charge q_A with the aid of the formula,[53]

$$E_{\rm ind} = -0.5\alpha_X q_A^2/r_{XA}^4 \qquad (2)$$

attraction energies 30–50% *larger* than calculated D_e values are found (Table VIII). This means that (i) the strength of the NG–Be interactions does not necessarily invoke other than electrostatic forces to explain the stability of $NGBe^{n+}$ and (ii) for the calculated NG–Be distances of $NGBe^{n+}$, formula 2, which is only valid for point charges, provides no longer a quantitative description of interaction energies.

A necessary condition for the validity of the above discussion is that the atomic polarizabilities α of the noble gas atoms are calculated correctly at the theoretical level employed in the investigation. It has been found that at the MP4(SDTQ)6/311G-(2df,2pd) level the calculated α values for He, Ne, and Ar deviate less than 10% from experimental results if the complete basis set of the NGX^{n+} cation is employed.[56]

The discussion of NG–BeO interactions using the experimental and theoretical results of the dipole moment and electron affinity of BeO points toward electrostatic interactions, although covalent contributions cannot completely be dismissed. Analysis of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ for $HeBe^{2+}$, $NeBe^{2+}$, $ArBe^{+}$, and $ArBe^{2+}$ (Table VI) reveals that there is more density in the internuclear region than found for **1–3**. Nevertheless, H_b values are either positive or close to zero (Table VI). When going from He to Ar, H_b becomes smaller (more negative), as has been found for **1–3**. But even for $ArBe^{2+}$, the calculated H_b result is far from the typical value found for a covalent NG–X bond (e.g., −1.0 for some HeC bonds[16]). We conclude that despite the large D_e values (20–68 kcal/mol, Table VIII) all interactions in $NGBe^{2+}$ are essentially electrostatic. *Since the partial charge of Be in NGBeO is definitely lower than 2, it is reasonable to conclude that NG–Be interactions in **1–3** are also electrostatic.*

5. Summary

Our theoretical results predict that HeBeO (**1**), NeBeO (**2**), and ArBeO (**3**) are stable toward dissociation of the noble-gas atom. The calculated dissociation energies D_0 at the highest level of theory used in our study and corrected by BSSE are 3.1 kcal/mol for **1**, 2.2 kcal/mol for **2**, and 7.0 kcal/mol for **3**. These values are lower bounds to the correct D_0 values because the BSSE is probably overestimated by the counterpoise method. In contrast to the NGBeO structures **1–3**, the NGLiF, NGBN, and HeLiH species **4–8** are calculated with much weaker NG–AB interactions, ≤0.1 kcal/mol.

The weakly interacting NG–AB systems **4–8** should be considered as van der Waals complexes which are bound by dipole-induced dipole forces. The electron density analysis of the NGBeO structures **1–3** reveals essentially charge-induced dipole interactions between the noble-gas atoms and BeO without any indication of covalent interaction. It cannot be excluded that attractive NG–Be interactions in **1–3** are partially enhanced by HOMO–LUMO interactions. However, all evidence points toward a classification of HeBeO, NeBeO, and ArBeO as unusually stable van der Waals complexes.

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Registry No. BeO, 1304-56-9; LiF, 7789-24-4; BN, 10043-11-5; LiH, 7580-67-8; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1.

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Theoretical Investigation of the Ground and a Few Excited States of the Co(Schiff base)Li Complexes

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Abstract: RHF-plus-correlation calculations have been performed on the ground and a few excited states of the complex $Co(foracim)_2Li$, chosen as a model of the Co(Schiff base)Li complexes. The wave functions thus obtained have been subjected to Mulliken population analysis and analyzed in terms of the orbitals of the separate constituent fragments to bring out effects of electronic σ-donation and π-back-donation between the cobalt atom and the ligand. The ground state of the isolated complex corresponds to an open-shell configuration of the Co^{II}/Li type and of A_1 symmetry, with the triplet and singlet components practically degenerate. A permanent magnetic moment of the order of at least 1.9 μ_B is predicted for the ground state of the complex. States corresponding to the configurations of the charge-transfer Co^{I}/Li^{+} type are higher in energy by more than 1 eV.

The complexes of the transition-metal atoms with planar-tetradentate Schiff bases (SB), like acacen, salen, and salophen, are of much interest from both theoretical and experimental points of view.

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 properties. However, only a limited number of theoretical studies of this type of molecule can be found in the literature.[1-5] Few Hartree–Fock (HF) calculations are available, essentially because

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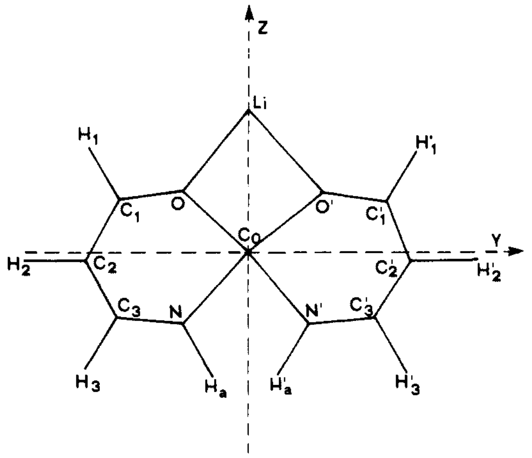

Figure 1. Geometry of the Co(foracim)$_2$Li (foracim ≡ formylacetaldehyde iminato ≡ OCHCHCHNH) complex in the *zy* plane. A C_{2v} symmetry has been imposed.

of the technical difficulties associated with the number of electrons; furthermore, the electronic correlation energy is usually neglected, although essential in many cases to obtaining the correct energy spectrum.

Such complexes have been the subject of experimental study because of their interesting reactivity, especially in connection with their capability for coordinating small molecules,[6,7] and also because of their characteristic magnetic and spectroscopic properties.[8] A class of compounds, which has been particularly analyzed in this context, is that constituted by the complexes of the cobalt with a planar-tetradentate Schiff base and an alkali metal atom (M), which exhibit the peculiarity of having simultaneously two metallic centers. Conductivity measurements have proved that these complexes do not dissociate appreciably, as ions, in solutions of THF and similar solvents, and this fact has been attributed to the presence of tightly bound ionic pairs.[9] Furthermore, these complexes are able to coordinate molecules with both nucleophilic and electrophilic sites, like CO_2, and this type of reactivity has been interpreted in terms of a bifunctional character for these complexes, with the alkali-metal ion as the acidic center. In particular, the reactions with CO_2 to give compounds of the type $[Co(SB)M(CO_2)(THF)_k]_n$ (SB = Schiff Base), whose solid-state structures have been determined for various SB and M,[6] have been studied intensively, also in view of a possible activation of the CO_2 and CO_2-like molecules toward reduction.

As a first step in developing theoretical understanding of the properties of such complexes, we present in this paper several results of accurate HF-plus-correlation calculations relative to a few electronic states of a molecule: Co(OCHCHCHNH)$_2$Li ≡ Co(foracim)$_2$Li, chosen as the simplest but at the same time chemically significant model of such bifunctional complexes. As shown in Figure 1, the (foracim)$_2$ ligand differs from a typical SB, like acacen [*N,N'*-ethylene bis(acetylacetoneiminate)], 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,[1,5] is chemically significant, and furthermore 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.

The purpose of this paper is to characterize at the level of an accurate HF-plus-correlation calculation the ground state of the system, to quantify effects like electronic σ-donation and π-back-donation between the cobalt and the ligand, to analyze the electronic structure of the lowest states of each molecular symmetry, and also to estimate the energy required for the homolitic and heterolitic dissociation of the complex into Co(SB) and Li.

In comparison with previous calculations[1-5] on similar molecules, we include explicitly the alkali-metal atom, evaluate the correlation energy, and analyze a few excited states of the complex. We think that, as can be seen from the analysis of our results, the theoretical study of such many-electron molecules requires both a sufficiently accurate HF calculation and a reliable evaluation of the correlation energy in order to resolve an electronic 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)$_2$Li molecule.

With regard to the geometry of the complex, we have imposed a planar C_{2v} structure using the experimental parameters of the solid [Co(salen)Li(THF)$_{1.5}$] [salen ≡ *N,N'*-ethylenebis(salicylideneaminate)][9] but projecting them in the plane that minimizes the sum of the square deviations from that structure and symmetrizing the two halves of the complex. The geometrical parameters, which concern the hydrogen atoms not present in the salen, have been derived from analogous organic molecules and are $R(N-H) = 1.02$ Å, $R(C-H) = 1.10$ Å, $\gamma(HCN) = 110°$, $\gamma(NCH) = 123°$, and $\gamma(OCH) = 118°$.

All the calculations have been carried out with a basis set of (14s, 9p, 6d/11s, 6p/11s/5s) spherical gaussian functions contracted to (8s, 4p, 3d/4s, 2p/5s/2s) for Co, first-row atoms, lithium, and hydrogen, respectively. This basis set corresponds to the Huzinaga double-ζ one[10] for the hydrogen and the first-row atoms, with the exception of the lithium whose basis set has been taken from ref 11. For cobalt we have used the (14s, 9p, 5d) basis contracted to (8s, 4p, 2d) of Wachters,[12] augmenting the p_z set with two diffuse functions ($\alpha_p = 0.24$ and $\alpha_p = 0.10$) 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.[13]

For evaluating the correlation energy, we have used a method proposed in previous papers[14-16] and applied successfully to several different molecular systems.[17-22] 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, Pratt,[23] and Levy,[24] 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 the solid-state physics, similar approaches based on the Hohemberg-Kohn theorem[25] are widely and successfully used.[26-28]

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

sym	states	confign	S	E_{HF}	E_c	E_T
A_1	1	$...23a_1^2 24a_1^1 25a_1^1/4a_2^2/6b_1^2/18b_2^2$	1	−1878.887 31	−3.859 20	−1882.746 51
			0	−1878.887 16	−3.859 23	−1882.746 39
	2	$...24a_1^2/4a_2^2/5b_1^2 6b_1^1 7b_1^1/18b_2^2$	1	−1878.819 56		
			0	−1878.818 28		
	3	$...24a_1^2/3a_2^2 4a_2^1 5a_2^1/6b_1^2/18b_2^2$	1	−1878.809 72		
			0	−1878.807 84		
	4	$...24a_1^2/4a_2^2/6b_1^2/17b_2^2 18b_2^1 19b_2^1$	1	−1878.373 74		
			0	−1878.369 63		
	5	$...24a_1^2/4a_2^2/6b_1^2/18b_2^2$	0	−1878.807 27	−3.889 15	−1882.696 42
A_2	1	$...24a_1^2 25a_1^1/3a_2^2 4a_2^1/6b_1^2/18b_2^2$	1	−1878.870 42	−3.858 90	−1882.729 32
			0	−1878.870 36	−3.858 89	−1882.729 25
	2	$...23a_1^2 24a_1^1/4a_2^2 5a_2^1/6b_1^2/18b_2^2$	1	−1878.823 18	−3.885 59	−1882.708 77
			0	−1878.822 95	−3.885 62	−1882.708 57
	3	$...24a_1^2/4a_2^2/5b_1^2 6b_1^1/18b_2^2 19b_2^1$	1	−1878.784 69	−3.885 43	−1882.670 13
			0	−1878.719 75	−3.890 25	−1882.610 00
	4	$...24a_1^2 25a_1^1/4a_2^2 5a_2^1/5b_1^2/18b_2^2$	1	−1878.591 85		
			0	−1878.591 67		
	5	$...24a_1^2/4a_2^2/6b_1^2 7b_1^1/17b_2^2 18b_2^1$	1	−1878.500 95		
			0	−1878.498 10		
B_1	1	$...24a_1^2 25a_1^1/4a_2^2/5b_1^2 6b_1^1/18b_2^2$	1	−1878.863 57	−3.859 03	−1882.722 60
			0	−1878.863 53	−3.859 03	−1882.722 56
	2	$...23a_1^2 24a_1^1/4a_2^2/6b_1^2 7b_1^1/18b_2^2$	1	−1878.839 02		
			0	−1878.837 47		
	3	$...24a_1^2/3a_2^2 4a_2^1/6b_1^2/18b_2^2 19b_2^1$	1	−1878.807 25		
			0	−1878.736 83		
	4	$...24a_1^2 25a_1^1/3a_2^2/6b_1^2 7b_1^1/18b_2^2$	1	−1878.627 55		
			0	−1878.627 26		
	5	$...24a_1^2/4a_2^2 5a_2^1/6b_1^2/17b_2^2 18b_2^1$	1	−1878.499 73		
			0	−1878.496 51		
B_2	1	$...24a_1^2/3a_2^2 4a_2^1/6b_1^2 7b_1^1/18b_2^2$	1	−1878.824 07	−3.885 07	−1882.709 14
			0	−1878.820 70	−3.885 28	−1882.705 98
	2	$...23a_1^2 24a_1^1/4a_2^2/6b_1^2/18b_2^2 19b_2^1$	1	−1878.801 89		
			0	−1878.743 12		
	3	$...24a_1^2/4a_2^2 5a_2^1/5b_1^2 6b_1^1/18b_2^2$	1	−1878.801 45		
			0	−1878.798 24		
	4	$...24a_1^2 25a_1^1/4a_2^2/6b_1^2/17b_2^2 18b_2^1$	1	−1878.566 44		
			0	−1878.562 61		

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

With respect to the standard CI methods 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[29] and therefore seems particularly appropriate in the case of large systems, like the metalloorganic 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[18] and formaldehyde.[19] 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 22.

Finally, we observe that since in our approach the correlation energy is evaluated separately, using a specific technique, it is not necessary to include correlation contributions via the unrestricted Hartree–Fock method, that, besides, 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 each symmtry of the Co(foracim)$_2$Li. To this end, we have performed several RHF calculations relative to different possible electronic configurations, chosen from among the most reasonable ones, thus obtaining various states that have been classified according to their spatial and spin symmetries. The results of such calculations are reported in Table I.

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, the only exceptions being the $^1A_1$ wave functions. In this case the HF wave functions for the higher $^1A_1$ states have been derived without any constraint with respect to the $^1A_1$ ones lower in energy, apart from that of the chosen configuration, and therefore the corresponding energy values, reported in Table I, are not in principle upper bounds to the exact energies. However, because of the very different nature and localization of the orbitals in the complex, we did not find problems of variational collapse for these states. Finally, we observe that for each symmetry several configurations can be proposed other than those of Table I, but none corresponding to an energy lower than that found as the lowest of each symmetry.

From the results of Table I we single out a few relevant points.

First, the lowest HF state is not represented by a $^1A_1$ closed-shell wave function but by a $^3A_1$ open shell. This fact suggests that the electronic structure of the ground stae of the complex does not correspond to a pair Co^I/Li$^+$ as usually assumed in experimental papers[9] but rather to a pair Co^{II}/Li, at least in the limit of the complex as an isolated molecule. This suggestion is confirmed by the analysis of the wave function proposed in the following section.

Second, we obtain an energy difference between the lowest singlet and the lowest triplet state of the A_1, A_2, and B_1 symmetries that is of the order of 10^{-4} au; this means that these states of the complex having the same spatial symmetry but different spin quantum number are quasi-degenerate at the HF level of approximation.

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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

sym	state	E	c_1	c_2	c_3	c_4	c_5
a. Triplet States							
$^3A_1$	1	−1878.887 31	1.0000	−0.017	−0.0007	−0.0006	
	2	−1878.820 15	0.0015	0.9727	−0.2322	0.0001	
	3	−1878.809 12	0.0010	0.2322	0.9727	0.0000	
	4	−1878.373 74	0.0006	−0.0001	0.0000	1.0000	
$^3A_2$	1	−1878.870 44	0.9999	0.0010	−0.0097	0.0039	0.0003
	2	−1878.823 21	−0.0012	0.9997	−0.0239	−0.0015	−0.0048
	3	−1878.784 67	0.0097	0.0239	0.9997	−0.0003	0.0029
	4	−1878.591 85	−0.0039	0.0015	0.0003	1.0000	0.0000
	5	−1878.500 95	−0.0003	0.0048	0.0030	0.0000	1.0000
$^3B_1$	1	−1878.863 68	0.9997	0.0047	−0.0131	0.0212	−0.0001
	2	−1878.839 37	−0.0060	0.9946	−0.1036	−0.0028	−0.0046
	3	−1878.806 89	0.0126	0.1037	0.9945	−0.0029	0.0001
	4	−1878.627 44	−0.0212	0.0030	0.0029	1.0000	0.0000
	5	−1878.499 72	0.0001	0.0046	−0.0006	0.0000	1.0000
$^3B_2$	1	−1878.824 27	0.9957	−0.0029	−0.0923	0.0003	
	2	−1878.801 89	0.0077	0.9986	0.0519	0.0009	
	3	−1878.801 26	0.0921	−0.0524	0.9944	−0.0002	
	4	−1878.566 44	−0.0003	−0.0010	0.0002	1.0000	
b. Singlet States							
$^1A_2$	1	−1878.870 39	0.9999	0.0007	0.0132	0.0039	0.0001
	2	−1878.822 96	−0.0006	1.0000	−0.0046	−0.0015	0.0047
	3	−1878.719 73	−0.0132	0.0045	0.9999	−0.0016	0.0069
	4	−1878.591 67	−0.0039	0.0015	0.0016	1.0000	0.0000
	5	−1878.498 08	0.0000	−0.0047	−0.0069	0.0000	1.0000
$^1B_1$	1	−1878.863 63	0.9998	0.0026	0.0024	0.0212	−0.0001
	2	−1878.837 59	−0.0025	0.9994	−0.0329	−0.0030	0.0047
	3	−1878.736 72	−0.0025	0.0328	0.9995	−0.0007	0.0015
	4	−1878.627 16	−0.0212	0.0030	0.0006	0.9998	0.0000
	5	−1878.496 50	0.0001	−0.0047	−0.0013	0.0000	1.0000
$^1B_2$	1	−1878.821 07	0.9957	−0.0581	−0.0723	0.0004	
	2	−1878.742 84	0.0567	0.9981	−0.0225	0.0004	
	3	−1878.798 15	0.0734	0.0183	0.9971	−0.0002	
	4	−1878.562 61	−0.0004	−0.0003	0.0002	1.0000	

To check whether the inclusion of the correlation energy changes this ordering of states, we have proceeded as follows. In order to estimate the importance of the mixing among different states that is responsible for the long-range part of the correlation energy, we have calculated the interaction matrix elements among the HF wave functions of the same symmetry, which are orthogonal among themselves, because of differences in their orbital occupation numbers, but mutually interacting as eigenfunctions of different HF operators. To this end, we have used a recently proposed technique[30] that allows a relevant simplification in the calculation of the matrix elements between Slater determinants orthogonal between themselves but constructed in terms of different sets of orbitals. The energy eigenvalues and eigenvectors, obtained by diagonalizing the corresponding Hamiltonian matrices, are given in parts a and b of Table II and show that the lowest state of each symmetry does not mix appreciably with the higher states of its symmetry and therefore that the long-range part of the correlation energy can be assumed negligible for these states.

We have not performed the corresponding CI calculation for the A_1 singlet states since the fact that they are not orthogonal among themselves does not allow us to exploit the simplifications discussed in ref 30 and thus makes such a calculation very heavy. However, if one includes in the CI matrix the same set of configurations as for the triplet A_1 states, the results should not significantly differ from those obtained in the case of the triplets: the only difference could be due to the presence of an extra state, the closed-shell $^1A_1$. For estimating the importance of its contributions to the lowest $^1A_1$ state, we have performed an MC–SCF calculation with a wave function of the type

$$\Psi = c_1|\ldots(24a_1\overline{25a_1} + 25a_1\overline{24a_1})| + c_2|\ldots 24a_1\overline{24a_1}| + c_3|\ldots 25a_1\overline{25a_1}|$$

Such a calculation is not strictly omogeneous with the previous (CI) one and probably includes larger correlation energy contributions; nevertheless, as the lowest root of the MC–SCF calculation, we have obtained an energy, $E = -1878.887\,734$, that is still very close, $|\Delta E| \sim 4 \times 10^{-4}$ au, to that of the lowest $^3A_1$ state. Furthermore, the corresponding wave function maintains a predominantly open-shell character: $c_1 \geq 0.99$.

To evaluate then the short-range part of the correlation energy, we have applied the approach proposed in ref 16 to the RHF wave functions of Table I. Such calculations have been performed for the three lowest states of the A_2 symmetries but only for the lowest state of the other symmetries. The results are reported in Table I.

We observe that the inclusion of the short-range correlation energy does not alter either the ordering of the A_2 states, as given by a simple HF calculations, nor the quasi-degeneracy between the lowest singlet and triplet states. Its main effect is the reduction, by about 0.7 eV, of the energy gap between the lowest and the first excited state of the symmetry. This is the reason why we have not performed such correlation energy calculations also for the higher states of the other symmetries.

From the results of Tables I and II, we conclude that the lowest electronic state of the Co(foracim)$_2$Li is described, in the independent-particle approximation, by the open-shell configuration $(\ldots 23a_1^2 24a_1 25a_1/\ldots 4a_2^2/\ldots 6b_1^2/\ldots 18b_2^2)$ of A_1 symmetry with the singlet and triplet components practically degenerate.

This degeneracy can be removed by including the relativistic components of the electronic Hamiltonian, whose contributions can be significant in the case of a transition-metal atom like the cobalt. In order to estimate this effect and thus to predict the order or magnitude of the magnetic moment of the Co(foracim)$_2$Li, we have taken into account for simplicity only the effects of the spin–orbit operator. From statistical considerations and from the analysis of the wave functions, which shows that the orbitals of the lowest $^3A_1$ state are very similar to the corresponding ones of the $^1A_1$ state and also that the singly occupied orbitals

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(30) Colle, R.; Fortunelli, A. *Chem. Phys. Lett.* **1988**, *144*, 493.

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

atom	$^3A_1$	$^3A_2$	$^3B_1$	$^3B_2$	$^1A_1$
Co	25.53	25.56	25.57	25.84	26.30
O	8.68	8.68	8.69	8.73	8.69
C_1	5.99	5.99	5.98	6.10	6.04
H_1	0.62	0.62	0.62	0.73	0.71
C_2	6.52	6.51	6.52	6.49	6.50
H_2	0.67	0.67	0.67	0.71	0.71
C_3	6.11	6.10	6.10	6.18	6.15
H_3	0.66	0.66	0.66	0.71	0.70
N	7.73	7.74	7.74	7.75	7.65
H_α	0.65	0.65	0.65	0.67	0.67
Li	3.19	3.19	3.19	2.05	2.05

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

exhibit a predominantly atomic character, one can conclude that the value of the magnetic moment should be much closer to that for a pure triplet state (2.8 μ_B) than to the value for a singlet state and not smaller than 1.9 μ_B. The experimental measurements, reported in ref 9 for the [Co(salen)Li(THF)$_{1.5}$], give a value for the magnetic moment of the order of 1.0 μ_B: this discrepancy could be attributed either to environment effects in the solid-state matrix or to problems in the experimental measurements.

Finally, we note that also the lowest states of the A_2 and B_1 symmetries are mutually quite close in energy and also similar in the nature of several occupied orbitals, as will be shown in the wave-function analysis of the following section: such a quasi-degeneracy can be removed by releasing the geometrical constraint on the C_{2v} symmetry of the complex, but such effects should be quite small since the experimental data of ref 9 correspond to a geometry only slightly distorted from planarity.

Analysis of the Wave Functions

In order to analyze the electron density distribution in the lowest state of each symmetry, we have performed a Mulliken population analysis of the HF wave functions of the various states of interest. Our results show that states with the same spatial symmetry but different spin quantum number have practically the same values of the gross atomic population (GAP), and thus in Table III we report the GAP only for the $^3A_1$, $^3A_2$, $^3B_1$, and $^3B_2$ lowest states and also for the $^1A_1$ closed-shell wave function.

From Table III we observe that the GAP's of $^3A_1$, $^3A_2$, and $^3B_1$ are practically coincident and correspond to a lithium with a slightly negative charge ($\simeq$0.19 au) and to a cobalt positively charged by about 1.45 au because of an electron transfer toward the oxygen and nitrogen atoms. Apart from the specific numerical values, which are affected by a certain roughness of the Mulliken population analysis, these results suggest that in such states the lithium retains much of its atomic character while the cobalt is essentially a Co^{II}. In the $^1A_1$ and $^3B_2$ states, instead, the lithium is essentially a positive ion, with a charge of about 0.95 au due to an electron transfer, which, in the case of $^1A_1$ closed shell, is of about 0.7 au toward the cobalt and 0.25 au toward the carbon hydrogen skeleton, while, in the case of $^3B_2$, it is of about 0.3 au toward the cobalt and 0.7 au toward the whole (foracim)$_2^{2-}$ ligand.

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, foracim$^-$ (in the geometry of the complex), and Li in the following states: Co^{II}(^{2}H: 1s^2/2s^{2}2p^6/3s^{2}3p^6/3d^7), foracim$^-$ (^{1}A: 1σ^2...16σ^2/1$\pi^2$2$\pi^2$3π^2) and Li(^{2}S: 1s^{2}2s^1). Note that we have chosen for the cobalt the ^{2}H state, which correlates with the energetically most favorable configuration for a d^7 atom in a square-planar field and that for this type of analysis the use of the orbitals of the pair Co^I/Li$^+$ instead of those of the pair Co^{II}/Li gives practically the same results. 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

Table IV. Expansion of the Highest Occupied Orbitals of a Few HF Wave Functions in Terms of the Orbitals of the Separate Fragments[a]

$4\gamma \pm (\mathrm{for}) = 1/\sqrt{2}[16\sigma(\mathrm{for}) \pm 16\sigma(\mathrm{for}')]$ $4\tau \pm (\mathrm{for}) = 1/\sqrt{2}[4\pi(\mathrm{for}) \pm 4\pi(\mathrm{for}')]$

$3\gamma \pm (\mathrm{for}) = 1/\sqrt{2}[15\sigma(\mathrm{for}) \pm 15\sigma(\mathrm{for}')]$ $3\tau \pm (\mathrm{for}) = 1/\sqrt{2}[3\pi(\mathrm{for}) \pm 3\pi(\mathrm{for}')]$

$2\gamma \pm (\mathrm{for}) = 1/\sqrt{2}[14\sigma(\mathrm{for}) \pm 14\sigma(\mathrm{for}')]$ $2\tau \pm (\mathrm{for}) = 1/\sqrt{2}[2\pi(\mathrm{for}) \pm 2\pi(\mathrm{for}')]$

$1\gamma \pm (\mathrm{for}) = 1/\sqrt{2}[13\sigma(\mathrm{for}) \pm 13\sigma(\mathrm{for}')]$ $1\tau \pm (\mathrm{for}) = 1/\sqrt{2}[1\pi(\mathrm{for}) \pm 1\pi(\mathrm{for}')]$

$^3A_1$	$23a_1^2$	$0.84\cdot d_{z^2}(\mathrm{Co}) + 0.51\cdot d_{x^2-y^2}(\mathrm{Co})$	$\epsilon = -0.473$
	$24a_1^1$	$0.84\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.50\cdot 3d_{z^2}(\mathrm{Co}) + 0.21\cdot 4s(\mathrm{Co})$	$\epsilon = -0.581$
	$25a_1^1$	$[-0.86\cdot 2s(\mathrm{Li}) + 0.42\cdot 3s(\mathrm{Li})] + 0.10\cdot 4s(\mathrm{Co})$	$\epsilon = -0.106$
	$4a_2^2$	$[0.95\cdot 3\tau_-(\mathrm{for}) + 0.14\cdot 1\tau_-(\mathrm{for})] - [0.19\cdot 3d_{xy}(\mathrm{Co}) - 0.15\cdot 4d_{xy}(\mathrm{Co})]$	$\epsilon = -0.343$
	$6b_1^2$	$0.96\cdot 3\tau_+(\mathrm{for}) + 0.22\cdot 1\tau_+(\mathrm{for})$	$\epsilon = -0.363$
	$18b_2^2$	$[0.86\cdot 4\gamma_-(\mathrm{for}) + 0.32\cdot 3\gamma_-(\mathrm{for}) - 0.24\cdot 1\gamma_-(\mathrm{for})] + [0.20\cdot 3d_{yz}(\mathrm{Co}) + 0.11\cdot 4d_{yz}(\mathrm{Co})]$	$\epsilon = -0.488$
$^3B_1$	$23a_1^2$	$[0.73\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.23\cdot 4s(\mathrm{Co})] + [0.53\cdot 4\gamma_+(\mathrm{for}) - 0.20\cdot 3\gamma_+(\mathrm{for})]$	$\epsilon = -0.489$
	$24a_1^2$	$[0.78\cdot 4\gamma_+(\mathrm{for}) + 0.30\cdot 3\gamma_+(\mathrm{for})] - [0.46\cdot 3d_{x^2-y^2}(\mathrm{Co}) + 0.18\cdot 4s(\mathrm{Co})]$	$\epsilon = -0.470$
	$25a_1^1$	$-0.86\cdot 2s(\mathrm{Li}) + 0.42\cdot 3s(\mathrm{Li})$	$\epsilon = -0.106$
	$4a_2^2$	$0.94\cdot 3\tau_-(\mathrm{for}) + [0.21\cdot 3d_{xy}(\mathrm{Co}) - 0.14\cdot 4d_{xy}(\mathrm{Co})]$	$\epsilon = -0.344$
	$6b_1^1$	$3d_{xz}(\mathrm{Co})$	$\epsilon = -0.620$
	$18b_2^2$	$[0.86\cdot 4\gamma_-(\mathrm{for}) + 0.33\cdot 3\gamma_-(\mathrm{for}) + 0.24\cdot 1\gamma_-(\mathrm{for})] + [0.20\cdot 3d_{yz}(\mathrm{Co}) + 0.11\cdot 4d_{yz}(\mathrm{Co})]$	$\epsilon = -0.490$
$^3A_2$	$23a_1^2$	$[0.68\cdot 3d_{z^2}(\mathrm{Co}) - 0.57\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.28\cdot 4s(\mathrm{Co})] + [0.16\cdot 2\gamma_+(\mathrm{for}) + 0.20\cdot 3\gamma_+(\mathrm{for}) - 0.21\cdot 4\gamma_+(\mathrm{for})]$	$\epsilon = -0.494$
	$24a_1^2$	$[0.90\cdot 4\gamma_+(\mathrm{for}) + 0.24\cdot 3\gamma_+(\mathrm{for})] - [0.20\cdot 3d_{x^2-y^2}(\mathrm{Co}) + 0.11\cdot 4s(\mathrm{Co})]$	$\epsilon = -0.477$
	$25a_1^1$	$[-0.86\cdot 2s(\mathrm{Li}) + 0.42\cdot 3s(\mathrm{Li})] + 0.10\cdot 4s(\mathrm{Co})$	$\epsilon = -0.106$
	$4a_2^1$	$3d_{xy}(\mathrm{Co})$	$\epsilon = -0.625$
	$6b_1^2$	$0.96\cdot 3\tau_+(\mathrm{for}) + 0.21\cdot 1\tau_+(\mathrm{for})$	$\epsilon = -0.365$
	$18b_2^2$	$[0.86\cdot 4\gamma_-(\mathrm{for}) + 0.32\cdot 3\gamma_-(\mathrm{for}) - 0.25\cdot 1\gamma_-(\mathrm{for})] - [0.20\cdot 3d_{yz}(\mathrm{Co}) + 0.11\cdot 4d_{yz}(\mathrm{Co})]$	$\epsilon = -0.492$
$^3B_2$	$23a_1^2$	$[0.57\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.49\cdot 3d_{z^2}(\mathrm{Co}) + 0.28\cdot 4s(\mathrm{Co})] - [0.48\cdot 4\gamma_+(\mathrm{for}) + 0.26\cdot 3\gamma(\mathrm{for})]$	$\epsilon = -0.410$
	$24a_1^2$	$[0.81\cdot 4\gamma_+(\mathrm{for}) - 0.19\cdot 3\gamma_+(\mathrm{for}) - 0.15\cdot 1\gamma_+(\mathrm{for})] - [0.35\cdot 3d_{z^2}(\mathrm{Co}) - 0.27\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.16\cdot 4s(\mathrm{Co})]$	$\epsilon = -0.407$
	$4a_2^1$	$3d_{xy}(\mathrm{Co})$	$\epsilon = -0.544$
	$6b_1^2$	$0.95\cdot 3\tau_+(\mathrm{for}) - 0.22\cdot 2\tau_+(\mathrm{for}) + 0.15\cdot 1\tau_+(\mathrm{for})$	$\epsilon = -0.305$
	$7b_1^1$	$[0.94\cdot 4\tau_+(\mathrm{for}) - 0.18\cdot 2\tau_+(\mathrm{for})] + [0.24\cdot 4d_{xz}(\mathrm{Co}) - 0.13\cdot 3d_{xz}(\mathrm{Co})]$	$\epsilon = -0.071$
	$18b_2^2$	$[0.88\cdot 4\gamma_-(\mathrm{for}) - 0.29\cdot 1\gamma_-(\mathrm{for}) + 0.14\cdot 3\gamma_-(\mathrm{for})] + 0.23\cdot 3d_{yz} + 0.12\cdot 4d_{yz}]$	$\epsilon = -0.425$
$^1A_1$	$23a_1^2$	$[0.83\cdot 3d_{z^2}(\mathrm{Co}) + 0.44\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.15\cdot 4d_{z^2}(\mathrm{Co})] + [0.17\cdot 2\gamma_+(\mathrm{for}) - 0.18\cdot 4\gamma_+(\mathrm{for})]$	$\epsilon = -0.354$
	$24a_1^2$	$0.80\cdot 3d_{x^2-y^2}(\mathrm{Co}) - 0.44\cdot 3d_{z^2}(\mathrm{Co}) + 0.34\cdot 4s(\mathrm{Co}) + 0.10\cdot 4d_{x^2-y^2}(\mathrm{Co})$	$\epsilon = -0.224$
	$4a_2^2$	$0.75\cdot 3\tau_-(\mathrm{for}) - 0.63\cdot 3d_{xy}(\mathrm{Co}) + 0.10\cdot 4d_{xy}(\mathrm{Co})$	$\epsilon = -0.245$
	$6b_1^2$	$0.90\cdot 3d_{xz}(\mathrm{Co}) + [0.34\cdot 2\tau_+(\mathrm{for}) + 0.25\cdot 4\tau_+(\mathrm{for})]$	$\epsilon = -0.244$
	$18b_2^2$	$[0.92\cdot 4\gamma_-(\mathrm{for}) - 0.21\cdot 1\gamma_-(\mathrm{for})] + [0.21\cdot 3d_{yz} + 0.13\cdot 4d_{yz}]$	$\epsilon = -0.417$

[a] ϵ indicates the HF eigenvalue of the orbital. All the quantities are given in atomic units.

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

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

$1\pi = 0.28\cdot 2p_x(\mathrm{O}) + 0.32\cdot 2p_x(\mathrm{C}_1) + 0.30\cdot 2p_x(\mathrm{C}_2) + 0.35\cdot 2p_x(\mathrm{C}_3) + 0.30\cdot 2p_x(\mathrm{N})$ $\epsilon = -0.310$

$2\pi = -0.45\cdot 2p_x(\mathrm{O}) - 0.38\cdot 2p_x(\mathrm{C}_1) + 0.37\cdot 2p_x(\mathrm{C}_3) + 0.40\cdot 2p_x(\mathrm{N})$ $\epsilon = -0.233$

$3\pi = -0.49\cdot 2p_x(\mathrm{O}) + 0.66\cdot 2p_x(\mathrm{C}_2) - 0.42\cdot 2p_x(\mathrm{N})$ $\epsilon = -0.063$

$4\pi = 0.47\cdot 2p_x(\mathrm{O}) - 0.58\cdot 2p_x(\mathrm{C}_1) + 0.59\cdot 2p_x(\mathrm{C}_3) - 0.56\cdot 2p_x(\mathrm{N})$ $\epsilon = +0.370$

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

various states of interest are reported in Table IV.

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 V. Furthermore, the orbitals that contribute most to the expansion of the higher occupied orbitals of the complex are the 3d, 4s, and 5s of the cobalt, the 2s and 3s of the lithium, and the 13–16 σ and 1–4 π of the foracim negative ion. The dominant component of the 16σ orbital is represented by the $2p_z$ functions centered on the oxygens, while the 13–15 σ orbitals are linear combinations of various sp^n hybrids centered on the oxygen, nitrogen, and carbons with s functions on the hydrogens; finally, the 1–4 π orbitals are Hückel-type combinations of the $2p_x$ of the oxygen, nitrogen, and carbon atoms (see Table V for a more detailed description).

This type of analysis, when applied to the $^3A_1$ HF ground-state wave function and to the corresponding $^1A_1$ open shell, whose orbitals are practically coincident, gives the following main results:

(a) The lower singly occupied orbital ($24a_1$) is predominantly a $3d_{x^2-y^2}$ of the cobalt with a minor s-type component also on the cobalt (virtual 4s), while the higher singly occupied orbital ($25a_1$) is essentially a diffuse s-type orbital on the lithium with a component on the 4s orbital of the cobalt, thus giving a weakly bound "lithium atom" (see below for the discussion of the fragmentation energy).

(b) There is a relevant ($\simeq$0.6 au) electron donation from the σ-system of the ligand to the d_{yz} and virtual orbitals of the cobalt.

(c) The π-system of the ligand is slightly more diffuse than in the separate fragments, because of the inclusion of the virtual 4π orbital of the foracim⁻ and the delocalization onto the $4d_{xy}$ and $4d_{xz}$ orbitals of the cobalt.

Considering now the states in which the lithium is essentially a positive ion (lowest $^{1,3}B_2$ states and $^1A_1$ closed shell), we see that the configuration lowest in energy corresponds to that of the $^3B_2$ state. In such a state the $3d_{x^2-y^2}$ and $3d_{z^2}$ of the cobalt are doubly occupied, while simultaneously one electron has been promoted from the $3d_{xy}$ of the cobalt to the first virtual orbital of the ligand π-system [$7b_1 \simeq 4\tau_+$]. Furthermore, there is a relevant ($\simeq$0.7 au) electron donation from the σ-system of the ligand to the d_{yz} and virtual orbitals of the cobalt, while the π-system of the ligand delocalizes also onto the $4d_{xy}$ and $4d_{xz}$ orbitals of the cobalt.

Finally, the $^1A_1$ closed-shell wave function, corresponding to a state in which the cobalt is formally a Co^{I}, gives an energy higher than that of the $^3B_2$ state by about 0.5 eV and is characterized by the expansion of the occupied 3d orbitals of the cobalt, by a slight reduction of the electron donation ($\simeq$0.5 au) from the σ-system of the ligand to the d_{yz} and virtual orbitals of the cobalt and by an appreciable ($\simeq$0.2 au) π-back-donation from the cobalt to the π-system of the ligand, that is also slightly more diffuse than in the separate fragments.

Using the results of such orbital analysis and the eigenvalues (ϵ au) of the HF operators reported in Table IV, we now discuss the ordering of the states as derived from our calculations. Let us consider the closed-shell $^1A_1$ wave function as the reference state: the eight valence electrons of the singly charged cobalt (Co^{I}), which in the isolated atom are described by the degenerate 3d orbitals, distribute among the following molecular orbitals, whose order in energy is characteristic of the d orbitals in a square-planar ligand field:

$$\begin{pmatrix} 23a_1[3d_{z^2}] \\ \epsilon = -0.354 \end{pmatrix}^2 < \begin{pmatrix} 4a_2[3d_{xy}] \\ \epsilon = -0.245 \end{pmatrix}^2 \simeq \begin{pmatrix} 6b_1[3d_{xz}] \\ \epsilon = -0.244 \end{pmatrix}^2 < \begin{pmatrix} 24a_1[3d_{x^2-y^2}] \\ \epsilon = -0.224 \end{pmatrix}^2$$

On the other hand, the HF eigenvalue of the lowest unoccupied orbital (LUMO: $25a_1$), which is essentially a diffuse s-type function centered on the lithium, is quite low in energy ($\epsilon = 0.007$ au). For estimating then the difference in energy between this closed-shell $^1A_1$ wave function and a triplet one obtained by promoting one electron from the highest occupied orbital (HOMO: $24a_1$) to the LUMO, one can use the formula $\Delta E = E(^3A_1) - E(^1A_1) = \epsilon_j^{\,t} - \epsilon_i^{\,s}$ where the $\epsilon_{i,j}^{\,s,t}$ are the Fock eigenvalues of the singly occupied orbital (j) of the open-shell triplet state and of the doubly occupied orbital (i) of the closed-shell singlet state. Approximating now the HF eigenvalue of the ($25a_1$) singly occupied orbital of the triplet state with that of the 2s orbital of the lithium atom: $\epsilon_j^{\,t} \simeq \epsilon(2s\ \mathrm{Li}) = -0.20$ au, we obtain the following rough estimate: $\Delta E = 0.02$ au, of the energy difference between the triplet and the optimized closed-shell $^1A_1$ function. By allowing now the rearrangement of the triplet wave function, one can easily predict that its energy will become lower than that of the closed-shell wave function, in accord with the results of Table I. Furthermore, from the pattern of the HF eigenvalues of the highest occupied orbitals of the A_1, A_2, and B_1 symmetries, one can also justify the calculated energy sequence of the lowest triplet states of the various symmetries: $E(^3A_1) < E(^3A_2) < E(^3B_1) < E(^3B_2)$.

Finally, in order to estimate the strength of the bond between the lithium and the $\mathrm{Co(foracim)_2}$ in the covalent $^3A_1$, $^3A_2$, and $^3B_2$ states of the $\mathrm{Co(foracim)_2Li}$, i.e. to evaluate the height of the barrier for the homolitic fragmentation of the complex, we have carried out separate RHF calculations for the ^2S state of the lithium atom and for the $\mathrm{Co(foracim)_2}$ molecule in the lowest $^2A_1$, $^2A_2$, and $^2B_1$ states, which correlate with the corresponding states of the complex. These RHF calculations have been performed by imposing on the $\mathrm{Co(foracim)_2}$ the same geometry as in the complex and by using the entire basis set described in the previous section, to automatically eliminate basis set superposition errors[31] in the evaluation of the fragmentation energy.

From such calculations we obtain that, at the HF level, the $^3A_1$, $^3A_2$, and $^3B_1$ states of the isolated complex are bound by about 0.8 eV with respect to the isolated fragments in the proper states (the inclusion of the correlation energy can only increase this energy gap). The fragmentation barrier for the $^1A_1$ closed-shell and $^3B_2$ states, where the lithium is essentially a positive ion, is obviously much higher than the previous one, about 7.3 eV, because of the electrostatic attraction between the fragments.

Conclusions

The main conclusions, that can be drawn from our analysis of the electronic states of the $\mathrm{Co(foracim)_2Li}$ are the following:

(1) The lowest states of the various symmetries can be classified in two groups, according to the different charge partition between the cobalt and the lithium. In particular, the $^{1,3}A_1$, $^{1,3}A_2$, and $^{1,3}B_1$ states are characterized by the presence of the pair $\mathrm{Co}^{\mathrm{II}}/\mathrm{Li}$ and are lower in energy with respect to the $^{1,3}B_2$ (and $^1A_1$ closed shell), characterized by the presence of an ionic lithium.

(2) The ground state of the molecule is represented, in the independent-particle approximation, by the open-shell configuration $(...23a_1^{\,2}24a_125a_1/...4a_2^{\,2}/...6b_1^{\,2}/...18b_2^{\,2})$ of A_1 symmetry with the triplet and singlet components practically degenerate. The main consequence of this fact is the prediction of a magnetic moment for the $\mathrm{Co(foracim)_2Li}$ in its ground state of the order of about 2.0 μ_B.

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(31) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(3) The $^{1,3}A_1$ states of the isolated complex are bound by about 0.8 eV with respect to the separate fragments, $Co(foracim)_2$ and Li, and are characterized by a relevant electronic σ-donation from the organic ligand to the cobalt and by a simultaneous expansion of the π-system.

(4) The $^{1}A_1$ closed-shell state exhibits an appreciable electronic π-back-donation from the cobalt to the ligand, with a reduced σ-donation from the ligand to the cobalt.

Finally, we observe that, at least a part of these results, which refer to the isolated molecule, can also be ascribed to the choice of lithium as the alkali-metal atom, its ionization potential being appreciably higher than that of the other alkali-metal atoms.

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The Role of Resonance and Inductive Effects in the Acidity of Carboxylic Acids

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Abstract: The normal inductive effects are shown to account for most of the enhanced acidity of carboxylic acids compared to alcohols. The contributions of these effects are determined using several extrapolations from nonconjugated systems. Further support is given from atomic population analyses of formic acid, formate ion, ethanol, and ethoxide ion. A comparison of the natural population analysis, integrated projection populations, and integrated Bader populations is given as well as the effects of varying the basis set (3-21+G, 6-31+G, 6-31+G*). Qualitatively, all population analyses agree that the carbonyl group in carboxylic acids is highly polarized and is the major contribution affecting the relative acidities of carboxylic acids and alcohols. Vinyl alcohol and vinyl alkoxide are included in the population analysis for comparison.

The greater acidity of carboxylic acids compared to alcohols is normally ascribed in current textbooks primarily to the resonance energy or, equivalently, increased charge delocalization in carboxylate ions compared to alkoxide ions; that is, in a carboxylate ion the charge is divided between two oxygens whereas in the alkoxide ion it is localized on only one.[2] This traditional view has been challenged by Siggel and Thomas[3] who found from a comparison of experimental photoelectron core-ionization energies with gas-phase acidities as well as from ab initio calculations that the gas-phase acidity difference between an alcohol and a carboxylic acid is determined by the potential at the proton in the neutral acid. That is, the acidity difference is already fully inherent in the ground-state electronic properties and is not due to differential effects in the product anions. This view was confirmed by our recent studies of projected electron density functions and difference functions of ethanol and formic acid and their anions.[4] The results of this study indicate that the carbonyl group is already so polar that little additional delocalization of charge can occur to the carbonyl oxygen.

In this paper we show that normal inductive effects can account for most of the enhanced acidity of carboxylic acids compared to alcohols and confirm that the charge delocalization in carboxylate ions plays only a small role.

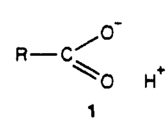
Table I. Correlation of Gas-Phase Acidities of Some Alcohols with σ_I

alcohol	$\sigma_I{}^a$	$\Delta H_{acid}{}^b$
CH_3CH_2OH	−0.01	376.1
$MeOCH_2CH_2OH$	0.11	372.5
F_2CHCH_2OH	0.32	367.0
CF_3CH_2OH	0.40	364.4

[a] Reference 8. [b] In kcal mol^{-1} from ref 7.

Inductive Effect of the Carbonyl Group

The new view assigns a much greater role to inductive effects than has been recently generally accepted. However, the inductive effect of a nearby polar carbonyl group had been considered as a significant factor in early theoretical studies. For example, in discussing the role of carboxylate resonance, Wheland recognized that inductive effects could be important: "...resonance of the present type may make a considerable contribution to the relatively great acid strength, *although the closeness of the large carbonyl group moment makes a decision difficult* (emphasis ours). Both the electrostatic and the resonance factors operate here to increase the acidity, and we cannot be sure how much of the observed effect must be attributed to each cause."[5] Pauling also wondered about the relative importance of resonance structure **1** in making the hydrogen more acidic and emphasized that the resonance energy of RCO_2^- is not known; however, he also wrote (regarding structure **1**), "The concept of resonance provides an obvious ex-



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[2] Some currently popular textbooks using essentially this argument are: Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn & Bacon: Boston MA, 1983; p 793. Solomons, T. W. G. *Fundamentals of Organic Chemistry*; Wiley: New York, 1982; p 602. Loudon, G. M. *Organic Chemistry*, 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1987; p 825. Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 3rd ed.; MacMillan: New York, 1985; pp 452–3. Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1977; pp 797–8. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987; p 6. Wade, L. G., Jr. *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1987; p 979. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 231.

[3] Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360.

[4] Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A., Jr. THEOCHEM **1988**, *165*, 309.

[5] Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: 1955; p 345.

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