Structure and Bonding in Binuclear Metal Carbonyls from the Analysis of Domain Averaged Fermi Holes. 2. $Fe_2(CO)_8^{2-}$ and $Fe_2(CO)_8$

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The nature of the bonding interactions in individual isomeric structures of the above carbonyls was studied using the analysis of domain averaged Fermi holes (DAFH). The main focus was directed on the confrontation of the picture of the bonding resulting from this analysis with the predictions of empirical 18-electron rule. This rule assumes, namely, the presence of direct metal−metal bond(s) for both carbonyls, but the detailed insights provided by the DAFH analysis show that the straightforward association of metal−metal bond with the favorable electron count only is too simplistic, and provided the actual structure of individual isomeric species is not taken into account, the predictions of this rule may fail. This is, e.g., the case of the C_{2v} isomer of the carbonylate anion $[Fe_2(CO)_8]^{2-}$ where the DAFH analysis denies the existence of direct metal−metal bond similarly as in the case the isoelectronic $Co_2(CO)_8$. Similar discrepancies between the predictions of the 18-electron rule and DAFH analysis were found also in the case of the C_{2v} isomer of the neutral $Fe_2(CO)_8$ carbonyl, where the DAFH analysis detects the presence of a single bent Fe−Fe bond rather than the double bond anticipated by the 18-electron rule.

Introduction

Transition metal carbonyls are fundamental constituents of modern organometallic chemistry. Besides continuing interest in the application of these species, e.g., in the catalysis and/or the synthesis of new materials with unusual properties,[1] the chemistry of metal carbonyls is interesting also because of the challenge it raises for the chemical theory in its efforts to elucidate and to rationalize the nature of bonding interactions especially in polynuclear species. The main question in this respect concerns the presence and/or the absence of a direct metal−metal bond. The simplest models of the bonding in transition metal carbonyls traditionally rely on the consideration of metal−metal distances and simple electron count exemplified by the so-called 18-electron rule.[2] On the basis of this approach, the existence of direct metal−metal bond was often assumed in various binuclear metal carbonyls.[3−6] Although there is no doubt that at least in some cases the above early models do indeed provide a realistic picture of the bonding, the results of more recent theoretical approaches based on sophisticated quantum chemical calculations suggest that the situation can often be much more complex. This is, e.g., the case of homoleptic binuclear carbonyls $Fe_2(CO)_9$ and $Co_2(CO)_8$, where the existence of direct metal−metal bond, anticipated on the basis of the 18-electron rule, was questioned using the analysis of orbital interactions,[7−10] the AIM analysis of electron density[11−13] and, most recently, also by the results of the analysis of the so-called domain averaged Fermi holes.[14] Our aim in this study is to follow up with the results of the above study[14] and to apply the same approach also to the elucidation of the structure and the nature of the bonding in other stable and/or transient binuclear iron carbonyls, namely the octacarbonylferrate(II) anion $[Fe_2(CO)_8]^{2-}$ and octacarbonyliron $Fe_2(CO)_8$ (hereafter "carbonylate" anion and neutral "carbonyl" respectively).

Theoretical Section

Although the formalism of the analysis of domain averaged Fermi holes (DAFH) was repeatedly described in various earlier studies,[15−18] we consider it useful to recall here the basic ideas of the approach to the extent necessary for the purpose of the present work. The domain averaged Fermi holes g_Ω can most straightforwardly be introduced via the definition in eq 1, in which $\rho(r_1)$ and $\rho(r_1,r_2)$ represent the diagonal elements of spinless first- and second-order density matrix respectively, and the integration is performed over the finite domain Ω.

$$g_\Omega(r_1) = \rho(r_1)\int_\Omega \rho(r_2)\,\mathrm{d}r_2 - 2\int_\Omega \rho(r_1,r_2)\,\mathrm{d}r_2 \qquad (1)$$

The importance of these holes for structural elucidations stems from the fact that their shape and information content depend on the particular choice of the domain Ω, over which the averaging (integration) is performed. Although it is in principle possible to generate and to analyze the holes averaged over the domains of arbitrary shape, we have shown in previous studies that especially interesting and chemically relevant structural information can be obtained only from the holes averaged over the domains defined on the basis of certain sound physical

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principles. This, is, above all, the case of the domains identified with the AIM atomic domains resulting from the virial partitioning of electron density.[19] In this case the holes provide the information about the actual valence state of a given atom in a molecule. Generated and analyzed can be, however, also more complex domains formed, e.g., by the union of several atomic domains corresponding to certain functional groups or interesting molecular fragments. In this case the holes provide the information about the electron pairs whose formal splitting is required for the isolation of the fragment from the rest of the molecule as well as about the electron pairs (chemical bonds, lone pairs), which remain intact within the fragment. The analysis of the holes consist in the diagonalization of the matrix representing the hole in the appropriate basis of atomic or molecular orbitals. The eigenvectors and eigenvalues resulting from this diagonalization are subsequently subjected to the so-called isopycnic transformation[20] which is a kind of localization procedure whose aim is to transform the original eigenvectors into the localized functions reminiscent of classical chemical bonds. The nature of the bonding interactions can then straightforwardly be deduced from the numerical values of the associated eigenvalues whose intepretation can be, moreover, significantly facilitated by the visual inspection of the corresponding transformed functions.

After having briefly reminded the basic idea of the proposed analysis, it is, however, important to realize that although the definition (eq 1) is completely general and can be applied at any level of the theory, most of the reported applications of DAFH analyses are nevertheless based on several simplifying approximations. The first one concerns the pair density, whose knowledge is the prerequisite for the construction of the hole (eq 1). This matrix is, namely, easily available only at the level of Hartree−Fock approximation where it can be calculated from the first-order density matrix, which can straightforwardly be extracted from any existing quantum chemical program. Within this approximation, the original eq 1 reduces to the formula (eq 2),

$$g_\Omega(r_1) = 2\sum_j^{\text{occ}}\sum_i^{\text{occ}} \langle\phi_i|\phi_j\rangle_\Omega \phi_i(r_1)\, \phi_j(r_1) \tag{2}$$

where the symbol $\langle\varphi_i|\varphi_j\rangle_\Omega$ denotes the element of the so-called AOM matrix (eq 3)

$$\langle\phi_i|\phi_j\rangle_\Omega = \int_\Omega \phi_i(r)\, \phi_j(r)\, \mathrm{d}r \tag{3}$$

The determination of the Fermi hole thus in this case primarily relies only on the availability of the elements of the corresponding AOM matrix and first applications of ab initio DAFH analysis were indeed performed at this inherently one-electron level of the theory.[21,22] The situation is, however, more complex when going beyond the scope of this approximation and although the first examples of the "exact" DAFH analyses based on explicitly correlated pair densities have recently been reported,[23,24] the application of such an approach is still restricted to relatively small, rather modest systems. In this connection it is therefore interesting to mention the possibility of the formal extension of DAFH analysis to DFT level of the theory. Within such an extension, which relies on the formal similarity of Hartree−Fock and Kohn−Sham wave functions, the Fermi hole is generated using the same formula (eq 2) with the sole difference that the AOM matrices are calculated from Kohn−Sham instead of Hartree−Fock orbitals. Here it is, of course, fair to say that such an extension is certainly a bit arbitrary, but as the results of such an approach proved to provide reasonable and realistic description of the bonding in various other systems,[25−28] we believe that the above approach can be accepted as a feasible alternative, especially for the structural investigations in inorganic chemistry. Moreover, the additional theoretical arguments corroborating the formal DFT extension of of DAFH analysis can be found in the recent study.[29]

In connection with the above DFT extension of DAFH analysis it is also necessary to mention another simplifying approximation that was widely used in previous applications, especially the study of metal−metal bonding in inorganic systems. This approximation concerns the determination of the integrals over the domain Ω and consists of replacing the AOM matrices in eq 2 calculated using the integration over the real AIM domains by the Mulliken-like approach, according to which the electron is associated with the domain of a certain atom if it is in the orbital localized on that atom. The main reason for the use of this approximation in this and earlier studies of metal−metal bonding,[14,25−28] was that it allowed us to avoid two important problems complicating the use of the "exact" DAFH analysis. One of them is that the conteporary computational tools, especially in the realm of transition metal chemistry, often rely on the use of basis sets of ECP type, which are known to produce the electron densities, whose integration is not always straightforward.[30−32] Another problem whose complicating impact on the use of the "exact" DAFH approach has also to be taken into account concerns the considerable computational demands of the integration over real AIM domains. The DAFH analysis requires, namely, the knowledge of the AOM matrices for all the atoms in the molecule, and the computational demands required for their generation can rapidly make the "exact" analysis unfeasible for bigger systems. In such cases, the approximate Mulliken-like form of DAFH analysis can represent the real alternative. Usefulness of such an approximate approach is straighforwardly corroborated by the available comparisons with the results of "exact" DAFH analysis, which shows that the picture of the bonding emerging from both approaches is generally very similar. Especially interesting in this respect is, e.g., the recent study of the bonding interactions in $Fe_2(CO)_9$ and $Co_2(CO)_8$,[14] where the absence of direct metal−metal bonding suggested by the approximate Mulliken-like DAFH approach was subsequently confirmed by the "exact" AIM generalized form of the approach.[33]

Computations

The analysis of DAFH is a two step process of which the first requires the generation of the reliable wave function for the studied molecules. For this purpose it is thus first necessarry to perform the complete optimization of the geometry of the studied molecules at the appropriate level of the theory. Based on the wave functions obtained at the equilibrium geometry, the second step consists of the construction of the Fermi holes (eq 2) for the chosen domain and in their subsequent analysis. As the results of earlier experimental and theoretical studies of $[Fe_2(CO)_8]^{2-}$ and $Fe_2(CO)_8$ suggest that each of these carbonyls can exist in several isomeric forms,[4,5,34−42] it was first necessary to localize the corresponding structures as critical points on the potential energy hypersurface. Optimized geometries of all the individual isomeric structures were generated using the Gaussian 98 program.[43] The calculations were performed at the B3LYP level of theory[44,45] using LANL2DZ and SDD bases and, for comparison, also the all-electron DZP basis, which was recently used in the thorough study of iron carbonyls by Schaeffer et al.[5] The results of the comparison are summarized in Tables 1−3. All of the localized isomeric structures of the carbonylate

TABLE 1: Relative Energies of Individual Isomers of $Fe_2(CO)_8$ and Its Dianion Calculated at the B3LYP/LANL2DZ, B3LYP/SDD and B3LYP/DZP Levels of Theory

symm	rel energy LANL2DZ	no. of imag freq	rel energy SDD	no. of imag freq	rel energy DZP	no. of imag freq
			$[Fe_2(CO)_8]^{2-}$			
D_{3d}	1.1	0	0.0	0	0.0	0
D_{2d}	0.0	0	1.6	0	2.7	0
C_{2v}	2.7	0	1.1	0	4.7	0
			$Fe_2(CO)_8$			
C_{2v}	0.0	1	0.0	0	0.0	0
D_{2h}	13.0	3	14.5	3	10.4	3

TABLE 2: Fe···Fe Interatomic Distances, Fe−Fe Bond Orders and ν_{Fe-Fe} Stretching Frequencies Calculated for Optimized Structures of Individual Isomers of the Carbonylate Anion at the B3LYP/LANL2DZ, B3LYP/SDD and B3LYP/DZP Levels of Theory

symmetry	LANL2DZ	SDD	DZP
	Fe···Fe Distance (Å)		
D_{3d}	2.854	2.910	2.924
D_{2d}	2.734	2.765	2.806
C_{2v}	2.627	2.631	2.651
	Fe···Fe Bond Order		
D_{3d}	0.436	0.380	0.436
D_{2d}	0.434	0.310	0.258
C_{2v}	0.248	0.222	0.060
	ν_{Fe-Fe} Stretch (cm^{-1})		
D_{3d}	157	149	151
D_{2d}	176	166	165
C_{2v}	226	228	227

TABLE 3: Fe···Fe Interatomic Distances, Fe−Fe Bond Orders and ν_{Fe-Fe} Stretching Frequencies Calculated for Optimized Structures of Individual Isomers of the Neutral Carbonyl $Fe_2(CO)_8$ at the B3LYP/LANL2DZ, B3LYP/SDD and B3LYP/DZP Levels of Theory

symmetry	LANL2DZ	SDD	DZP
	Fe···Fe Distance (Å)		
C_{2v}	2.417	2.438	2.443
D_{2h}	2.519	2.551	2.543
	Fe···Fe Bond Order		
C_{2v}	0.580	0.716	0.568
D_{2h}	0.950	0.798	0.774
	ν_{Fe-Fe} Stretch (cm^{-1})		
C_{2v}	230	232	231
D_{2h}	190	183	189

anion $[Fe_2(CO)_8]^{2-}$ corresponded to true minima on the PE hypersurface, but slight differences in the relative stability of individual isomers depending on the basis set can nevertheless be observed. Although for the LANL2DZ basis, the most stable isomer is predicted, consistent with the findings of the earlier study,[38] to correspond to the structure of D_{2d} symmetry, the calculations using the SDD and DZP basis set consistently predict the most stable isomer to correspond to the structure of D_{3d} symmetry. To demostrate to what extent the nature of the bonding of all individual isomers depends on the particular type of the structure, we report the results of DAFH analysis for all the three isomeric structures of dianion $[Fe_2(CO)_8]^{2-}$.

Similar detailed analysis of the potential energy hypersurface was performed for the neutral carbonyl $Fe_2(CO)_8$, for which the existence of several isomeric structures was also previously reported. The calculations were again performed at the B3LYP level of the theory using the LANL2DZ, SDD and DZP basis. In keeping with earlier suggestions,[5,39,40] we have been able to detect the existence of the structures of C_{2v} and D_{2h} symmetry. The most stable of these structures corresponds in all cases to the isomer of C_{2v} symmetry, but individual computational methods slightly differ in the classification of the nature of this structure as a critical point on the PE hypersurface. The C_{2v} structure was found to represent the true minimum on the hypersurface only for SDD and DZP basis sets, whereas for the LANL2DZ basis the minimum energy structure exhibits one negative eigenvalue of the force constant matrix (Table 1). For this reason, and also to maintain the consistency with other systems analyzed in this study, we report the results of DAFH analysis of the bonding interactions in this most stable isomer just for the structure generated at B3LYP/SDD level of the theory, for which the molecule exists as a true minimum on the PE hypersurface.

A slightly more complex situation is for the isomer of D_{2h} symmetry. In this case, namely, the vibrational analysis revealed the existence of three negative eigenvalues of the force constant matrix. This, of course, throws some doubts on early spectroscopic assignments according to which just the nonbridged isomer could be the best candidate for the isolation in the cryogenic matrix,[40] but as the clarification of this apparent discrepancy will certainly require further studies, we leave the problem open. Nevertheless, because of theoretical interest in the nature of the bonding in this particular isomer, we perfomed and report the results of the DAFH analysis also for this nonbridged structure.

The DAFH analysis of both the carbonylate anion and the neutral carbonyl was performed using the WinFermi program,[46] which is available upon request. For all the studied species, the analysis was performed for the structures resulting from the geometry optimizations at B3LYP/SDD and, for comparison, also the B3LYP/LANL2DZ level of the theory. The comparison has shown that with the only exception of the C_{2v} isomer of $Fe_2(CO)_8$, where the corresponding structures differ in the number of imaginary frequencies (only the SDD structure is true minimum), the results of DAFH analysis are only a little sensitive to the actual basis set used and the final picture of the bonding is qualitatively similar for both cases. The same little sensitivity to the quality of the basis set is also evident from Tables 2 and 3, which summarize the comparison of the calculated values of Fe···Fe distances, Fe−Fe bond orders[47] and the frequencies of IR Fe−Fe stretching vibrations. The numerical results of DAFH analysis of all the studied species are summarized in Tables 4−8 and the visual display of the DAFH eigenvectors in Figures 1−5. The pictures were generated using GaussView Program at B3LYP/SDD level of the theory.

Results and Discussion

$[Fe_2(CO)_8]^{2-}$. The carbonylate ion of the above formula is formed in the reaction of $Fe_2(CO)_9$ with methanolic KOH and can be isolated in the form of stable ammonium salt $(Et_4N)_2[Fe2(CO)_8]$.[35] The ion is isoelectronic with the neutral cobalt carbonyl $Co_2(CO)_8$, but in contrast to this molecule, whose most stable arrangement corresponds to the species of C_{2v} symmetry, the carbonylate ion exists in the solid state in the form of the structure of D_{3d} symmetry.[34−36] The situation is, however, slightly different in solution where the Raman spectroscopic studies revealed the existence of the tautomeric equilibria between the bridged and nonbridged forms.[37] The nature of the corresponding species was then specified by the detailed quantum chemical analysis of the potential energy

TABLE 4: Summary of the Results of the Analysis of the DAFH Associated with the Fe(CO)$_2$Fe Fragment of the C_{2v} Isomer of the Carbonylate Anion [Fe$_2$(CO)$_8$]$^{2-}$

eigenvalue	degeneracy	interpretation
Electron Pairs and Chemical Bonds Not Involved in the Bonding of the Bridging Ligands		
2.00	2	1s^2 (O)
2.00	2	1s^2 (C)
1.99	2	σ(CO)
1.99	2	σ(O)
1.99	8	inner shells on Fe
1.98	4	π(CO)
1.64−1.67	6	d(Fe)
0.75−0.76	4+2	broken valences of σ(FeC)t bonds
Electron Pairs Involved in the Bonding with the Bridging Ligands		
1.87	2	σ(FeC)$_b$
1.52	2	nonbonding electron pairs on metals
1.87	1	3c−2e FeC$_b$Fe bond

TABLE 5: Summary of the Results of the Analysis of the DAFH Associated with the Fe(CO)$_4$ Fragment of D_{3d} Isomer of the Carbonylate Anion [Fe$_2$(CO)$_8$]$^{2-}$

eigenvalue	degeneracy	interpretation
Electron Pairs and Chemical Bonds Not Involved in the Fe−Fe Bonding		
≈2.00	4	1s^2 (O)
≈2.00	4	1s^2 (C)
≈2.00	4	σ(CO)
≈2.00	4	σ(O)
≈2.00	8	π(CO)
≈2.00	4	inner shells on Fe
1.98−1.99	2+2	d(Fe)
1.94−1.99	3+1	σ(FeC)$_t$ bonds
Electron Pairs Involved in the Fe−Fe Bonding		
1.01	1	broken valence of σ(FeFe) bond

TABLE 6: Summary of the Results of the Analysis of the DAFH Associated with the Fe(CO)$_4$ fragment of D_{2d} Isomer of the Carbonylate Anion [Fe$_2$(CO)$_8$]$^{2-}$

eigenvalue	degeneracy	interpretation
Electron Pairs and Chemical Bonds Not Involved in the Fe−Fe Bonding		
≈2.00	4	1s^2 (O)
≈2.00	4	1s^2 (C)
≈2.00	4	σ(CO)
≈2.00	4	σ(O)
≈2.00	4	inner shells on Fe
≈1.97; ≈1.99	4+4	π(CO)
≈1.95; ≈ 1.99	2+2	d orbitals on Fe
≈1.93; ≈1.97	2+2	σ(FeC)$_t$ bond
Electron Pairs Involved in the Fe−Fe Bonding		
1.02	1	broken valence of σ(FeFe) bond

TABLE 7: Summary of the Results of the Analysis of the DAFH Associated with the Fe(CO)$_2$Fe Fragment of the C_{2v} Isomer of the Neutral Carbonyl Fe$_2$(CO)$_8$

eigenvalue	degeneracy	interpretation
Electron Pairs and Chemical Bonds Not Involved in the Bonding of the Bridging Ligands		
2.00	2	1s (O)
2.00	2	1s (C)
1.99	2	σ(CO)
1.99	2	σ(O)
1.99	8	inner shells on Fe
1.98	4	π(CO)
1.72−1.74	6	d(Fe)
0.75−0.78	4+2	broken valences of σ(FeC)t bonds
Electron Pairs Involved in the Bonding with the Bridging Ligands		
1.91	1	3c−2e FeC$_b$Fe bond
1.90	2	σ(FeC)$_b$
1.72	1	bent Fe−Fe bond

TABLE 8: Summary of the Results of the Analysis of the DAFH Associated with the Fe(CO)$_4$ Fragment of D_{2h} Isomer of the Neutral Carbonyl Fe$_2$(CO)$_8$

eigenvalue	degeneracy	interpretation
Electron Pairs and Chemical Bonds Not Involved in the Fe−Fe Bonding		
2.00	4	1s^2 (O)
2.00	4	1s^2 (C)
1.99	4	σ(CO)
1.99	4	σ(O)
1.99	8	π(CO)
1.99	4	inner shells on Fe
1.98	3	d(Fe)
1.93; 1.98	2 + 2	σ(FeC)$_t$
Electron Pairs Involved in the Fe−Fe Bonding		
eigenvalue	Degeneracy	interpretation
1.03	1	broken valence of σ(FeFe) bond
1.00	1	broken valence of π(FeFe) bond

hypersurface, in which the existence of three isomeric structures of D_{3d}, D_{2d} and C_{2v} symmetry was detected.[38] The existence of the species of so many different structures represents, of course, an important challenge to the bonding theory and our aim in this study is to demonstrate to what extent the nature of the bonding interactions in individual isomers depends on the particular type of the structure. The main question we are going to address concerns the presence and/or absence of a direct iron−iron bond. The presence of such a bond is, namely, anticipated for the above ion by the 18-electron rule, but as it will be shown, the detailed insights provided by the DAFH analysis suggest that the actual picture of the bonding is more complex and the existence of an iron−iron bond depends, besides simple electron count, also on the actual structure of individual isomeric species.

C_{2v} Structure. To demonstrate the apparent inadequacy of early empirical tools based on simple electron count, let us start our discussion of the bonding in the above carbonylate ion by the confrontation of the predictions of the 18-electron rule with the results of DAFH analysis just for this particular isomer of the anion. This C_{2v} isomer is isoelectronic and isosteric with the most stable structure of neutral cobalt carbonyl Co$_2$(CO)$_8$ for which the existence of direct Co···Co bond was seriously questioned by sophisticated theoretical techniques[7−13] including the recent DAFH analysis.[14] As it will be shown, a similar discrepancy with the expectations based on the 18-electron rule is observed also in the case of [Fe$_2$(CO)$_8$]$^{2-}$ anion. To demonstrate the close resemblance of both systems, the results of the DAFH analysis will be reported below. As the main goal is the elucidation of the nature of the bonding interactions between the metal atoms and the bridging ligands, the natural focus for the DAFH analysis is the hole averaged over Fe(CO)$_2$Fe fragment. The numerical results of the analysis are sumarized in Table 4 and the graphical form of the eigenvectors decisive for the bonding in the fragment is displayed in Figure 1.

As it is possible to see from the table, the analysis yields 37 (essentially) nonzero eigenvalues. Twenty of them are very close to 2, and the inspection of the associated eigenvectors shows that they correspond to electron pairs of 1s^2 core electron pairs on C and O of the bridging ligands (4×), the electron pairs of

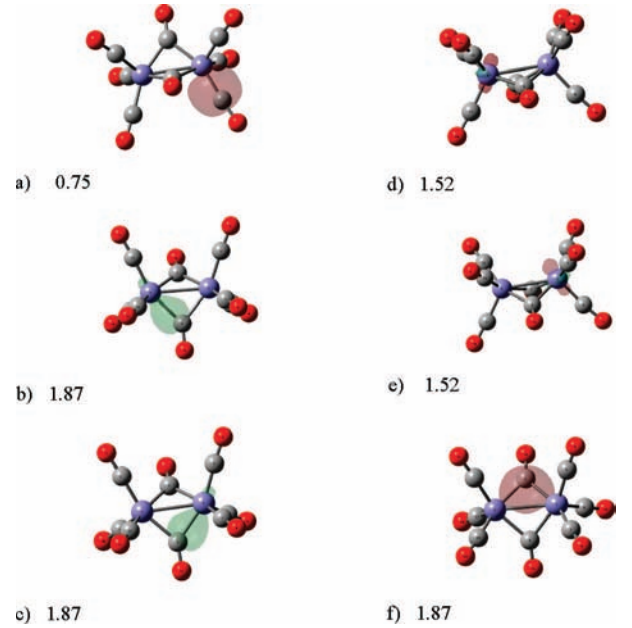


Figure 1. Graphical display of selected eigenvectors of DAFH associated with the $Fe(CO)_2Fe$ fragment of the C_{2v} isomer of the carbonylate anion $[Fe_2(CO)_8]^{2-}$.

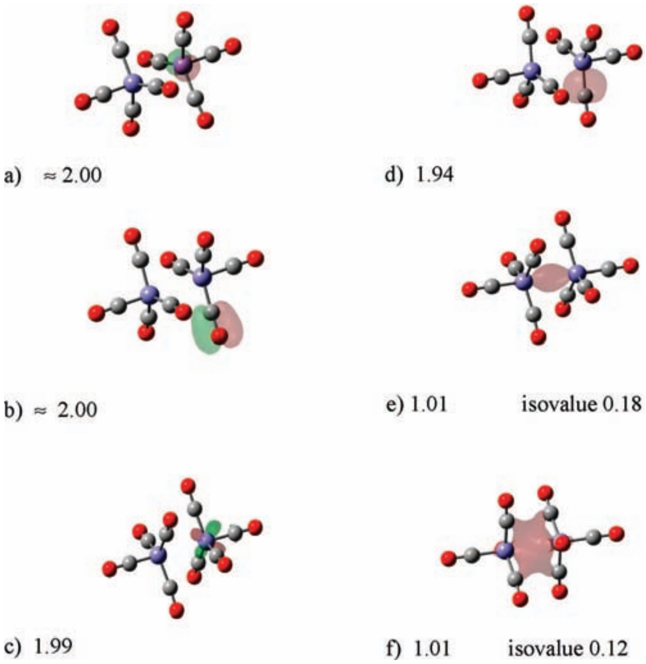
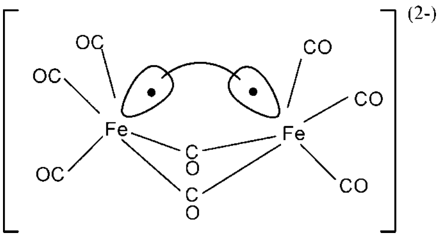
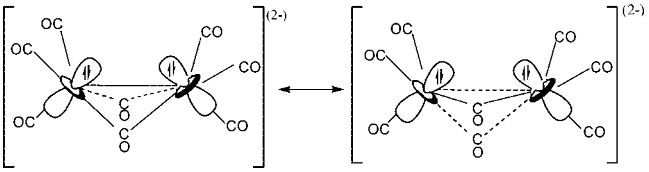


Figure 2. Graphical display of selected eigenvectors of DAFH associated with the $Fe(CO)_4$ fragment of the D_{3d} isomer of the carbonylate anion $[Fe_2(CO)_8]^{2-}$.

SCHEME 1



SCHEME 2



σ_{CO} (2×) and π_{CO} (4×) bonds of the bridging ligands, σ lone pairs on the oxygen atoms of the bridging ligands (2×) and 8 electron pairs of completely filled 3s and 3p shells on the Fe atoms.

In addition to these electron pairs, which are not involved in the bonding within the fragment, there is a group of six eigenvalues ranging from 1.64−1.67, for which the inspection of the associated eigenvectors shows that they correspond to nonbonding d orbitals on Fe, whose presence was anticipated for the $Fe(CO)_3$ fragment on the basis of symmetry considerations.[7−10] Although the fact that these eigenvalues deviate from the ideal value of 2 suggests that the corresponding d orbitals are slightly involved in the interactions with the ligands, the closer inspection of the associated eigenvectors shows that these interactions are predominantly directed toward the terminal ligands so that their contribution to the bonding within $Fe(CO)_2Fe$ fragment is only marginal. The same is true of the eigenvectors associated with the group of six eigenvalues ranging from 0.75−0.76, whose inspection shows that they correspond to six free or broken valences created by the formal splitting of Fe−C bonds with terminal ligands. (Figure 1a). In keeping with the suggested interpretation, the corresponding eigenvalues can be regarded as contributions of iron to unevenly shared electron pair of terminal Fe−C bonds.

The bonding with the bridging ligands is thus necessarily due to the remaining five electron pairs whose presence can be anticipated on the basis of the isolobal analogy.[41,48] In this connection it is interesting to remark that although the existence of five bonding electron pairs could be, at least in principle, compatible with the existence of bent metal−metal bond (Scheme 1), the inspection of the DAFH eigenvectors associated with these five crucial electron pairs shows that the actual picture of the bonding is quite different.

The form of the corresponding eigenvectors is displayed in Figures 1b−f. The most important structural feature emerging from the inspection of the electron pairs in Figure 1 is the impossibility to bind both bridging ligands by “ordinary” localized Fe−C bonds. The inspection of this figure shows, namely, that there are only two localized electron pairs that are available for the bonding of two bridging ligands (Figure 1b,c). This result is very interesting because exactly the same situation was observed in the case of the isoelectronic $Co_2(CO)_8$ and the close parallel with this carbonyl is reflected also in the bonding of the second bridging ligand. As it is possible to see from Figure 1, the bonding of this ligand is due to the electron pair, associated with the eigenvalue 1.87 (Figure 1f), which is very reminiscent of a multicenter (3c−2e) bond, whose presence was also detected in the DAFH analysis of $Co_2(CO)_8$.[14] The close resemblance of both systems is finally underlined also by the remaining two eigenvectors (Figure 1d,e) for which the DAFH analysis implies the association with nonbonding pairs on the metal atoms. We can thus see that the parallel between both isoelectronic carbonyls is indeed complete. This implies, however, also the close resemblance in the final picture of the bonding, which can be described by the same qualitative scheme involving the resonance of two three-center bonded structures as in the case of the cobalt carbonyl (Scheme 2).

As the absence of direct Fe−Fe bond suggested by the above DAFH analysis of the bonding interactions in the C_{2v} isomer of the carbonylate anion is evidently inconsistent with the empirical predictions of the 18-electron rule, it was of interest to see whether similar discrepancies can be observed also for the other isomeric structures of the $[Fe_2(CO)_8]^{2-}$ dianion. The most interesting in this respect is, of course, the isomer of D_{3h} symmetry.

***D_{3d}* Structure.** This isomer of the carbonylate anion exists in the form of the stable ammonium salt $[NEt_4]_2(Fe_2(CO)_8)$, whose electron count, structural arrangement with relatively short Fe···Fe distance, and the absence of the bridging ligands makes it an ideal candidate for the existence of the direct Fe−Fe bond. To contribute to the elucidation of the nature of the bonding in the this isomer of the carbonylate anion, the above qualitative considerations will be confronted with the insights provided by the DAFH analysis.

Because of close direct proximity of the metal atoms, the most straightforward way of detecting the eventual existence of Fe−Fe bond is to analyze the hole averaged over the fragment $Fe(CO)_4$ formed by the symmetrical splitting of the molecule. The advantage of such a choice of the fragment is that provided a metal−metal bond is present, the isolation of the fragment from the rest of the molecule formally splits that bond and such a splitting can straightforwardly be detected by the existence of DAFH eigenvectors corresponding to "free" or "broken valences". Consistent with widely accepted interpretation of DAFH analysis, such "broken valences" are assciated with the eigenvalues close to 1 and the eventual appearance of such eigenvalues thus provides a straightforward indication of the existence and multiplicity of the corresponding metal−metal bond. The complete list of the eigenvalues resulting from the DAFH analysis DAFH analysis is given in the Table 5 and the suggested interpretation is supported by the graphical display of selected DAFH eigenvectors, depicted in Figure 2.

As can be seen from the table, the DAFH analysis of the $Fe(CO)_4$ fragment yields 37 nonzero eigenvalues of which 36 are close to 2 and the remaining one is close to 1. In keeping with the expectation, the eigenvalues close to 2 do indeed correspond to the chemical bonds and/or the electron pairs that remain intact in the fragment. These electron pairs, some of which are displayed in Figure 2a−d evidently do not contribute to the metal−metal bonding and need not be considered any longer. This implies that the eventual contribution to the metal−metal bond is necessarily connected with the only remaining eigenvector, whose association with the eigenvalue close to 1 suggests its possible intepretation as a "broken valence" of a formally broken Fe−Fe bond. Such an interpretation is then also straightforwardly corroborated by the inspection of the corresponding eigenvector (Figure 2e) whose shape suggests that the corresponding metal−metal bond has the character of a single σ bond. We can thus see that in contrast to the previous case of the C_{2v} isomer, the results of DAFH analysis and the predictions of the 18-electron rule are in the case of the D_{3d} isomer completely consistent and both point to the existence of a direct Fe−Fe bond. This result is very interesting because of its possible implications concerning the reliability of the 18-electron rule. The observed differences in the picture of bonding of different isomeric structures show, namely, that the straightforward association of the presence and/or absence of direct metal−metal bond with mere electron count without taking into account the actual structure of the individual species is evidently too simplistic.

In addition to confirming the existence of a direct Fe−Fe bond, the DAFH analysis of the bonding situation also reveals further detailed insights into the nature of the corresponding Fe−Fe bond. These insights follow from the detailed inspection of the form of the eigenvector associated with the "broken valence" of a formally split metal−metal bond for various isovalues. Thus, although the inspection of the corresponding eigenvector at higher isovalue is useful for the fundamental classification of the bond as a σ(Fe−Fe) bond (Figure 2e), the display of the same eigenvector using lower isovalues reveals subtler details, suggesting that the electron pair involved in this bond also participates in the interactions with the terminal ligands (Figure 2f). In this connection it is interesting to remark that similar interactions are not apparently exceptional and their existence was proposed in earlier theoretical studies[11,49,50] aiming at the rationalization of the specific features of metal−metal bonding in non-supported metal carbonyls like $Mn_2(CO)_{10}$.[26]

After having demonstated the existence of a direct Fe−Fe bond in the D_{3d} isomer of the carbonylate anion, let us confront, in the following part, the detailed insights into the nature of the bonding interactions with the predictions of 18-electron rule also for the remaining D_{2d} isomer of the carbonylate anion.

***D_{2d}* Structure.** Another stable species whose existence was detected by the quantum chemical analysis of the PE hypersurface[38] of the carbonylate anion, is the unbridged isomer corresponding to a structure of the D_{2d} symmetry. As the basic structural features of this isomer are in many respects (electron count, close direct adjacency of metal atoms, the absence of bridging ligands) similar to what was observed in the previous case of the isomer of D_{3d} symmetry, one can expect that these common features of both species will also be reflected in the similarity of the bonding interactions. If this is indeed the case, the existence of the direct Fe−Fe bond, detected previously in the case of the D_{3d} isomer can also be expected in the D_{2d} isomer. In the following part, the results of DAFH analysis for the D_{2d} isomer of the carbonylate anion will be reported. As the main focus was the detection of direct Fe−Fe bond, the natural choice for the analysis is again the Fermi hole averaged over the fragment $Fe(CO)_4$ formed by the symmetrical splitting of the molecule. The results of the analysis are summarized in Table 6, and the suggested interpetation is again corroborated by the graphical display of selected DAFH eigenvectors depicted in Figure 3.

The inspection of the table shows that the analysis yields again 37 nonzero eigenvalues, of which 36 are close to 2 and the remaining one is close to 1. This result is very interesting because the resulting pattern of the eigenvalues exactly matches that in the previous case of D_{3d} isomer. As it is possible to see from the comparison of Tables 5 and 6, the above quantitative resemblance is also straightforwardly reflected in the similarity of the bonding interactions in both systems. On the basis of the interpretation suggested in Table 6, the picture of the bonding in D_{2d} isomer can be described as follows. The eigenvalues close to 2 correspond to chemical bonds and/or electron pairs that remain intact in the fragment. Some of these electron pairs, whose detailed interpretations are summarized in Table 6, are displayed in Figure 3a−d. These electron pairs evidently do not contribute to the metal−metal bonding and need not be considered any longer. This implies that any bonding interactions between the metal atoms thus has to be again due to the only remaining eigenvector associated with the eigenvalue close to 1. Such eigenvectors are interpreted as "free" or "broken" valences and the fact that the analysis yielded just one such eigenvalue thus straightforwardly implies that the isolation of the $Fe(CO)_4$ fragment from the rest of the molecule again requires the formal splitting of one electron pair Fe−Fe bond. The more detailed insight into the nature of such a bond comes

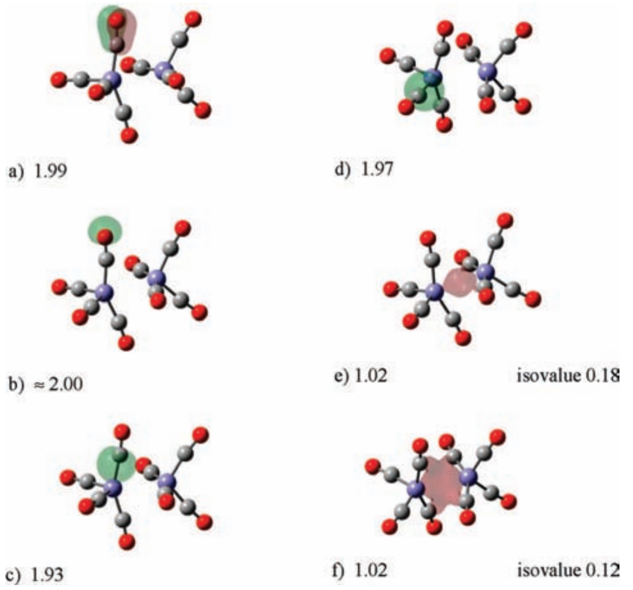


Figure 3. Graphical display of selected eigenvectors of DAFH associated with the $Fe(CO)_4$ fragment of the D_{2d} isomer of the carbonylate anion $[Fe_2(CO)_8]^{2-}$.

from the inspection of the corresponding eigenvector whose form indeed confirms that metal−metal bond in D_{2d} isomer has the character of σ(Fe−Fe) bond (Figure 3e) and, moreover, that similarly as in the case of D_{3d} isomer, the electron pair of this bond participates in the interactions with the terminal ligands (Figure 3f).

This result is again very interesting because we encounter here another example where the existence of metal−metal bond, anticipated on the basis of favorable electron count, is again made possible only because of the presence of favorable structural arrangement.

Another example demonstrating the decisive role of favorable electron structure in determining the nature of the bonding interactions is provided by the confrontation of the results of DAFH analysis with the predictions of the 18-electron rule in the case of the neutral carbonyl $Fe_2(CO)_8$.

$Fe_2(CO)_8$. Unlike the closely related dianion, the neutral carbonyl $Fe_2(CO)_8$ is an extremely unstable species whose transient existence has been detected among the products of low temperature UV/vis photolysis of $Fe_2(CO)_9$.[39] This original discovery has subsequently stimulated more detailed low temperature spectroscopic study,[40] in which the existence of two isomeric forms, one bridged and one unbridged was reported. Although the structure of the bridged isomer was assigned to correspond to the species of C_{2v} symmetry, the structure of unbridged isomer was not assigned with certainty but it was suggested that it could correspond to the species of D_{2h} symmetry, earlier suggested by Hoffmann.[41] These early experimental observations have subsequently been complemented by the thorough theoretical analysis by Xie et al.[5] in which the existence of the isomeric structures of both C_{2v} and D_{2h} symmetry was indeed reported. Consistent with this earlier study[5] we have also been able to detect the existence of the stationary points on the potential energy hypersurface that correspond to the structures of both C_{2v} and D_{2h} symmetry. For all the basis sets compared, the most stable isomer is that of C_{2v} symmetry, but despite marginal differences in the calculated optimized geometries, the nature of the corresponding critical points was found to be sensitive to the actual basis set used. The original assignment of bridged C_{2v} structure as the minimum on the PE hypersurface was confirmed only at the B3LYP/DZP and B3LYP/SDD levels of the theory; for the LANL2DZ basis the presence of one negative eigenvalue of the force constant matrix was observed. For this reason and also to maintain the consistency with other systems analyzed in this study, we report in the following part the results of DAFH analysis of the bonding interactions in the most stable C_{2v} isomer of $Fe_2(CO)_8$ just for the structure generated at B3LYP/SDD level of the theory.

C_{2v} Structure. The nature of the bonding in this molecule was previously studied in the thorough study of binuclear homoleptic iron carbonyls,[5] in which the existence of direct double Fe═Fe bond in the C_{2v} isomer of the above carbonyl was advocated on the basis of the 18-electron rule and interatomic Fe···Fe distances. As, however, the accumulating examples of the disagreement between the predictions of these empirical rules and the conclusions of more sophisticated theoretical approaches were repeatedly being reported,[11−14] it was of interest to see whether the suggested existence of double Fe═Fe bond is indeed compatible with the detailed insights provided by the DAFH analysis. The analysis was again performed for the hole averaged over the $Fe(CO)_2Fe$ fragment involving metal atoms and the bridging ligands. The numerical results are summarized in Table 7, and the graphical display of the crucial eigenvectors responsible for the bonding within the fragment is in Figure 4.

The most interesting conclusion resulting from the DAFH analysis of this isomer of $Fe_2(CO)_8$ concerns its straightforward mutual links with the picture of the bonding observed above for the closely related dianion $Fe_2(CO)_8{}^{2-}$. The close parallel between both systems is clearly suggested already by the number of nonzero eigenvalues, where the observed drop from 37 for carbonylate dianion to 36 for neutral carbonyl straightforwardly reflects the difference in the number of available electron pairs. Quite in keeping with the expectation, the more detailed inspection of the individual eigenvalues and associated eigenvectors shows that the above drop has no impact on the electron pairs and/or broken bonds not directly involved in the bonding within the fragment and their number as well as populations are for both systems the same (see Tables 4 and 7). The whole difference between the two systems thus concentrates just in the number and the form of the electron pairs responsible for the bonding within the $Fe(CO)_2Fe$ fragment. While in the case of the carbonylate anion the bonding was found to be due to five "active" electron pairs, in the case of the neutral carbonyl this number drops to four and as it will be show below, the observed differences in the picture of the bonding of the neutral $Fe_2(CO)_8$ and the above ion can straightforwardly be related just to the above change. To reveal the above relation, it is useful to compare the form of the corresponding "active" electron pairs depicted in Figure 4 with those resulting from the DAFH analysis of the anion (Figure 1). Such a comparison shows that three of four and/or five electron pairs responsible for the bonding within the fragment are in both cases practically the same. The inspection of the corresponding figures (1b,c,f vs 4a,b,c) shows that two of these electron pairs are involved in the localized chemical bonds between the metal atoms and one of the bridging ligands and the remaining one, involved in the bonding of the second ligand, is more delocalized and its form is reminiscent of multicenter 3c−2e bond. This result is very important as the existence of delocalized multicenter bonding suggests that the bonding in this carbonyl exhibits similar features of electron deficiency that were previously detected in other bridged metal carbonyls.[14] Irrespective of this resemblance, the important differences in the final picture of the bonding in

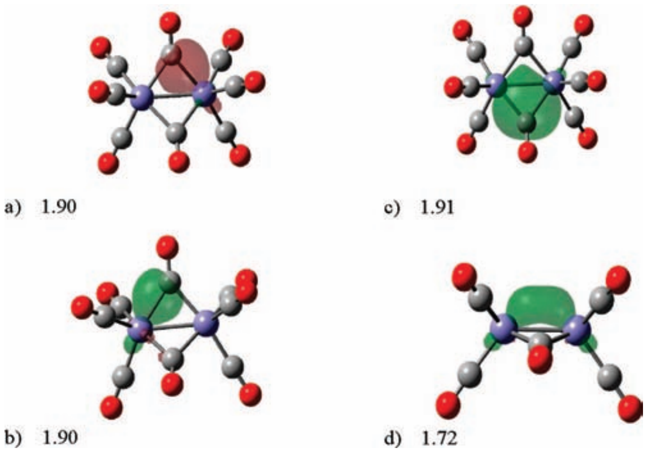


Figure 4. Graphical display of selected eigenvectors of DAFH associated with the Fe(CO)$_2$Fe fragment of the C_{2v} isomer of the neutral carbonyl Fe$_2$(CO)$_8$.

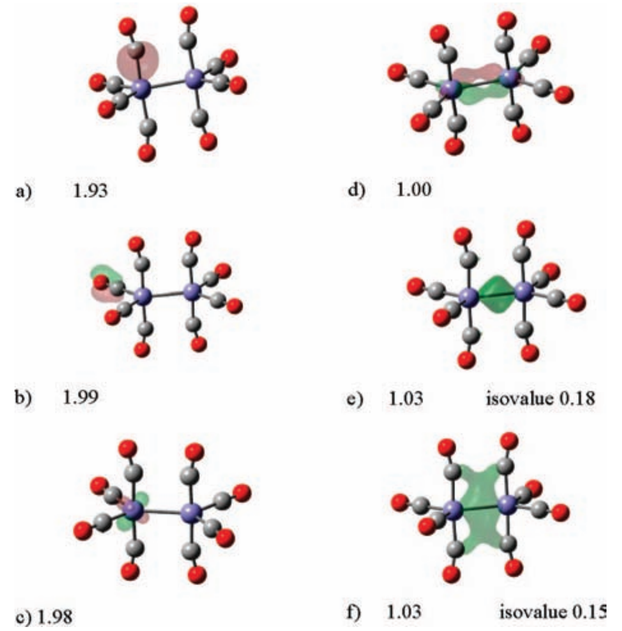


Figure 5. Graphical display of selected eigenvectors of DAFH associated with the Fe(CO)$_4$ fragment of the D_{2h} isomer of the neutral carbonyl Fe$_2$(CO)$_8$.

the neutral carbonyl Fe$_2$(CO)$_8$ and its dianion nevertheless exist and, as it will be shown, their existence is straightforwardly due to the differences in the number of remaining electron pairs.

In contrast to the carbonylate anion, where the DAFH analysis excluded (similarly as in the case of isoelectronic Co$_2$(CO)$_8$[14]), the existence of a direct Fe—Fe bond, the same analysis of the neutral carbonyl suggests the presence of such a bond. Such a conclusion straightforwadly follows from the inspection of the form of the remaining fourth "active" DAFH eigenvector associated with the eigenvalue 1.91 (Figure 4d), which corresponds to the in-phase bonding combination of d$_{z^2}$ orbitals on the metals. The existence of such a direct bond in the neutral carbonyl, as well as its absence in the carbonylate anion, can be understood by referring to the orbital interaction diagram (Scheme 3), from which the mutual interplay of the presence and/or absence of direct metal—metal bond and the number of available electron pairs in the system is straightforwardly evident.

On the basis of the above results of the DAFH analysis, the structure of the neutral carbonyl can be characterized by the resonance Scheme 4.

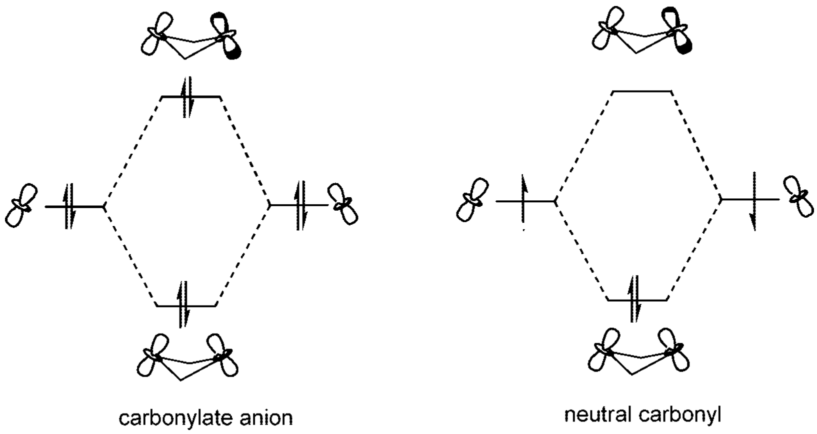
The picture of the bonding suggested by the above scheme is very interesting not only because of demonstrating the close link between the nature of the bonding interactions and the electron count but also because it again clearly shows that the predictions based just on the simple electron count without considering subtler details of the electron structure of individual molecules are not necessarily reliable and can fail. This is just the case of Fe$_2$(CO)$_8$ and its dianion where the 18-electron rule predicts the existence of double and single Fe—Fe bonds, respectively, whereas the above presented DAFH analysis suggests the existence of single Fe—Fe bond in the neutral carbonyl and its complete absence in the dianion.

***D_{2h}* Structure.** Irrespective of the fact that the existence of three negative eigenvalues of the force constant matrix is apparently inconsistent with the early experimental expectations considering the D_{2h} isomer as the best candidate for the trapping in cryogenic matrix,[40] the nature of the bonding interactions in this isomer of Fe$_2$(CO)$_8$ still represents an important challenge for the bonding theory. The reason is again the discrepancy between the anticipations based on the 18-electron rule and isolobal analogy,[41,48] which both predict the existence of Fe=Fe double bond, and the results of a more recent computational study[5] in which the authors claim that in spite of the relatively short Fe···Fe interatomic distance, "there is no evidence for Fe=Fe double bond from the structural perspective". To contribute to the eludication of the above inconsistency, the results of DAFH analysis of the D_{2h} isomer of Fe$_2$(CO)$_8$ are reported below.

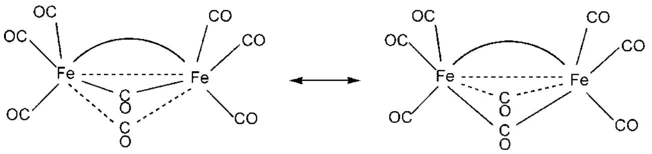
As the structural arrangement is again favorable for the existence of metal—metal bond, the most straightforward way to detect the eventual presence of such a bond in the DAFH analysis is to analyze the hole averaged over the fragment Fe(CO)$_4$ formed by the symmetrical splitting of the molecule. The numerical results of the DAFH analysis are summarized in the Table 8 and the suggested interpretation is supported by the graphical display of selected DAFH eigenvectors, presented in Figure 5.

The inspection of the table shows that the DAFH analysis yields 37 nonzero eigenvalues of which 35 are equal or very close to 2, and the remaining two are close to 1. The eigenvectors associated with the eigenvalues close to 2 evidently correspond to chemical bonds and core and/or lone electron pairs that remain intact in the fragment (Figure 5a—c). These electron pairs are irrelevant for the metal—metal bonding and need not be again considered. The decisive role in determining the nature of the bonding interactions between the metal atoms thus necessarily belongs only to the remaining two eigenvectors associated with the eigenvalues close to 1. According to traditional interpretation, such eigenvectors are interpreted as "free" or "broken" valences and the fact that the analysis yields just two such free valences thus clearly suggests the existence of double Fe=Fe bond in the D_{2h} isomer of the neutral Fe$_2$(CO)$_8$ molecule. Such an intepretation is then also straightforwardly corroborated by the inspection of the shape of the two above eigenvectors associated with the "broken valence" of the formally split Fe=Fe bond, which shows that one of the eigenvectors is very reminiscent of localized orbital of π(Fe—Fe) (Figure 5d) bond and the other corresponds to the σ component of the Fe=Fe bond (Figure 5e). Here it is also interesting to remark that similar to the previous case of D_{3d} and D_{2d} isomer

SCHEME 3



SCHEME 4



of the carbonylate anion, the σ(Fe−Fe) bond is also involved in the interactions with the terminal ligands (Figure 5f).

The detection of direct metal−metal bond in the D_{2h} isomer of the neutral carbonyl is again very important because of its possible impact on the reliability of 18-electron rule. The agreement between the predictions of 18-electron rule and the picture of the bonding provided by the DAFH analysis is namely observed again only in one particular (D_{2h}) isomer of the carbonyl, whereas in the case of the isomeric C_{2v} species the predictions of both approaches again differ. The existence of similar discrepancy is, of course, very interesting not only because it implies that empirical electron count rules can no longer be considered as completely general trustworthy tool but also because it demonstrates that the detailed understanding of the nature of the bonding interactions requires more detailed insights that take into account the actual structure of the studied molecules.

Conclusions

The reported DAFH analysis of the bonding interactions in the studied binuclear carbonyls has provided new interesting insights that throw new light on early empirical tools like the 18-electron rule. In contrast to this rule, which assumes the presence of direct metal−metal bonds in both the above carbonyls, the reported analysis shows that the favorable electron count is only one of the factors determining the nature of the bonding interactions and that the realistic description of the bonding requires to take into the account also the actual structure of the molecule in any particular case. The detailed insights provided by DAFH analysis revealed the nature of the complex interplay between the above factors and we believe that its further systematic application to other molecules with nontrivial bonding pattern can provide useful insights allowing the deeper understanding of the picture of the bonding in such systems.

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Supporting Information Available: Optimized coordinates and total energies for all the studied systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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