-called Kramers doublets, which can therefore appear in an EPR experiment as standard doublets. Our calculations give an energy difference between the two Kramers doublets of ΔE_{so} = 0.00282 au; this splitting ensures that only one of the two doublets is populated at room temperature ($\Delta E_{so} \approx 2.8\ kT$ at T = 298 K), but it is not sufficient to modify appreciably the energy spectrum ($\Delta E_{so} \approx 0.076$ eV).

Let us therefore discuss our predictions for the energy spectrum of Co(foracim)$_2$ in the range of energies that is of interest for comparison with the experimental results, i.e. the near-infrared and visible regions, 3500–22000 cm^{-1}. This will allow us to give an assignment for the various observed bands attributed to d–d transitions.

We note that for the states which fall in this energy interval the long-range part of the correlation energy gives minor contributions, except for the three lowest $^2B_2$ standard doublet states, which strongly interact among themselves. Therefore, in Table III we report as calculated values of the energy for all the other states simply the sum of the RHF energy plus the short-range part of the correlation energy evaluated through the method given in ref 24. The energy value reported for the $^2B_2$ state, instead, has been obtained by applying the corresponding generalized method as explained in ref 25 to the three-determinant wave function derived from the CI among the three lowest $^2B_2$ standard doublet states.

In Table III we compare the results of our calculations for the Co(foracim)$_2$ energy spectrum with the experimental transition energies of the Co(acac(−)pn) molecule and also propose the assignment of the various transitions. We refer to the Co(acac(−)pn) molecule, since it is chemically quite similar to our model complex and is the most thoroughly studied; however, due to the differences between our model ligand (foracim)$_2$ and acac(−)pn, we cannot expect a complete quantitative agreement between the calculated and the observed spectra, and our purpose is essentially that of reproducing the main features of the electronic spectra of the whole class.

Table III. Calculated Electronic Spectral Data for Co(foracim)$_2$ Compared with the Experimental Spectral Data for Co(acac(−)pn) Obtained by the Application of Isotropic Absorption (ΔE(abs)) and Circular Dichroism (ΔE(CD)) Spectroscopies

state	ΔE_{calc}	ΔE_{exptl}(abs)	ΔE_{exptl}(CD)
$^4B_1$			
$^4A_2$	1820		
$^4A_1$	2060	3970	
$^4B_2$	2100	4300	
$^2A_1$	5710	5550	
$^2A_2$	9500	8500	
$^2B_1$	10860		15630
$^2B_2$	17720		18000
$^4B_2$	18510		19500
$^2B_1$	20710	20600	20700
$^4A_2$	22260		22000

As regards the d–d part of the spectra, these features can be summarized as consisting as follows: (a) a characteristic band at 8500–9000 cm^{-1}; (b) a group of bands beween 15000 and 20000 cm^{-1} that are obscured by intense intraligand absorptions just over 20000 cm^{-1}; (c) a group of bands between 3500 and 6000 cm^{-1} and maybe below difficult to observe and of controversial interpretation, because of the technical problems in recording spectra below 4000 cm^{-1} and because of the mixing with infrared overtones of ligand vibrations (note that sometimes the whole group has been attributed to such overtones[41]).

As can be seen from Table III, there is a pretty good qualitative agreement between the calculated and observed spectra, the only relevant deviations concerning the lower transitions (calculated at about 2000 cm^{-1} instead of about 4000 cm^{-1}) and a transition calculated at 10800 cm^{-1}, which seems to be related to the experimental one at 15600 cm^{-1}.

The most relevant results of our analysis are as follows: (a) d–d transitions are predicted in the near- and medium-infrared region, a part of the spectrum of controversial attribution. In particular our results support the attribution of the bands below 6000 cm^{-1} to d–d metal transitions and suggest the presence of a further unobserved low-lying band. (b) These transitions are assigned to excitations from the $^4B_1$ ground state to the three lowest quartet states of A_1, A_2, and B_2 symmetry.

Another prediction that can be made on the basis of our results concerns with the intensities of the various bands. The assignment of the ground state to a quartet implies that the spin-forbidden

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(40) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, England, 1961.

(41) Hitchman, M. A. *Inorg. Chem.* **1977**, *16*, 1985.

Table IV. Mulliken Gross Atomic Populations of the Different Atoms in $Co(foracim)_2$ for the Various States of Interest[a]

atom	$^4A_1$	$^4A_2$	$^4B_1$	$^4B_2$	$^2A_1$	$^2A_2$	$^2B_1$	$^2B_2$
Co	25.74	25.72	25.73	25.72	25.78	25.81	25.80	25.78
O_a	8.58	8.58	8.57	8.53	8.57	8.57	8.57	8.56
C_1	6.01	6.01	6.02	6.14	6.01	6.01	6.01	6.02
H_1	0.66	0.66	0.66	0.66	0.66	0.66	0.66	0.66
C_2	6.53	6.53	6.53	6.29	6.53	6.52	6.52	6.52
H_2	0.69	0.69	0.69	0.69	0.69	0.69	0.69	0.69
C_3	6.14	6.14	6.15	6.32	6.15	6.15	6.14	6.15
H_3	0.67	0.67	0.67	0.67	0.67	0.67	0.66	0.67
N_a	7.68	7.69	7.68	7.68	7.67	7.67	7.68	7.67
H_a	0.66	0.66	0.66	0.66	0.65	0.65	0.65	0.65

[a] The numbering of the atoms is taken from Figure 1.

transitions to doublet states are much less intense than the transitions to other quartet states. In effect, among the transitions below 20000 cm^{-1}, whose intensities can be measured, those corresponding in our assignment to the spin-forbidden ones are less intense by a factor approximately equal to 5.

Analysis of the Wave Function

In order to analyze the electron density distributions of the lowest doublet and quartet states of each symmetry, we have performed a Mulliken population analysis of the RHF wave functions of the various states of interest. Our results show that states with the same orbital occupation but different spin numbers (we refer to the quartets and the corresponding two nonstandard doublets) have practically the same values of the gross atomic population (GAP), and therefore, we report in Table IV the GAP only for the lowest standard doublet and quartet of each symmetry.

From Table IV we observe that the GAP's are very similar for all the states considered, the only relevant exception being the atomic population on the cobalt atom, which is about 25.73 for the doublet states and about 25.80 for the quartets. There is therefore a slightly increased electron density on the cobalt atom ($\Delta \approx 0.1$) in the quartet states with respect to the doublet ones.

Another interesting point to be observed is the fact that the net charge on the cobalt atom is predicted to be +1.2–1.3 au instead of +2.0 au as formally described. This is in agreement with other calculations on transition-metal complexes, according to which the net charge on the metal is rather lower than the formal one, probably because of delocalization on the ligand orbitals.

To further analyze the nature of these wave functions, we have expanded their occupied orbitals in terms of the orbitals of the separate fragments. By using the previously described basis set, we have calculated the RHF wave functions for Co and $foracim^-$ (in the geometry of the complex) in the following states: $Co^{II}(^2H)$, $1s^2/2s^22p^6/3s^23p^63d^7$; $foracim^-(^1A)$, $1\sigma^2...16\sigma^2/1\pi^22\pi^23\pi^2$. Note that we have chosen for cobalt the ^2H state, which correlates with the energetically most favorable configuration for a d^7 atom in a square-planar field. The orbitals from such RHF calculations have then been centered on the proper positions of the complex, mutually orthogonalized through the Löwdin procedure, and finally used in the expansion of the occupied orbitals of the complex. The relevant contributions to the expansion of the highest occupied orbitals of the various states of interest are reported in Tables V and VI. We observe that the orbitals of the fragments distribute among the four irreducible representations of the molecular C_{2v} point group as shown in Table VII. Furthermore the orbitals that contribute most to the expansion of the highest occupied orbitals of the complex are the 3d and 4s of cobalt and the 13σ–16σ and 1π–4π of $foracim^-$ (negative ion). The dominant component of the 16σ orbital is represented by the $2p_z$ functions centered on the oxygens, while the 13σ–15σ orbitals are linear combinations of various sp^n hybrids centred on the oxygen, nitrogen, and carbon atoms with s functions on the hydrogens; finally the 1π–4π orbitals are essentially Hückel-type combinations of the $2p_x$ orbitals of the oxygen, nitrogen, and carbon atoms (see Table VII for a more detailed description).

This type of analysis when applied to the $^4B_1$ ground state wave function gives the following main results: (a) The three singly occupied orbitals are essentially 3d orbitals of the cobalt; more in detail, we find that $23a_1$ is a $3d_{x^2}$ orbital with a relevant contribution of $3d_{z^2-y^2}$, $4a_2$ is a pure $3d_{xy}$ orbital, and $19b_2$ is a $3d_{yz}$ orbital only slightly mixed with the 16σ orbital of the two $foracim^-$ ligands. (b) The highest 3d orbital is the $3d_{yz}$ one, as expected, and the energy sequence of the others is $3d_{xy} > 3d_{x^2} \approx 3d_{z^2-y^2} > 3d_{xz}$. (c) The $3d_{xz}$ orbital is completely mixed up with the 2π orbital of the $foracim^-$ ligand and contributes to the $5b_1$ doubly occupied orbital, while the $6b_1$ (doubly occupied) orbital is es-

Table V. Expansion of the Highest Occupied Orbitals of a Few HF Wave Functions in Terms of the Orbitals of the Separate Fragments: Quartet States[a]

state	orbital	expansion	ϵ
$^4A_1$	$22a_1^2$	$0.33(4s(Co)) + 0.50(3d_{x^2}(Co)) - 0.62(3d_{z^2-y^2}(Co)) + 0.30(3\gamma_+(for))$	−0.963
	$23a_1^2$	$0.25(3d_{z^2-y^2}(Co)) + 0.21(3d_{x^2}(Co)) - 0.13(4d_{x^2}(Co)) - 0.15(3\gamma_+(for)) - 0.61(4\gamma_+(for))$	−0.839
	$4a_2^1$	$0.98(3d_{xy}(Co))$	−0.613
	$6b_1^1$	$0.99(3d_{xz}(Co))$	−0.343
	$18b_2^2$	$0.62(3\gamma_-(for)) - 0.17(3d_{yz}(Co))$	−0.873
	$19b_2^1$	$0.14(4\gamma_-(for)) + [-0.92(3d_{yz}(Co)) + 0.25(4d_{yz}(Co))]$	−0.519
$^4A_2$	$22a_1^2$	$[0.44(3d_{x^2}(Co)) - 0.12(4d_{x^2}(Co)) - 0.13(3d_{z^2-y^2}(Co))] + 0.58(4\gamma_+(for))$	−0.854
	$23a_1^1$	$0.96(3d_{z^2-y^2}(Co)) + 0.19(3d_{x^2}(Co)) + 0.12(4s(Co))$	−0.470
	$4a_2^2$	$0.68(3\tau_-(for)) - [0.19(3d_{xy}(Co)) - 0.17(4d_{xy}(Co))]$	−0.610
	$6b_1^1$	$0.99(3d_{xz}(Co))$	−0.607
	$18b_2^2$	$[0.62(4\gamma_-(for)) + 0.20(3\gamma_-(for)) - 0.19(2\gamma_-(for))] + 0.17(3d_{yz}(Co))$	−0.871
	$19b_2^1$	$-0.15(4\gamma_-(for)) + [0.93(3d_{yz}(Co)) - 0.25(4d_{yz}(Co))]$	−0.871
$^4B_1$	$22a_1^2$	$-0.58(3d_{x^2}(Co)) - 0.80(3d_{z^2-y^2}(Co))$	−0.915
	$23a_1^1$	$-0.79(3d_{x^2}(Co)) + 0.57(3d_{z^2-y^2}(Co))$	−0.610
	$4a_2^1$	$0.98(3d_{xy}(Co))$	−0.608
	$5b_1^2$	$0.57(2\tau_+(for)) - 0.53(3d_{xz}(Co)) + 0.19(4d_{xz}(Co))$	−0.889
	$6b_1^2$	$-0.68(3\tau_+(for))$	−0.669
	$19b_2^1$	$0.16(4\gamma_-(for)) + [0.92(3d_{yz}(Co)) - 0.25(4d_{yz}(Co))]$	−0.529
$^4B_2$	$22a_1^2$	$0.80(3d_{x^2}(Co)) + 0.57(3d_{z^2-y^2}(Co))$	−0.564
	$23a_1^1$	$-0.80(3d_{z^2-y^2}(Co)) + 0.57(3d_{x^2}(Co))$	−0.549
	$4a_2^1$	$-0.68(3\tau_-(for)) + [0.20(3d_{xy}(Co)) - 0.17(4d_{xy}(Co))]$	−0.610
	$5b_1^2$	$0.54(2\tau_+(for)) - 0.61(3d_{xz}(Co))$	−0.879
	$6b_1^1$	$0.69(3\tau_+(for))$	−0.669
	$19b_2^2$	$-0.92(3d_{yz}(Co)) + 0.26(4d_{yz}(Co))$	−0.618

[a] ϵ indicates the HF eigenvalue of the orbital. All the quantities are given in atomic units. $4\gamma_\pm(for) = 1/\sqrt{2}[16\sigma(for) \pm 16\sigma(for')]$, $4\tau_\pm(for) = 1/\sqrt{2}[4\pi(for) \pm 4\pi(for')]$, $3\gamma_\pm(for) = 1/\sqrt{2}[15\sigma(for) \pm 15\sigma(for')]$, $3\tau_\pm(for) = 1/\sqrt{2}[3\pi(for) \pm 3\pi(for')]$, $2\gamma_\pm(for) = 1/\sqrt{2}[14\sigma(for) \pm 14\sigma(for')]$, $2\tau_\pm(for) = 1/\sqrt{2}[2\pi(for) \pm 2\pi(for')]$, $1\gamma_\pm(for) = 1/\sqrt{2}[13\sigma(for) \pm 13\sigma(for')]$, $1\tau_\pm(for) = 1/\sqrt{2}[1\pi(for) \pm 1\pi(for')]$.

Table VI. Expansion of the Highest Occupied Orbitals of a Few HF Wave Functions in Terms of the Orbitals of the Separate Fragments: Doublet States[a]

state	orbital	expansion	ϵ
$^2A_1$	$22a_1{}^2$	$-0.85(3d_{x^2}(Co)) - 0.51(3d_{z^2-y^2}(Co))$	−0.842
	$23a_1{}^1$	$0.85(3d_{z^2-y^2}(Co)) - 0.50(3d_{x^2}(Co))$	−0.528
	$4a_2{}^2$	$0.21(3d_{xy}(Co)) - 0.67(2\tau_-(for))$	−0.611
	$6b_1{}^2$	$0.22(3d_{xz}(Co)) - 0.67(2\tau_+(for))$	−0.669
	$18b_2{}^2$	$-0.61(4\gamma_-(for)) - 0.21(3\gamma_-(for)) + 0.18(3d_{yz}(Co))$	−0.867
$^2A_2$	$22a_1{}^2$	$0.65(3d_{x^2}(Co)) - 0.60(3d_{z^2-y^2}(Co)) + 0.16(3\gamma_+(for))$	−0.886
	$23a_1{}^2$	$0.22(3d_{z^2-y^2}(Co)) - 0.12(3d_{x^2}(Co)) - 0.62(4\gamma_+(for))$	−0.850
	$4a_2{}^1$	$0.99(3d_{xy}(Co))$	−0.572
	$5b_1{}^2$	$-0.48(2\tau_+(for)) - [0.71(3d_{xz}(Co)) - 0.13(4d_{xz}(Co))]$	−0.856
	$6b_1{}^2$	$0.22(3p_x(Co)) - 0.15(1\tau_+(for)) - 0.67(3\tau_+(for))$	−0.673
	$18b_2{}^2$	$0.61(4\gamma_-(for)) + 0.20(3\gamma_-(for)) + 0.18(3d_{yz}(Co))$	−0.871
$^2B_1$	$22a_1{}^2$	$0.32(3d_{x^2}(Co)) - 0.67(3d_{z^2-y^2}(Co)) - 0.37(4\gamma_+(for))$	−0.894
	$23a_1{}^2$	$-0.12(3d_x2(Co)) + 0.51(3d_{z^2-y^2}(Co)) - 0.52(4\gamma_+(for))$	−0.829
	$4a_2{}^2$	$0.24(3d_{xy}(Co)) - 0.67(3\tau_-(for))$	−0.611
	$6b_1{}^1$	$0.99(3d_{xz}(Co))$	−0.569
	$18b_2{}^2$	$0.61(4\gamma_-(for)) + 0.21(3\gamma_-(for)) + 0.18(3d_{yz}(Co))$	−0.870
$^2B_2$	$22a_1{}^2$	$[0.34(3d_{x^2}(Co)) - 0.13(4d_{x^2}(Co))] + 0.18(3d_{z^2-y^2}(Co)) + 0.59(4\gamma_+(for))$	−0.828
	$23a_1{}^0$	$-0.38(3d_{z^2-y^2}(Co)) - 0.34(4d_{z^2-y^2}(Co)) + 0.23(3d_{x^2}(Co)) + 0.24(4d_{x^2}(Co)) - 0.62(3p_z)$	+0.243
	$4a_2{}^2$	$-0.67(3\tau_-(for)) + [0.17(3d_{xy}(Co)) - 0.18(4d_{xy}(Co))]$	−0.607
	$5b_1{}^2$	$-0.60(2\tau_+(for)) - [0.47(3d_{xz}(Co)) - 0.20(4d_{xz}(Co))]$	−0.903
	$6b_1{}^2$	$-0.67(3\tau_+(for)) - 0.16(1\tau_+(for)) + 0.24(3p_x(Co))$	−0.665
	$19b_2{}^1$	$[-0.92(3d_{yz}(Co)) + 0.25(4d_{yz}(Co))] + 0.15(4\gamma_-(for))$	−0.456

[a] ϵ indicates the HF eigenvalue of the orbital. All the quantities are given in atomic units. $4\gamma_\pm(for) = 1/\sqrt{2}[16\sigma(for) \pm 16\sigma(for')]$, $4\tau_\pm(for) = 1/\sqrt{2}[4\pi(for)$ ● $4\pi(for')]$, $3\gamma_\pm(for) = 1/\sqrt{2}[15\sigma(for) \pm 15\sigma(for')]$, $3\tau_\pm(for) = 1/\sqrt{2}[3\pi(for) \pm 3\pi(for')]$, $2\gamma_\pm(for) = 1/\sqrt{2}[14\sigma(for)$ ● $14\sigma(for')]$, $2\tau_\pm(for) = 1/\sqrt{2}[2\pi(for) \pm 2\pi(for')]$, $1\gamma_\pm(for) = 1/\sqrt{2}[13\sigma(for) \pm 13\sigma(for')]$, $1\tau_\pm(for) = 1/\sqrt{2}[1\pi(for) \pm 1\pi(for')]$.

Table VII. Symmetry Properties of the Cobalt and $(foracim)_2{}^{2-}$ Orbitals within the C_{2v} Molecular Point Group and HF Eigenvalues (ϵ) and Expansion Coefficients of the Lowest π Orbitals of $(foracim)_2{}^{2-}$ in Terms of the $2p_x$ Orbitals of the Carbon, Oxygen, and Nitrogen Atoms[a]

sym	Co	$(foracim)_2{}^{2-}$
A_1	s, p_z, $d_{z^2-y^2}$, d_{x^2}	$\gamma_+ = 1/\sqrt{2}[\sigma(for) + \sigma(for')]$
A_2	d_{xy}	$\tau_- = 1/\sqrt{2}[\pi(for) - \pi(for')]$
B_1	p_x, d_{xz}	$\tau_+ = 1/\sqrt{2}[\pi(for) + \pi(for')]$
B_2	p_y, d_{yz}	$\gamma_- = 1/\sqrt{2}[\sigma(for) - \sigma(for')]$

expansion	ϵ
$1\pi = 0.28(2p_x(O)) + 0.32(2p_x(C_1)) + 0.30(2p_x(C_2)) + 0.35(2p_x(C_3)) + 0.30(2p_x(N))$	−0.310
$2\pi = -0.45(2p_x(O)) - 0.38(2p_x(C_1)) + 0.37(2p_x(C_3)) + 0.40(2p_x(N))$	−0.233
$3\pi = -0.49(2p_x(O)) + 0.66(2p_x(C_2)) - 0.42(2p_x(N))$	−0.063
$4\pi = 0.47(2p_x(O)) - 0.58(2p_x(C_1)) + 0.59(2p_x(C_3)) + 0.56(2p_x(N))$	+0.370

[a] All the quantities are given in atomic units.

sentially constituted by the 3π orbital of the foracim$^-$.

As regards the other quartet states, only slightly higher in energy, the d-orbital energy sequence is almost the same as for $^4B_1$, the only exceptions being the $^4B_2$ state, in which the singly occupied $3d_{x^2}$ and $3d_{z^2-y^2}$ orbitals are higher in energy than the remaining singly occupied $3d_{yz}$.

It is interesting to apply this type of analysis also to the $^2A_2$ state, which is the lowest doublet state. The main results obtained are as follows: (a) The singly occupied orbital is a $3d_{z^2-y^2}$ orbital well mixed with $3d_{x^2}$. (b) The energy ordering of the d orbitals is $3d_{yz} \gg 3d_{z^2-y^2} > 3d_{xy} \approx 3d_{xz} > 3d_{x^2}$, with the $3d_{yz}$ orbital unoccupied and the lowest doubly occupied $3d_{xy}$ and $3d_{xz}$ appreciably mixed with the 2π orbitals of foracim$^-$ and lower in energy than other orbitals corresponding to almost pure 3π orbitals of foracim$^-$.

The situation is similar for the other lowest standard doublet states of each symmetry, again with the exception of the $^2B_2$ state, in which the $3d_{yz}$ orbital is singly occupied.

Conclusions

The main conclusions that can be drawn from our analysis of the electronic states of $Co(foracim)_2$ are the following: (a) The ground state of the molecule is represented, in the independent-particle approximation, by a quartet state of B_1 symmetry corresponding to the open-shell configuration $(...22a_1{}^2 23a_1{}^1/...3a_2{}^2 4a_2{}^1/...6b_1{}^2/...18b_2{}^2 19b_2{}^1)$ and very close in energy ($\Delta E \approx$ 0.2–0.3 eV) to a group of quartet states of different symmetry. This is in contrast with previous theoretical calculations,[5] which give a $^2A_1$ state as the lowest one. (b) The four components of the $^4B_1$ ground state are split by the spin–orbit interactions into two Kramers doublets separated in energy by about 0.076 eV, so that at room temperature only the lowest one is appreciably populated and appears in the EPR experiments as a standard doublet state. (c) It is possible to give assignments for the various bands observed in the near-infrared and visible regions and also to suggest the existence of an unobserved low-lying state, whose corresponding transition is probably obscured by vibrational transitions.

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