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The electronic structure of $Co_4(CO)_{12}$ and $Co_3S(CO)_9$

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Abstract

The bonding in $Co_4(CO)_{12}$, $Co_3S(CO)_9$ and $Co_3P(CO)_9$ is compared by means of general bond indices analysis, band structure analysis and the valent atomic orbitals approach. The existence of direct Co–Co bonds was found in all the compounds under consideration. These bonds are of a complex nature with all the Co valence orbitals — 3d, 4s and 4p — being involved in the bonding. The similarity of the local valent structure of the Co atoms in all the compounds was demonstrated. The interactions of the orbitals of e symmetry play an important role in the Co–S bonding in $Co_3S(CO)_9$.

Introduction

In transition metal clusters one can find two types of bonds between the metal atoms: direct bonding and bonding through the bridging atoms or ligands. In the latter case the question arises about the existence of direct metal–metal bonds. Both the theoretical and experimental data are controversial [1–4].

In this communication we present the results of comparative analyses of bonding in the cobalt carbonyl clusters $Co_4(CO)_{12}$ and $Co_3X(CO)_9$ (X=S, P). The ground state geometrical structure of tetrametal dodecacarbonyls, $M_4(CO)_{12}$, is either the idealized T_d form with all terminal ligands or the C_{3v} form in which one face of the tetrahedron is bridged on all three edges by carbonyl ligands [4] (Fig. 1). The C_{3v} structure is the one found experimentally for cobalt dodecacarbonyl, but it is believed that the energy difference between these two forms does not exceed several kcal mol^{-1} [5]. The $Co_3S(CO)_9$ cluster belongs to the group of compounds that can be regarded as the result of the isolobal (or almost isolobal) substitution of one of the $Co(CO)_3$ fragments by the main group element atom or by some radical. The $Co_3S(CO)_9$ and $Co_3P(CO)_9$ molecules have the approximate C_{3v} spatial symmetry without bridging CO groups but with the μ_3-X bridging atom. The $Co_3S(CO)_9$ molecule is of particular interest because of its stability with the 'extra' electron on the strongly antibonding molecular orbital [6, 7]. At the same time, the phosphor atom in $Co_3P(CO)_9$ is inclined to form additional bonds through its lone pair [8]. The main purpose of this paper is to study and to compare the electronic structure of $Co_3S(CO)_9$, $Co_3P(CO)_9$ and both $Co_4(CO)_{12}$ forms with special attention to the problems of Co_3–S bonding and direct metal–metal bonding. We use the data obtained for $Co_4(CO)_{12}$ for further discussion of the chemistry and photochemistry of this cluster.

Apart from the quantitative electron counting rules [9] and the general discussion based on the Extended Hückel Theory (EHT) studies [10, 11] there are as yet few published electronic structure calculations of tetrametal carbonyl clusters. Freund *et al.* [12] used the CNDO method to compare the MO diagrams and orbital populations for several mononuclear and binuclear carbonyls and for two conformations of $Co_4(CO)_{12}$. Holland *et al.* [13] in the framework of the self-consistent X_α method examined the effect of different ligand environments on the electronic structure, spectra and electrochemistry of $Co_4(CO)_{12}$ and its derivatives. As for the $Co_3S(CO)_9$ cluster, Chesky and Hall [6] studied the electronic structure of $Co_3S(CO)_9$ and of several related compounds by the parameter-free Fenske-Hall MO method. Dahl and co-workers [7] used the qualitative molecular orbital approach to show the antibonding nature of the MO occupied by the unpaired electron. Subsequent comparative experimental investigations of the related compounds $FeCo_2(CO)_9X$ (X=S, Se, Te) confirmed their conclusion [14].

Details of the molecular orbital calculations

For the molecular orbital calculations we used the restricted Hartree-Fock method in the extended INDO

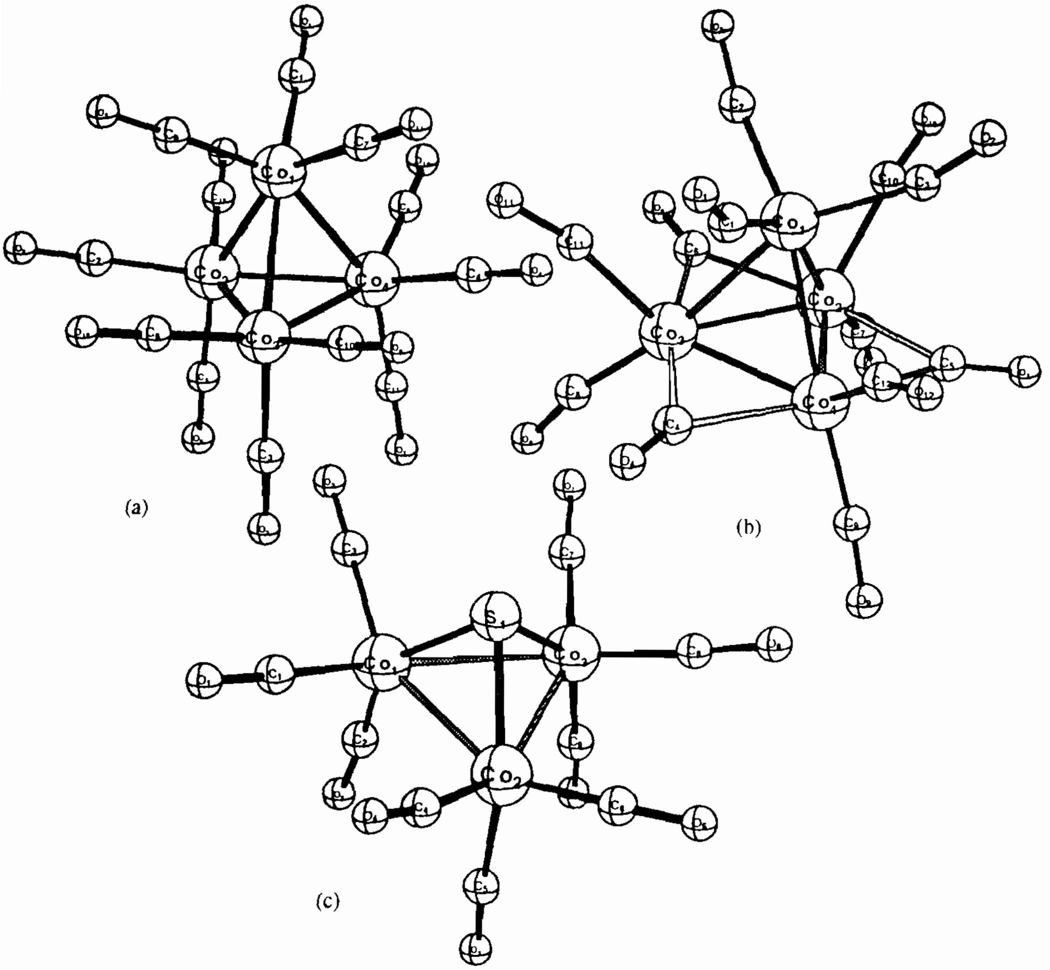


Fig. 1. The molecular structure of $Co_4(CO)_{12}$ (T_d (a) and C_{3v} (b)) and $Co_3S(CO)_9$ (c)

approximation [15, 16]. For the excited states the configuration interaction (CI) method was applied. Details of the parametrization scheme are given in the Appendix.

For $Co_3S(CO)_9$ we took the experimental X-ray structure [17]. The mean values of the interatomic distances are: Co–Co 2.646, Co–S 2.137, Co–C 1.777, C–O 1.148 Å; the average value of the O–C–Co angle is 174.7°. The largest deviations from the mean values are: R(C–O) 0.07 Å, R(Co–C) 0.15 Å. The distances between the Co atoms in $Co_3S(CO)_9$ are larger than in $Co_4(CO)_{12}$, and the Co–CO distances are slightly larger than $R(Co_b–C_l)$, but much shorter than the other bonds of cobalt with the terminal CO groups in $Co_4(CO)_{12}$. Because we wanted to exclude the influence of the geometry on the results of the comparative analysis of the bonding in two $Co_3X(CO)_9$ molecules, for $Co_3P(CO)_9$ we took the same geometry as for $Co_3S(CO)_9$.

The INDO calculations of $Co_4(CO)_{12}$ were performed for the experimental C_{3v} geometry taken from the refs. 18 and 19 and for two (T_d and C_{3v}) model structures. In both model structures R(Co–Co) = 2.488, R(Co–C) = 1.878, R(C–O) = 1.150 Å. These bond lengths were also used in the calculations of structural elements of $Co_4(CO)_{12}$: the naked Co_4 cluster and the CO molecule. Thus any possible differences in the calculated bonding characteristics of these two model structures are due to the electronic and symmetry effects but not to the variations in the bond length.

In the case of the experimental structure we used the X-ray structural data [18, 19] with the averaged values of the bond length and angles to form the molecule with C_{3v} symmetry. In this structure there are four different sorts of CO groups: coordinated to the apical Co atom, CO_a ($R(Co_a–CO_a) = 1.9329$ Å, $\angle Co_a–C_a–O_a = 160.0°$, $\angle C_a–Co_a–C_a = 101.92°$); terminal CO groups, bonded to basal metal atoms, Co_b: ligands above the basal plane – the 'upper' CO ($R(Co_b–C_u) = 1.9563$ Å, $\angle Co_a–C_a–O_a = 167.87°$) or under the basal plane – the 'lower' CO groups ($R(Co_b–C_l) = 1.7393$ Å, $\angle Co_b–C_l–O_l = 167.09°$, $\angle C_l–Co_b–O_l = 104.40°$). For these terminal CO groups R(C–O) = 1.0223 Å. The bridging CO ligands lie in

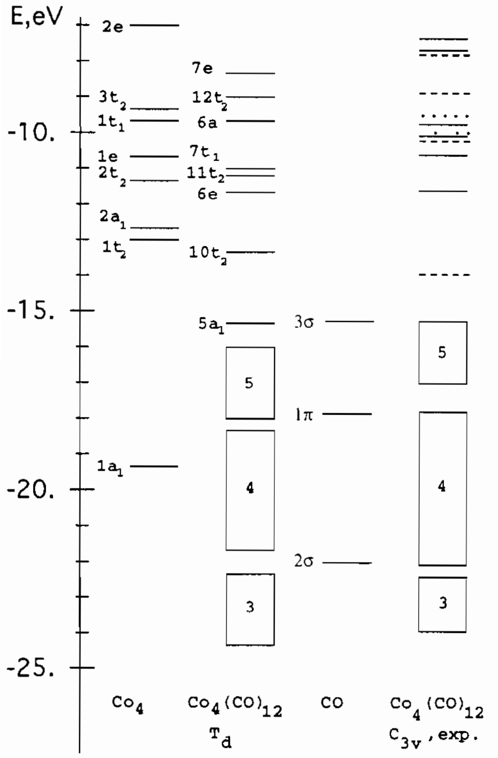


Fig. 2. The molecular orbital diagrams for the two $Co_4(CO)_{12}$ structures, the naked cluster Co_4 and the CO molecule Only the occupied MOs are displayed. The numbering of MOs includes the lowest occupied orbitals which are not shown on the diagram The MO symmetry for C_{3v} conformation. ----- a_1, · · · · · a_2, ——, e

the same plane as the basal Co atoms with $R(Co_b–C_b) = 2.0806$, $R(C–O)_b = 1.182$ Å.

The molecular orbital diagrams for the T_d and two C_{3v} structures of $Co_4(CO)_{12}$, the $^1A_1$ electronic state of the metal cluster Co_4 (this state is not the lowest one) and the CO molecule are shown in Fig. 2. The MO energies, calculated for the experimental geometry of $Co_4(CO)_{12}$, are in good agreement with the photoelectron spectrum of this compound, which shows two main bands: one broad band of the ionization of the metal core with the maximum at 8.9 eV and the intense broad CO band with the maximum at 15.8 eV [13].

The bonding analysis for large molecules

In the modern computational quantum chemistry of large molecules the important problem is how to describe the results of calculations in the same clear, compact and understandable form as in qualitative models. The individual examination of each of numerous MOs is fruitless if possible at all; the global characteristics (atomic charges, cumulative bond indices) are very useful in comparative studies but cannot give deeper insight into the intimate mechanism of bond formation. In our study we used the intermediate approach based on the analysis of the groups of MOs ('bands') with common bonding properties. Our approach also includes the examination of the local valent structure of atoms or ligands and the use of several indices to describe the bonding between the pairs of atoms. The Wiberg index [20]

$$W(A\text{–}B) = \sum_{\mu\in A}\sum_{\nu\in B}(P_{\mu\nu})^2 \qquad (1)$$

is equal to the bond order between atoms A and B. The next index, $E^{cov}(A\text{–}B)$ [21, 22], is the covalent component of the two-center contribution to the total molecular electronic energy:

$$E^{cov}(A\text{–}B) = 2\sum_{\mu\in A}\sum_{\nu\in B}\beta_{\mu\nu}P_{\mu\nu}S_{\mu\nu} - 1/2\gamma_{AB}\sum_{\mu\in A}\sum_{\nu\in B}(P_{\mu\nu})^2 \qquad (2)$$

In our program the $E^{cov}(A\text{–}B)$ indices are calculated only for the systems with the closed shell configuration.

In the formulas (1) and (2) $S_{\mu\nu}$ is the overlap integral between the atomic orbitals μ and ν, $P_{\mu\nu}$ is the non-diagonal element of bond order matrix ($P_{\mu\nu} = 2\Sigma c_{\mu i}c_{\nu i}$ where the summation goes over all occupied MO i) and $\beta_{\mu\nu} = 1/2(\beta_A + \beta_B)$, β_A and β_B being the one-electron parameters of INDO method. It is necessary to note that parameters β are negative, and so usually the $E^{cov}(A\text{–}B)$ is also negative.

These bond indices are based on the assumption that the interaction between atoms depends on the overlap of their atomic orbitals and on the nodal structure of the resulting molecular orbitals in the region between these atoms. These assumptions enter the formulas (1) and (2) through the overlap integrals $S_{\mu\nu}$ and the MO coefficients $c_{\mu i}$. All these indices represent (although in different ways) the *total* bonding ability between two atoms in the molecule. In simple molecules it is often possible to correlate every MO with a certain type of interaction: σ or π, covalent or donor and so on. Analyzing the MOs one can understand the origin and the nature of interatomic bonding in the molecule under consideration. Using the overlap population concept it is also possible to express the contribution from each of the molecular orbitals to the total bonding between atoms A and B; for the MO i this contribution equals $\Sigma_{\mu\in A}\Sigma_{\nu\in B}S_{\mu\nu}c_{\mu i}c_{\nu i}$.

In the case of infinitely large systems (for instance crystals) it is possible to present the contribution of the individual molecular or crystal orbital to the overlap population between particular pairs of atoms as a function of the orbital energy [23]. The resulting COOP (crystal orbital overlap population) curves enable one to ascertain the bonding characteristics of the levels in the given energy range with respect to any pair of atoms.

Large molecules form an intermediate case between small molecules and crystals. The energy intervals between the molecular orbitals are small, but not sufficiently small to form a continuum. On the other hand, the MOs in such compounds are usually delocalized and bonding between atoms is distributed among molecular orbitals lying in a certain energy interval. So it is more instructive to consider not the single molecular orbitals but the groups with the common (but of course not the same) bonding properties and the electron density distribution. It is reasonable to expect that if a significant part of the electron density of the group of MOs rests on some pair of atoms then there is an interaction, either bonding or antibonding, between these atoms that originate from this group of MOs. That is the reason why both of these characteristics are useful in dividing the MOs in the groups whose bonding properties are to be analyzed.

In the framework of the INDO method (or any other method that takes electron–electron interactions explicitly into account) the atom–atom pair interaction energy is not additive relative to the summation over the MOs because of the second term in formula (2) and of the coulomb interaction. The only additive part of this energy is the first term in formula (2). We propose to use the components of this term as a measure of the input from the MO ϕ_i to the bonding between the atoms A and B:

$$B_i(\text{A–B}) = -2\sum_{\mu\in A}\sum_{\nu\in B}\beta_{\mu\nu}S_{\mu\nu}c_{\mu i}c_{\nu i} \qquad (3)$$

Then the index $B_{i-j}(\text{A–B}) = \Sigma_k B_k(\text{A–B})$ is a measure of the overall ability of the MOs ϕ_i–ϕ_j to bond the atoms A and B. The result of summation of $B_i(\text{A–B})$ (or $B_{i-j}(\text{A–B})$) over all occupied MOs is equal to the first term in formula (2) (taken with the opposite sign). The sign in formula (3) is chosen to produce a positive sign of $B_i(\text{A–B})$ for the bonding interactions and negative for the antibonding interactions.

Starting from the usual population analyses [24] we came to the index $A_{i-j}(X)$, which represent the atomic population connected with the MOs i–j.

In the analysis of the bonding in the cobalt clusters we also used the concept of the valent molecular (VMO) or atomic (VAO) orbitals. These orbitals are obtained by the diagonalization of the bond-order matrix block involving indices of the orbitals belonging to some atom or selected ligand [21']. The valent activities of the valent orbitals, V_λ, are closely connected with their effective occupancy n_λ:

$$V_\lambda = 2n_\lambda - n_\lambda^2 \qquad (4)$$

There is a close interrelation between the VAOs effective occupation number and the type of the bond in which this VAO takes part. Orbitals that form covalent bonds have n_λ values close to 1; the low values of n_λ show that the corresponding VAO takes part in the bond with the electronic density partly transferred to this orbital from, for instance, a lone pair with the resulting n_λ' slightly less than 2.

The general bonding properties in $Co_4(CO)_{12}$ and $Co_3S(CO)_9$

Let us first discuss the total bond indices $E^{\text{cov}}(\text{A–B})$ and $W(\text{A–B})$ for the ground states of $Co_4(CO)_{12}$ and $Co_3S(CO)_9$ and of the lowest excited state of $Co_4(CO)_{12}$ (Table 1). For the free CO molecule $E^{\text{cov}}(\text{C–O}) = 58.348$ eV and $W(\text{C–O}) = 2.555$. In the model T_d and C_{3v} structures with $R(\text{C–O}) = 1.15$ Å and in $Co_3S(CO)_9$ the C–O bond strength for all the terminal ligands is almost the same and does not depend substantially on the symmetry of the cluster or on the position of the ligand in the C_{3v} structure. The bond strength in the bridging CO groups is considerably reduced The changes in the bond indices for the 'experimental' C_{3v} geometry as compared with the 'model' structure reflect the differences in the bond lengths. The C–O bond indices group around two values – one for the terminal and the other for the bridging ligands. This explains the existence of two C–O stretching frequencies in the IR spectrum of $Co_4(CO)_{12}$ (2055 and 1866 cm^{-1}, [25]).

For bridging ligands each single bond is weaker than for terminal groups, but because each bridging ligand is connected with two cobalt atoms in total these ligands are bonded more strongly than the terminal ones.

The tetrahedral $Co_4(CO)_{12}$ molecule can be regarded as a model system with neither bridging CO groups in the basal plane nor an extra electron in the antibonding orbital. The bonding parameters of this structure are used as the reference characteristics of the direct Co–Co bonds in the cobalt carbonyl clusters.

Our calculations reveal the existence of direct Co–Co bonding in both trigonal $Co_4(CO)_{12}$ and $Co_3S(CO)_9$ molecules. The order of these bonds is about the half of the direct Co–Co bond in tetrahedral $Co_4(CO)_{12}$. This is enough to reduce the Co–S–Co angle to 72–76° in the $Co_3X(CO)_9$ clusters (X = S, Se, Te) [14, 17], which is much smaller than the typical values of 100–105° in the pyramidal molecules with an apical sulfur atom [26]. On the other hand, these bonds are possibly not strong enough to produce the local minimum on the electronic density distribution in the region between the Co atoms (as was found both experimentally and theoretically for the Co dimer with the bridging CO groups $Co_2(CO)_8$ [26]. The Co–S bond order slightly

TABLE 1. Bond indices E^{cov}(A–B) (in eV) and W(A–B) for the different structures of $Co_4(CO)_{12}$ and for $Co_3S(CO)_9$

	E^{cov}(A–B), $^1A_1$			W(A–B), $^1A_1$			W(A–B), $^3A_1$		W(A–B)
	T_d	C_{3v}, mod.	C_{3v}, exp.	T_d	C_{3v}, mod	C_{3v}, exp.	C_{3v}, mod.	C_{3v}, exp.	$Co_3S(CO)_9$
Co_a–Co_b	10.468	9 289	9.706	0.701	0.634	0.669	0.440	0.448	0.743[a]
Co_b–Co_b		7.110	7.780		0.342	0 406	0.339	0.387	0 486
Co_a–C_a	20.770	20.764	18.643	0.902	0.900	0 784	0.894	0.775	0 986[b]
Co_b–C_u		21 265	18.286		0.946	0 770	0.946	0.745	
Co_b–C_t		20.090	23.007		0.862	0 949	0.856	0.943	
Co_b–C_b		17 447	14.914		0.708	0.678	0.687	0.668	
$(C–O)_a$	55.744	55 722	65.492	2.264	2.267	2.375	2.263	2.375	2.265[c]
$(C–O)_u$		55.642	66.119		2.266	2.413	2.254	2.392	
$(C–O)_t$		55 767	64 715		2 299	2.316	2.268	2.316	
$(C–O)_b$		51.990	50.763		1.992	2.027	2.015	2.027	

[a] Co–S bond. [b] Average value for Co–CO interactions. [c] Average for $(C–O)_u$ and $(C–O)_t$

exceeds the Co_a–Co_b bond order in $Co_4(CO)_{12}$, but also does not attain the single bond value of 1.0. In trigonal $Co_4(CO)_{12}$ the weakening of the direct Co–Co bonds is compensated by the appearance of the bridging Co–(CO)–Co bonds and the consequent stabilization of the basal plane.

In $Co_3S(CO)_9$, where there are no bridging ligands, the stabilization is achieved through the interactions Co–S and Co–Co that are stronger than in trigonal $CO_4(CO)_{12}$. These interactions, however, are weaker than in $Co_3P(CO)_9$; in this compound $W(P–Co) = 0.915$ (that is very close to the single bond value of 1.0) and $W(Co–Co) = 0.643$.

The band bonding analysis for the cobalt clusters

The bonding properties of the CO molecule orbitals are well known [4]. As for the Co_4 cluster, the occupied MOs of symmetry a_1 and t_2 are bonding, t_1 is antibonding and the MOs 1e and 2e are essentially non-bonding (see Fig. 2).

The results of the band bonding analysis for the cobalt carbonyls are given in Tables 2–5. These data show that the overall band structures of all the systems under consideration are similar. This is not trivial, because the transformation of $Co_4(CO)_{12}$ from T_d to C_{3v} geometry is not simple symmetry lowering, but it is followed by the appearance of the bonds to the bridging ligands. The C_{3v} molecular orbitals reflect this new bonding scheme and therefore cannot be regarded simply as a result of the splitting of the T_d molecular orbitals in the field of the lower symmetry.

The MOs of the first band are localized on the CO groups. Their energies and bond indices B_{i-j}(C–O) are close to the related characteristics of the free CO molecule: $\epsilon_{1\sigma} = -42.1$ eV, $B_{1\sigma}(C–O) = 13.55$ eV. The only exception is the C–O bond index for the bridging CO ligands, which is reduced by about 10% as compared with the T_d structure, but this reduction is compensated for by the $(C–O)_b$ input to the second band. The MOs of this second band are delocalized over all atoms of the clusters and are responsible for the Co–Co (or Co–Co and Co–S) and Co–C bonds. The cobalt atoms participate in the MOs of this band through the 4s orbitals.

The MOs of the third group correlate with the non-bonding 2σ MO of CO. These MOs contribute significantly to the Co–C bonding. The MOs of the fourth band are derived from the 1π bonding orbitals of the CO molecule (the bond index $B_{1\pi}$(C–O) for the free CO molecule is equal to 8.8). This value is almost conserved for the terminal ligands ($B(C–O)_t$ for the fourth band equals 8.2–8.7). As for the bridging ligands, their 1π bonding ability is partly transferred to the fifth band.

The molecular orbitals of the fifth band participate essentially in the Co–CO bonds and in the intraligand bonds, especially for the bridging CO groups in the C_{3v} structure.

All these bands are well distinguished in the case of $Co_4(CO)_{12}$. In the case of $Co_3S(CO)_{12}$ we used in our calculations the real (not symmetrized) crystal structure of this compound. This led to removal of the degeneracy of the MOs and to a more uniform distribution of the MO energy levels within the energy interval -28.5 to -20.2 eV. The loss of the relatively high symmetry also manifests itself in the spreading of the input to the corresponding σ or π bonding over the wider energy interval. Indeed in the C–O bands

TABLE 2. Atomic localization indices A_{i-j}(Co) and A_{i-j}(CO) for the occupied MOs and for the lowest virtual MOs of $Co_4(CO)_{12}$[a] For the band numbering see Tables 3–5

Band	i	j	T_d		C_{3v}					
			4(Co)	12(CO)	(Co_a)	3(Co_b)	$3(CO)_a$	$3(CO)_u$	$3(CO)_1$	$3(CO)_b$
1	1	12	0 756	23 242	0.239	0.963	5.818	5 885	5 855	5 239
2	13	16	2 104	5 895	0.485	1.514	1.276	1 039	1 238	2.446
3	17	24	1 643	14 353	0.477	1.391	3.713	3 714	4.066	2.636
4	25	49	2 683	47.305	0.672	2 389	12.359	12 558	12.999	9.011
5	50	60	2.678	19 324	0.794	2 272	4 519	4.445	3.716	6.256
6	61	78	27 292	8 704	6.619	19.221	2.012	2.044	1.785	4.313
7	79	84	5.847	6 151	1.218	3.396	0.928	1.519	3.106	1.835

[a] The indices are multiplied by the number of equivalent atoms or ligands; $A_i(CO)=A_i(C)+A_i(O)$.

TABLE 3 Bond indices B_{i-j}(A–B) for the groups of the occupied MOs (ϕ_1–ϕ_{78}) and virtual MOs ϕ_{79}–ϕ_{84} of the tetrahedral $Co_4(CO)_{12}$ Energies of MOs, ϵ_i, are in eV

Band	i	j	ϵ_i	ϵ_j	B(Co–Co)	B(Co–CO)	B(C–O)
1	1	12	−49 5	−42.5	0.242	0 970	13.210
2	13	16	−35 0	−28.8	1.491	1 890	0.033
3	17	24	−24 5	−22.6	0.113	2.097	0.026
4	25	49	−21.5	−18.3	0.487	1.339	8.186
5	50	60	−18 1	−16.2	0.107	1 950	1.240
6–8	61	78	−15 3	−8.6	1.852	0.613	−0.783
6	61	66	−15 2	−11.5	1.532	0 230	−0 098
7	67	72	−11 1	−11.0	−0.432	0.408	−0.288
8	73	78	−9 6	−7.5	0.753	−0 025	−0 398
9	79	84	−1 9	−1.3	−0.842	−0.805	−1 234

TABLE 4 Bond indices B_{i-j}(A–B) for $Co_4(CO)_{12}$ (C_{3v} model structure). MO energies are close to the corresponding values from Table 3 (see also Fig 2) Bond indices for the non-bridging (terminal, CO_t) groups are averaged over CO_a, CO_u and CO_t

Band	i	j	$B(Co_a–Co_b)$	$B(Co_b–Co_b)$	$B(Co–C_t)$	$B(Co_b–C_b)$	$B(C–O)_t$	$B(C–O)_b$
1	1	12	0.495	0 596	1.087	1.635	13 245	11 861
2	13	16	1.380	1.419	1 532	1.864	0.026	1 205
3	17	24	0.181	0.213	2 266	1.423	−0 015	0 152
4	25	49	0.396	0 346	1 364	1.223	8.643	5 893
5	50	60	0 231	0.265	2 013	0 881	0.810	2 719
6–8	61	78	1 112	0 264	0 555	0.497	−0.810	−1 071
6	61	66	0.990	0 948	0 211	−0.012	−0.182	0.252
7	67	72	−0.724	0 320	0.327	−0 095	−0.300	0 029
8	73	78	0 845	−0 952	0.018	0 605	−0.324	−1 353
9	79	84	−0.627	−0 618	−0.668	−0 207	−1.456	−1 368

interval (−28.5 to −20.2 eV) it is possible to distinguish only two bands with the C–O bonding distributed between these two bands. For this reason it seems preferable to regard the $Co_3S(CO)_9$ molecular orbitals from this energy interval as forming the single C–O bonding band. The width of this band (8.3 eV) is equal to the total width of the three C–O bands in $Co_4(CO)_{12}$. The value of the B_{i-j}(C–O) index for this C–O band (9.64 eV) is only slightly larger than the sum of the B_{i-j}(C–O) indices over the three C–O bands in tetrahedral (9.45 eV) and trigonal (9.44 eV) $Co_4(CO)_{12}$. The same holds also for the $Co_3P(CO)_{12}$ cluster.

In all of the systems under consideration the most pronounced changes in bonding come from the highest (6–8) groups of the occupied MOs mostly localized on the Co_4 or the Co_3S core. The main input to this group of MOs arises from the 3d orbitals of the cobalt atoms. These bands are well distinguished by their Co–Co and Co–CO bonding properties. In Tables 3–5 the cumulative indices for the groups of the three upper bands are

TABLE 5. Bond indices $B_{i,j}$(A–B) for the groups of the occupied MOs of $Co_3S(CO)_9$. Energies of MOs are in eV

Band	i	j	ϵ_i	ϵ_j	B(Co–Co)	B(Co–S)	B(Co–C)	B(C–O)	Charge localization
1	1	9	−49.8	−45.6	0.219	0.045	1.140	13.622	CO
2	10	13	−36.6	−29.4	1.500	1.420	2.410	−0.040	CO, (Co,S)
3	14	28	−28.5	−24.2	0.563	1.448	3.734	4.749	CO
4	29	46	−23.7	−20.2	0.199	0.340	2.435	4.895	CO
5–8	47	62	−19.8	−13.0	0.473	1.192	−0.095	−0.673	Co, S
5	47	49	−19.8	−18.3	0.560	1.645	−0.039	0.069	Co, S
6	50	55	−17.5	−16.0	−0.312	0.164	0.310	−0.224	Co
7	56	61	−15.4	−13.8	0.764	−0.615	−0.042	−0.359	Co, S
8	62		−13.0		−0.539	−0.002	−0.324	−0.159	Co

also given. In the case of $Co_3S(CO)_9$ the single occupied MO of the symmetry a_2 forms the individual 'band'. This MO is localized in the plane of the basal Co atoms; its lobal structure is the same as is shown on Fig. 6 in ref. 14 and Fig. 8 in ref. 6. Two upper (the 7th and the 6th) bands can be reasonably correlated with the two peaks in the lower energy part of the PE spectrum of $Co_3S(CO)_9$ [6].

From the data of Tables 3 and 4 it follows that the strong reduction of the Co–Co bond strength in the C_{3v} form of $Co_4(CO)_{12}$ is connected with the less bonding and more antibonding interactions in the bands 6–8. For the bands of the doubly occupied MO of $Co_3S(CO)_9$ the antibonding Co–Co interactions (band 6) are not as strong as in $Co_4(CO)_{12}$, T_d, but the bonding Co–Co interactions (bands 5, 7) are much weaker. So the existence of the unpaired electron on the antibonding MO $9a_2$ is not the only cause for the weakening of the Co–Co bonds in $Co_3S(CO)_9$. Probably this is the more common effect connected with the lowering of the symmetry.

In the work of Chesky and Hall [6] the fragment bond analysis was carried out for the upper group of MOs, which approximately corresponds to the bands 7–5 of Table 5. MOs $14a_1$ and 20e are Co–Co bonding, MO $13a_1$ is Co–S antibonding; the group of close lying MOs $12a_1$–19e is localized primarily on the Co atoms and represents Co–CO interactions. The MOs $11a_1$ and 16e are Co–S bonding. The corresponding data of Table 5 are in accord with these results, but our 'band' approach permits a more detailed description of *all* interactions *simultaneously* to be obtained, thereby demonstrating the advantage of this method over qualitative MO analysis.

The valent structure of the cobalt, sulfur and phosphorus atoms

The structure of the valent (self-consistent hybrid) atomic orbitals, VAO, for Co, S and P atoms is presented in Tables 6 and 7.

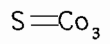
TABLE 6. Effective occupancies (n_λ), valent activities (V_λ), composition and bonds formed by the valent atomic orbitals (VAO) of the X atom in $Co_3X(CO)_{12}$ (X = S, P)

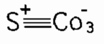
X = S				
λ	1	2	3	4
n_λ	1.08	1.44	1.50	1.98
V_λ	0.98	0.80	0.75	0.03
Composition	$3s-3p_z$	$3p_x$, $3p_y$		$3s+3p_z$
Bonds	covalent, Co	covalent + donor, Co		lone pair
X = P				
λ	1	2	3	4
n_λ	0.90	1.03	1.08	1.96
V_λ	0.99	1.00	0.99	0.07
Composition	$3s-3p_z$	$3p_x$, $3p_y$		$3s+3p_z$
Bonds	covalent, Co	covalent, Co		lone pair

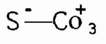
The main difference between phosphorus and sulfur derivatives lies in the character of the π-type bonds formed by the VAOs composed of the $3p_x$, $3p_y$ atomic orbitals of the main group atoms. In $Co_3P(CO)_9$ there are two purely covalent π-type bonds; adding the 3s-$3p_z$ σ-type VAO and using the almost equal occupancies of the initial VAOs it is possible to form three new equivalent hybrid orbitals. Each of these orbitals is directed to one of the Co atoms, so in total there are three covalent P–$(Co)_3$ bonds. In $Co_3S(CO)_9$ the $3p_x$, $3p_y$ and the (3s-$3p_z$) valent orbitals have different occupancies so that such a hybridization procedure is no longer possible. For this reason there are two types of S–Co_3 bonds in this molecule: the covalent one of the σ-type and two of the π-type formed by the sulfur $3p_\pi$AOs and by the Co_3 group orbitals of the appropriate symmetry (irreducible representation e). This additional π-type component increases the sulfur atom valent activity up to $V_s = 2.56$, which is higher than the formal sulfur valency of 2. The bonding between the sulfur atom and Co_3 fragment can be represented as the superposition of three valent structures:

TABLE 7. The structure of valence atomic orbitals (VAO) for the Co atoms: their effective occupancies (n), valent activities (V), composition (AO) and the atoms or ligands with which this VAO forms chemical bonds (the line 'bonds') The total atomic valent activities V_{Co} are also shown

Co in $Co_4(CO)_{12}$, T_d, $V=5.69$									
n	0.33	0.33	0.38	0.51	1.21	1 21	1.77	1.78	1 78
V	0 56	0.56	0.68	0.76	0.96	0 96	0 41	0.40	0 40
AO	3d	3d	4s + 4p	4s − 0 3(4p)	4p + 3d		$3d_\pi$	$3d_{x^2-y^2}$, $3d_{z^2}$	
Bonds	CO	CO	CO	Co	Co	Co	CO	CO	CO
Co_a in $Co_4(CO)_{12}$, C_{3v}, $V=5.48$									
n	0.33	0.33	0.36	0.46	1 24	1.24	1 78	1.78	1.78
V	0.55	0.55	0.60	0.70	0.94	0 94	0 40	0.40	0.40
AO	$4p_x$, $4p_y$		$4p_z$	4s	3d + 4p		3d	3d	3d
Bonds	CO	CO	CO	Co_b	Co_b	Co_b	CO	CO	CO
Co_b in $Co_4(CO)_{12}$, C_{3v}, $V=5\ 26$									
n	0.31	0 33	0.33	0 42	1.05	1 50	1.80	1.80	1 80
V	0.52	0 56	0.56	0.67	1.00	0 75	0.40	0.40	0.40
AO		4p		4s	$3d_{z^2}$	3d	3d	3d	3d
Bonds	CO_b	CO_t	CO_t	CO_t	CO_a	CO_b	CO_t	CO_t	CO_t
Co in $Co_3S(CO)_9$, $V=5.13$									
n	0.34	0.36	0.38	0 47	1 09	1 45	1 74	1.78	1 82
V	0.56	0.59	0 61	0 72	0.98	0.53	0 44	0 38	0 32
AO		4p		4s	$3d_{z^2}$	$3d_{xy}$	$3d_{xz}$	$3d_{yz}$	$3d_{x^2-y^2}$
Bonds	S	CO	CO	CO	S, Co, CO	CO, Co		CO	


1


2


3

It is possible to estimate the weights of these structures taking into account the calculated total valent activity (2.56) and the number of valent electrons on the sulfur atom (~6). These weights are 0.36 for structure **1** and 0.32 for structures **2** and **3**. So the bonding between S and the Co_3 fragment is of the mixed covalent + donor − acceptor character.

There is a small but noticeable difference in the local electronic structure of the P and S atoms in the corresponding $Co_3X(CO)_9$ derivatives. The effective occupancy of the phosphorus lone pair is only 1.96 compared with 1.98 of the sulfur lone pair. So the most stable 8-electron shell is not completed in $Co_3P(CO)_9$. The relatively low occupancy of the phosphorus lone pair can be related to the chemical properties of this cluster, which does not appear to be stable unless the phosphorus lone pair is complexed to external metals [8].

The main features of the VAOs of the cobalt atoms remain the same in all clusters. The first four VAOs with the effective occupancy of 0.3–0.5 (electron accepting orbitals) are the pure 3s,4p AOs or their linear combinations. The orbitals with $n_\lambda = 1.7$–1.8 (mainly 3d cobalt AOs) can be considered as the Co lone pairs that act as the electron donors. In each cluster there is at least one VAO with the occupancy 1.05–1.25 which takes part in the covalent bond. The last VAO is either of the covalent ($Co_4(CO)_{12}$ T_d; Co_a in the trigonal $Co_4(CO)_{12}$) or of the mixed covalent-donor type with $n_\lambda = 1.45$–1.50 (Co_b in the trigonal $Co_4(CO)_{12}$ and $Co_3S(CO)_9$). This change of the effective occupation number is followed by the disappearance of the VAOs 4p component. This is the only noticeable difference between the valent (hybrid) structure of the apical (including all of the Co atoms in $Co_4(CO)_{12}$) and basal cobalt atoms. This is rather unexpected because the $Co(CO)_3$ fragments in $Co_3S(CO)_9$ look more like the corresponding apical groups in the tetracobalt carbonyls. The common feature of the basal Co atoms in both molecules is the lower local symmetry as compared with the apical atoms (the loss of the threefold axis). So it seems that the general reason for weakening the Co–Co bonds in the trigonal systems is the lower molecular symmetry relative to the reference tetrahedral cluster. This suggestion is confirmed by the analysis of the total valent activity of the Co atoms ((Table 6). As was mentioned above, the reduction of the Co–Co bond order in trigonal $Co_4(CO)_{12}$ can be explained by the transfer of part of their valent activity to the new bridging bonds. But this does not explain the total decrease of the valency of the basal cobalt atoms compared with the V_{Co} in tetrahedral $Co_4(CO)_{12}$.

The data in Tables 6 and 7 and the results of the band analysis show that the bonds formed by the Co atoms are of mixed nature (both covalent and donor-acceptor) and that all of the valent AOs (4s,4p and 3d) participate in the bonding. According to Chesky and Hall [6], the 3d Co orbitals play an important role in Co–Co and Co–S bonding. These authors used the double-exponent 3d functions of Richardson *et al.* [27]. At the same time Rodrigez *et al.* [28, 29] in recent studies of the cobalt and iron silicide clusters came to the conclusion that M–Si bonds arise mainly as the results of sp–sp interactions. The reason seems to be in the very compact 3d orbitals used in refs. 28 and 29: the 3d Slater exponent is 3.73 for Fe and 3.95 for Co. This lead to a very small overlap of the 3d metal orbitals and only electrostatic 3d interactions. The *ab initio* calculations show [30, 31] the important role of the diffuse 3d basis functions. In our preliminary calculations of the Ni_2 molecule we were able to reproduce on the INDO level the results of *ab initio* calculations of the relative energies of the low lying electronic states only after the inclusion of the additional diffuse component in the two-exponent 3d function of Richardson *et al.* [27] (see 'Appendix'). The more diffuse 3d functions ensure better overlap between the AOs of the Co atoms and the other atoms. It is natural to suggest that without such an overlap the antibonding nature of the singly occupied MO a_2 could not manifest itself so clearly. According to our results, this MO mainly consists of the 3d Co atomic orbitals. This is in accord with the experimental ESR data for $Co_3S(CO)_9$ [14]. It seems that the use of multiexponential 3d functions rather than the simple Slater orbitals can lead to a more reasonable description of the nature of the bonds formed by the transition metal atoms.

The ligand valent activities and their σ-donor and π-acceptor components and the VMO occupancies are listed in Table 8. The bridging ligand valent activities are larger than those of the terminal CO ligands. In the case of the terminal ligands the σ-donor component is larger than the π-acceptor one; for the bridging ligands the bonding with the metal core is predominantly of π-back-donor character. The data on the partial indices B_i(C–O) (Tables 3–5) confirm these conclusions. The data in Table 8 also show that although the occupancy of the σ valent atomic orbital of the bridging CO ligand is strongly reduced owing to the charge transfer to two of the neighboring Co atoms, the pronounced back-donation leads to larger effective electronic populations on the bridging relative to the terminal CO groups. This explains the formation of H bonds between the OH groups and the bridging CO of the $Co_4(CO)_{12}$ adsorbed on the zeolites [32]. The more negative charge on the bridging CO groups was also found by Bauschlicher for $Fe_2(CO)_9$ [2].

TABLE 8. Valent activities V, their σ-donor, V_σ, and π-acceptor, V_π, components and VMOs occupation numbers, n_λ, for the CO groups in the C_{3v} model structure of $Co_4(CO)_{12}$

	Type of CO group			
	$(CO)_d$	$(CO)_u$	$(CO)_1$	$(CO)_b$
V	1.31	1.34	1.22	2.06
V_σ	0.66	0.67	0.63	0.88
V_π	0.60	0.62	0.54	1.04
n_σ	1.58	1.57	1.61	1.35
n_π	0.33	0.34	0.29	0.65

The excited states of $Co_4(CO)_{12}$

The results of the electronic spectrum calculations for $Co_4(CO)_{12}$ (the 'experimental' structure) are reported in Table 9. We included in the CI calculations all single excitations with $|\epsilon_j - \epsilon_i| < 10.3$ eV (in total 56 configurations). Table 9 also contains our suggested assignment of the experimental spectral bands [7]. The data from Tables 1 and 4 can be used to predict the changes in the electron density distribution and bond strength connected with the electronic excitation. The experimentally observed bands correspond to the excitations within the metal core, so one can not expect substantial charge redistribution during these transitions, as well as the changes in the bonding between the apical Co atom and the basal Co atoms (see indices B(Co–Co) in Tables 1–3).

The energies of the lowest singlet–triplet transitions are equal to (in eV): 0.96 ($^3A_1$), 1.41 (^3E), 1.90 ($^3A_1$) and 2.23 (^3E). Since the lowest triplet states are expected to play an important role in the photochemical reactions, we studied more thoroughly the $^3A_1$ and ^3E electronic states, generated by the transitions between MO 26e (HOMO) and 27e (LUMO) ($\phi_{77,78} \rightarrow \phi_{79,80}$). For these excited states the redistribution of the electron density is negligible. The values of the Wiberg indices (Table 1) confirm the proposed weakening of the Co_a–Co_b bonds. The unpaired electrons are localized within the metal core, the spin density for Co_a being equal to 0.62. The spin density of each basal cobalt atom is equal to 0.28. The main part of the spin density is on the $3d_{xz}$ and $3d_{yz}$ orbitals; the spin density on the orbitals $3d_{x^2-y^2}$, $3d_{xy}$ is less by a factor of two.

Both of the excitations ($^1A_1 \rightarrow {}^3A_1$ and $^1A_1 \rightarrow {}^3E$) lead to the weakening of the bonds between basal and apical Co atoms. However, there is a difference between the reactivity of these excited states. The active mode for the $^3A_1$ state is an A_1 vibration, which is followed by the symmetrical lengthening of all three Co_a–Co_b bonds. One of the vibrational modes in the ^3E state leads to

TABLE 9 The calculated electronic transition energies and oscillator strengths for $Co_4(CO)_{12}$

Calculated values		Experiment [13]		Assignment
E (eV)	*f*	*E* (eV)	*f*	
2.11	0	1.88	1300	A_2 26e→27e
2.29	0.026	2.29	3000	E 26e→27e
2.37	0			A_2 26e→27e
2.70	0.001	2.69	5500	E 25e→27e
3.30	0.024	3.31	19000	E 26e→$21a_1$, $20a_1$→27e, 26e→$7a_2$
3.44	0.004			E $20a_1$→27e, 25e→27e
3.54	0.001			E 26e→$7a_2$, ($19a_1$→27e)
3.62	0			A_1 25e→27e
3.63	0.033	3.65	13000	E $19a_1$→27e, 26e→$21a_1$, (25e→$21a_1$)
3.83	0.015			A_1 $20a_1$→$21a_1$, (24e→27e)
3.96	0			A_2 $20a_1$→$7a_2$
4.04	0.001			E 24e→27e, 25e→$7a_2$
4.15	0.001			A_1 24e→27e
4.23	0.080			E 25e→$7a_2$, 24e→27e

the 'butterfly' structure. This structure can be more easily attacked by the other molecules to form new intermediates [33].

Conclusions

We have analyzed the electronic structure and bonding in the cobalt carbonyl clusters using the general bond indices analysis, the band structure analysis and the valent atomic orbitals approach. The existence of direct Co–Co bonds was found in all the compounds under consideration. These bonds are complicated with all the Co valence orbitals —3d,4s and 4p — being involved in the bonding. The similarity of the local valent structure of the Co atoms in all the compounds was demonstrated. The interactions of the orbitals of e symmetry play an important role in the Co–S bonding in $Co_3S(CO)_9$.

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References

1 A.A. Low, K L Kunze, P.J. MacDougall and M B Hall, *Inorg Chem*, *30* (1981) 1079
2 Ch Bauschlicher, *J. Chem Phys*, *84* (1986) 872
3 A. Veillard and M.-M. Rohmer, *Int J. Quant Chem*, *42* (1992) 965.
4 Ch. Elschenbroich and A. Salzer, *Organometallics A Concise Introduction,* VCH, Weinheim, 1989, pp. 226–227
5 R H Crabtree, *The Organometallic Chemistry of the Transition Metals,* Wiley, New York, 1988, pp 316–320
6 P T. Chesky and M B Hall, *Inorg Chem*, *22* (1983) 2998
7 D L Stevenson, C H Wei and L.F Dahl, *J Am. Chem Soc*, *93* (1971) 6027
8 K.H Whitmire, in H.W Roesky (ed), *Rings, Clusters and Polymers of Main Group and Transition Elements,* Elsevier, New York, 1989, p 503
9 S.P. Gubin, *Khimia Klasterov, Osnovi klassifikazii i stroenia,* Nauka, Moscow, 1987, Ch. 2, and refs. therein (in Russian).
10 R Hoffman, B E.R Schilling, R Bau, H.D Kaesz and D M P Mingos, *J Am Chem Soc*, *100* (1978) 6088.
11 M C Manning and W C Trogler, *Coord Chem. Rev*, *38* (1981) 89.
12 H -H. Freund and G Hohlneicher, *Theor Chim. Acta, 51* (1979) 145
13 G F Holland, D E. Ellis and W C Trogler, *J Am Chem Soc*, *108* (1986) 1884.
14 Ch E. Strouse and L F Dahl, *J Am Chem Soc*, *93* (1971) 6033
15 A D Bacon and M C Zerner, *Theor Chim Acta, 53* (1979) 21.
16 V.I Baranovski, O.V Sizova and N V. Ivanova, *Russ J Struct Chem*, *3* (1990) 382.
17 C.H Wei and L F Dahl, *Inorg Chem*, *6* (1967) 1229
18 C H Wei, *Inorg Chem*, *8* (1969) 2384.
19 F H. Carre, F A Cotton and B A. Frenz, *Inorg Chem*, *15* (1976) 380
20 K W. Wiberg, *Tetrahedron, 28* (1968) 1441.
21 V.I Baranovski, O V. Sizova and N V. Ivanova, *Russ. J Struct Chem*, *17* (1976) 478
22 S. Sakaki, M. Nachikawa and A Ohiosi, *J Am Chem Soc*, *102* (1980) 4062
23 R Hoffman, *Solids and Surfaces A Chemist's View on Bonding in Extended Structures,* VCH, Weinheim, Germany, 1988.
24 R S Mulliken, *J Chem Phys., 23* (1955) 1833, 1841
25 S P Tunik, V P. Krym and A.B Nikolski, *Metalloorg Khim*, *3* (1990) 283 (in Russian).
26 I. Hargittai, *The Structure of the Volatile Sulphur Compounds,* Akademiai Kiado, Budapest, 1985.
27 J.W Richardson, R R Powell and W C Nieupoort, *J Chem Phys*, *38* (1961) 769

28 L.J. Rodriguez, F. Ruette, G.R. Castro, E.V. Ludena and A J. Hernandez, *Theor Chim. Acta, 77* (1990) 39.

29 G. Urbina-Villalba, L J. Rodriguez, G.R. Castro and F. Ruette, *J Comput Chem., 13* (1992) 867.

30 C.W. Bauschlicher, S.R. Langhoff and P.R. Taylor, *Adv Chem Phys, 77* (1990) 103

31 S. Langhoff and C. Bauschlicher, *Ann Rev. Phys Chem., 39* (1988) 181.

32 R.L. Schneider, R.F. Howe and K.L. Watters, *Inorg. Chem, 23* (1984) 4600

33 R D. Pearson, *Symmetry Rules in Chemical Reactions,* Wiley, New York, 1976

34 H.G Benson and A. Hudson, *Theor. Chim Acta, 23* (1971) 259

35 E. Tondello, G. De Michelis, L. Oleary and L. Di Sipio, *Coord. Chem Rev., 2* (1967) 65.

36 Ch.E. Moore, *Atomic Energy Levels,* Vol. 2, National Bureau of Standards, Washington, DC, USA, 1952, Circ No 467.

37 K. Ohno, *Theor. Chim. Acta, 2* (1964) 219.

Appendix

We used the restricted Hartree-Fock (RHF) method in the extended INDO approximation in which all non-zero one-center two electron integrals [ab|cd], where a, b, c and d are 3d and (or) 4p AOs of the transition metal atom, are taken into account [15, 16]. This makes the results invariant to the rotation of the coordinate system and ensures the degeneracy of the energy levels in the high symmetry molecules. For the excited states the method of configuration interaction (CI) was applied.

The atomic parameters U_{ss}, U_{pp}, F^0, G^1 and G^3 for C and O are those of Benson and Hudson [34]. The Slater-Condon parameters for Co (in eV) are from ref. 35. Using these parameters and spectroscopic data for several lowest electronic states of Co^0, Co^+ and Co^{2+} (averaged with respect to the quantum number J) [36] we calculated the values of the parameters U_{ii} and $F^0(i,j)$ for cobalt. These values are (in eV):

F^0(s,s)	F^0(s,p)	F^0(s,d)	F^0(p,p)	F^0(p,d)	F^0(d,d)
9.659	8.404	11.137	7.600	9.390	15.018

U_{ss}	U_{pp}	U_{dd}
−95.473	−78.164	−122.098

The Slater-Condon and $U_{\mu\mu}$ parameters for the S atom were also estimated with the use of the data from Moore's tables [36]: $F^0 = 12.760$, $F^2(\mathrm{p,p}) = 4.537$, $G^1(\mathrm{s,p}) = 3.075$, $U_{ss} = -80.874$, $U_{pp} = -74.285$ eV.

Two-center parameters γ_{AB} were calculated by Ohno's formula [37]. The values of parameters β^0 are (in eV): $\beta^0{}_s(\mathrm{Co}) = -7.4$, $\beta^0{}_p(\mathrm{Co}) = -3.5$, $\beta^0{}_d(\mathrm{Co}) = -15.5$, $\beta_{s,p}(\mathrm{S}) = -8$, $\beta^0{}_s(\mathrm{C}) = -17.0$, $\beta^0{}_p(\mathrm{C}) = -15.0$, $\beta^0{}_s(\mathrm{O}) = -27.0$ and $\beta^0{}_p(\mathrm{O}) = -25.0$. The radial atomic functions for s and p AOs are approximated by the Slater orbitals with ζ equal to 1.625 (C), 2.275 (O), 1.816 (S), 1.55 (4s Co), 1.2 (4p Co). For 3d AO of Co we used the triple-zeta function obtained by adding a diffuse component to Richardson's [27] double-zeta function: $R(3d) = 0.5365\ \ \phi_3(5.55) + 0.6245\ \ \phi_3(1.90) + 0.0967\ \ \phi_3(0.70)$.