Peculiarities of Multiple Cr−Cr Bonding. Insights from the Analysis of Domain-Averaged Fermi Holes

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The recently proposed methodology known as the analysis of domain-averaged Fermi holes was applied to reveal the nature and peculiarity of metal−metal bonding interactions in two recently reported complexes with an ultrashort, presumably quintuple Cr−Cr bond. The results of the analysis straightforwardly confirm the considerable reduction of the Cr−Cr bond order resulting from depletion of the electron density from one of the electron pairs involved in the metal−metal bonding. Because of this depletion, the Cr−Cr bond can be best classified as the effective quadruple bond, with the contribution of another weak component corresponding to the antiferromagnetic coupling of electrons in one of the available δ-electron pairs.

Introduction

Since its discovery in the 1960s, the phenomenon of metal−metal bonding has been the focus of continuous interest of experimental and theoretical studies. In addition to the new perspectives that the discovery of the molecules containing directly bonded metal atoms enriched the traditional paradigms of transition-metal chemistry,[1−3] another, apparently even more stimulating impetus for the development of this new field of chemistry came from the observation that not only can the corresponding bonds have the character of multiple bonds but also their multiplicities can exceed the usual limits known from organic chemistry.[14−16] Besides vigorous activity in the preparation and structural characterization of new compunds with unusual bond multiplicitites, the discovery of the phenomenon of metal−metal bonding has also immediately raised the challenge for the chemical theory to provide the background for elucidation of the nature of the underlying bonding interactions. The first successful model of multiple metal−metal bonding was suggested by Cotton,[4,5,9,11] who related the existence of such bonds to interactions of incompletely filled shells of available d orbitals on the metals. Using this elementary molecular orbital (MO) model, the existence of a quadruple metal−metal bond in molecules like $Re_2Cl_8^{2-}$ has been attributed to interactions of the metals in the valence state configuration d^4−d^4, which results in bonding involving one σ, two π, and one δ components. The possibility of involving the contributions of a metal−metal δ bond suggested, however, also the existence of metal−metal bonds of even higher multiplicity,[17−23] and these predictions have subsequently been vindicated by the reported synthesis of stable molecules with quintuple Cr−Cr.[24−27] Although the qualitative description based on simple MO analyses, as well as ultrashort interatomic distances, seems to be straightforwardly consistent with the presumed quintuple multiplicity Cr−Cr bond, the more recent insights based on sophisticated theoretical analyses suggest, however, that the nature of the bonding interactions in the realm of metal−metal bonding can be much more intricate.[28−45] An example in this respect can be, e.g., the discussions concerning the discrepancy between the number of electron pairs involved and the effective multiplicity of metal−metal bonds. In order to contribute to the elucidation of the peculiarities of Cr−Cr bonding, we report in this study the picture of the bonding interactions in two recently reported complexes with an ultrashort Cr−Cr bond,[25−27] resulting from the analysis of domain-averaged Fermi holes (DAFHs).[46−48] Because of valuable insights provided by the reported DAFH analyses for different types of metal−metal bonds,[30,37,49,50] we believe that application of the same methodology can contribute to a deeper understanding of the nature of the bonding interactions also for the widely discussed Cr−Cr bond.

Theoretical Section. Because the methodology of the analysis of DAFHs is sufficiently reported in previous studies,[46,47] we restrict ourselves only to a brief review of the basic ideas to the extent necessary for the purpose of this study. The most straightforward way of introducing the DAFHs (eq 1) is via the appropriate integration of the so-called pair correlation function.[51]

$$\begin{aligned} C(r_1, r_2) &= 2\rho(r_1, r_2) - \rho(r_1)\,\rho(r_2) \\ g_\Omega(r_1) &= -\int_\Omega C(r_1, r_2)\,\mathrm{d}r_2 \\ g_\Omega(r_1) &= \rho(r_1)\int_\Omega \rho(r_2)\,\mathrm{d}r_2 - 2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2 \\ &= \rho(r_1)\,N_\Omega - 2\int_\Omega \rho(r_1, r_2)\,\mathrm{d}r_2 \end{aligned} \tag{1}$$

In this equation, $\rho(r_1)$ and $\rho(r_1,r_2)$ denote the ordinary first-order and pair density, respectively, and integration (averaging) is via the finite domain Ω. The choice of the domain is, in principle, arbitrary and analyzed could be the holes averaged over the domains of arbitrary shape and size, but in previous studies, we have shown that especially useful and chemically relevant information can be extracted from the holes (1) only if the domains Ω are derived from sound physical principles. One

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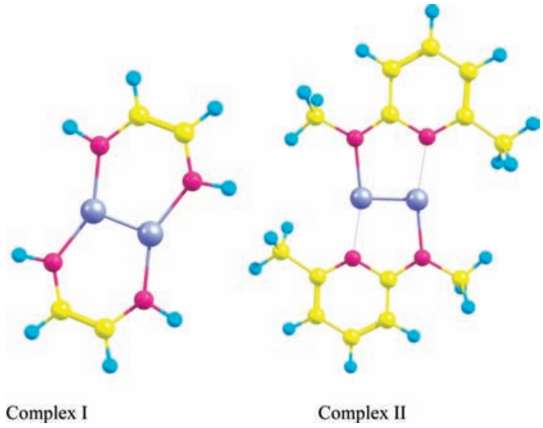
of such possibilities is, e.g., to identify the domains Ω, with the AIM atomic domains resulting from virial partitioning of the electron density.[52] In such a case, the holes have been shown to provide information about the actual valence state of the corresponding atom in a molecule. Analyzed and discussed can be, however, also more complex domains formed by the formal union of several atomic domains corresponding, e.g., to certain functional groups or interesting molecular fragments. In such a case, the hole reveals the broken or "dangling" valences created by formal splitting of the bonds required to isolate a given fragment from the rest of the molecule as well as the electron pairs (bonds, lone pairs, etc.) that remain intact within the fragment. The above information is being extracted from the holes (1) via the analysis that involves first the diagonalization of the matrix representing the hole in the appropriate basis. The eigenvalues and eigenvectors resulting from this diagonalization are then, in the second step, subjected to the isopycnic transformation,[53] whose aim is to convert the original (delocalized) eigenvectors to more localized functions reminiscent of classical chemical concepts of bonds, lone pairs, etc., in terms of which chemists are used to thinking of molecules and their structures. The resulting picture of the bonding can then straightforwardly be deduced from the inspection of the form of the corresponding localized functions and the numerical values of the associated eigenvalues. Thus, while the eigenvalues close to 2 typically correspond to electron pairs of chemical bonds, lone pairs, etc., the broken or dangling valences can generally be identified with the localized functions associated, for nonpolar bonds, with the eigenvalues close to 1. In the case of polar bonds, the significant deviations from unity can be observed and the actual values can then be regarded as the contributions of individual atoms to the unevenly shared electron pair of the corresponding bond.

Results and Discussion

In order to contribute to the clarification of the bonding interactions in the Cr−Cr bond, we report in this study the results of the DAFH analysis for the two systems closely related to recently reported Cr complexes with an ultrashort Cr−Cr bond. The first of them is the complex reported by Kreisel et al.[25] with the experimental Cr−Cr bond length 1.80 Å, which was in the calculations simplified by replacement of the bulky 2,6-diisopropylphenyl groups by hydrogen atoms (complex I). The same type of simplification was also used in the theoretical modeling[25] of the complex, and our use of the same systems thus opens the possibility of the straightforward comparison of both studies. The second system we analyzed was related to the Cr complex reported in the study by Noor et al.[27] (Cr−Cr bond length 1.75 Å) and, similar to in the previous case, the original complex was simplified for computational purposes by replacing the bulky substituents by methyl groups (complex II). The calculations comprised first the complete optimization of the geometry of the studied complexes. These calculations were performed using the *Gaussian98* program[54] at the same level of the theory as that in the studies,[25,27] i.e., BLYP/6-311G for complex I and BLYP/TZVP for complex II, respectively. The resulting geometrical parameters exactly reproduced the data reported in the studies[25,27] (calculated Cr−Cr bond distance 1.76 Å vs experimental value 1.80 Å for complex I and 1.72 Å (calculated) vs 1.75 Å (experimental) for complex II).

On the basis of the generated wave functions, the next step involved the construction of the DAFH for the selected fragments and their subsequent analysis. The analysis was performed using our program *WinBader*, which is available upon request. For both systems, two types of domains were analyzed. One of them was associated with the fragment Cr−Cr involving both metal atoms and the resulting picture of the bonding was complemented by the analysis for the domain involving one of the Cr atoms only.



Before reporting the results of the DAFH analyses for the two above systems, we, nevertheless, consider it useful to briefly comment on the relevance of the computational methods used in the context of recent computational studies,[22,28,42,43] in which the authors strongly advocate for the use of post-Hartree−Fock multiconfigurational treatment. There is, of course, no doubt that for the quantitatively reliable description of the systems with ultrashort ultraweak metal−metal bonds such a level of the theory is certainly to be preferred, but the accumulating evidence of numerous computational studies clearly suggests that the qualitative classification of metal−metal-bonding interactions can apparently be achieved using less demanding approaches.[21,23,30,31,37,48−50] An example can be the recent studies in which the peculiarities of metal−metal bonding such as the discrepancy between the number of electron pairs involved and the actual (effective) bond order[30−32] or the existence of the bonding interactions transcending the traditional Lewis model of a shared electron pair[48] could satisfactorily be revealed using the DAFH analysis at the density functional theory (DFT) level.

In view of these encouraging results, it was of interest to see what picture of the bonding will result from the same approach for a nowadays widely discussed Cr−Cr bond, and in the following part, the results of such analysis will be reported.

Complex I. The nature of Cr−Cr bond in this molecule was first discussed in the study by Kreisel et al.,[25] whose analysis of MOs revealed that the peculiarity of this bond arises from the fact that although there is indeed five bonding electron pairs involved in metal−metal bonding; only four of them are predominantly localized between the metal atoms, while the remaining one (HOMO−2) displays strong delocalization toward the neighboring N ligands (Figure 1).

This, of course, raises the question of the classification of this bond because, as a result of the above delocalization, which removes part of the electron density from the region between the metal atoms, the discrepancy between the number of electron pairs involved and the actual Cr−Cr bond multiplicity can be expected. Such an expectation was indeed confirmed, and on the basis of NRT analysis, the authors report the effective Cr−Cr bond order 4.28. A similar reduction of the Cr−Cr bond order was also reported in the recent studies,[42,45] where, on the basis of the calculated value of effective Cr−Cr bond order, the authors prefer to classify the bond as a quadruple bond rather than a quintuple bond. In connection with this numerical result,

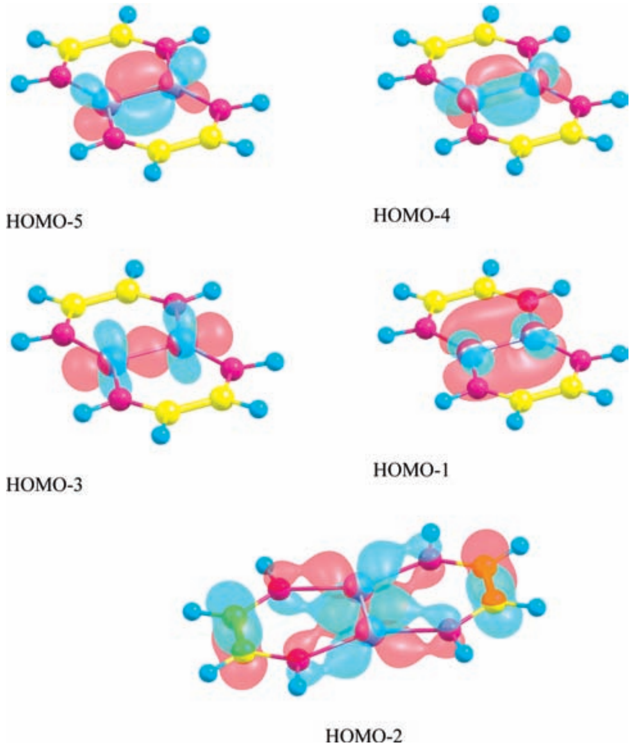


Figure 1. Occupied MOs corresponding to five electron pairs involved in complex I in metal−metal bonding.[11] Pictures were generated using the *ChemCraft* program.

it is useful to remark that qualitatively the same reduction of that Cr−Cr bond order has been observed also in our calculations, where despite the fact that a single-determinant DFT level is used, the values of the Wiberg−Mayer bond index[55,56] (3.94) as well as its AIM generalized counterpart (SEDI)[57−59] (3.76) are also straightforwardly consistent with the quadruple multiplicity of the Cr−Cr bond. As will be shown, a qualitatively very similar picture of the bonding emerges also from the DAFH analysis. In order to elucidate the nature of the Cr−Cr bonding interactions, let us discuss first the results of the DAFH analysis for the fragment Cr−Cr involving both metal atoms. In such a case, the most relevant information provided by the analysis concerns the detection of electron pairs that remain intact within the fragment as well as the "broken" valences formed by the formal splitting of Cr−ligand bonds required to isolate the fragment from the rest of the molecule. The numerical results of the analysis are summarized in Table 1. Inspection of the table shows that the DAFH analysis yields in this case 27 (essentially) nonzero eigenvalues. A closer inspection of the graphical form of the associated eigenvectors shows that 10 of them, equal to 2.00, correspond to electron pairs of completely filled 1s, 2s, and 2p inner shells on both metals. In addition to these core electron pairs, there is another group of eight eigenvalues ranging from 1.985 to 1.997, for which inspection of the associated eigenvectors shows that they correspond to electron pairs of completely filled 3s and 3p valence shells on the metals (Figure 2a,b). These electron pairs, as well as the previous core pairs, are of no relevance for metal−metal bonding in the molecule and need not be considered any longer. The same is also true of another four eigenvectors associated with the degenerate group of eigenvalues equal to 0.297, whose inspection shows that they evidently correspond to "dangling" valences of formally broken bonds between the metal atoms and the ligands (Figure 2c).

TABLE 1: Numerical Results of the DAFH Analysis of Complex I[a]

eigenvalue	degeneracy	interpretation
2.000	10	electron pairs of completely filled K and L inner shells on Cr
1.997	2	$3p_z^2$ electron pair on Cr
1.996	4	$3s^2$ and $3p_y^2$ electron pairs on Cr
1.985	2	$3p_x^2$ electron pair of Cr
1.981	1	electron pair of the $(d-d)_\pi$ bond
1.964	1	electron pair of the $(d-d)_\sigma$ bond
1.854	1	electron pair of the $(d-d)_\pi$ bond
1.817	1	electron pair of one component of the $(d-d)_\delta$ bond
1.095	1	partially populated component of the $(d-d)_\delta$ bond
0.297	4	broken valences of Cr−ligand bonds

[a] The calculated eigenvalues of the Fermi hole averaged for the fragment Cr−Cr, together with the interpretation of the corresponding eigenvectors.

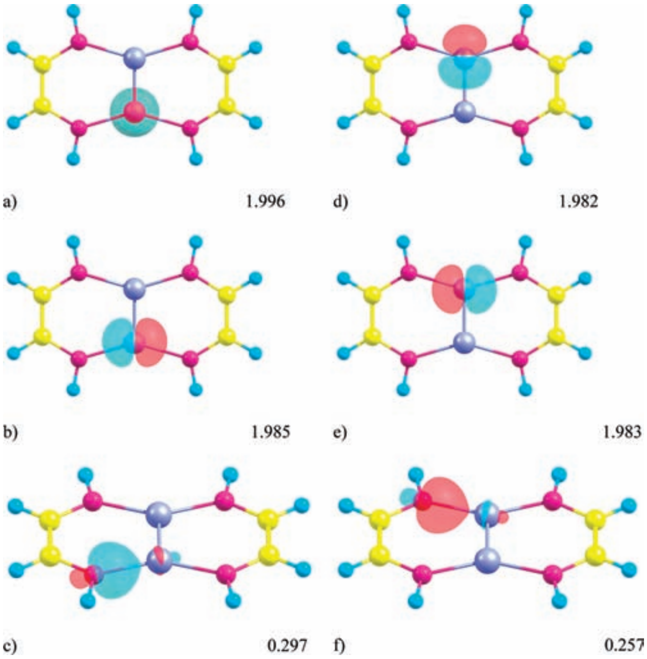


Figure 2. Results of the DAFH analysis for complex I. Selected eigenvectors of the Fermi holes associated with the electron pairs of completely filled inner shells on Cr and broken valences of Cr−ligand bonds for the holes averaged over the fragment Cr−Cr (left column) and the domain involving one Cr atom (right column), respectively.

In keeping with the traditional interpretation, the high deviations of these eigenvalues from unity indicate high polarity of Cr−(N) ligand σ bonds, and the degree of polarity can roughly be estimated by the actual value 0.297, which can be regarded as the contribution of the Cr atom to an unevenly shared electron pair of the above formally broken bond. After elimination of the contributions of the formally broken Cr−ligand bonds, it is obvious that the bonding interactions within the Cr−Cr fragment have to be due to eigenvalues associated with the five remaining nonzero eigenvalues. This result is very interesting because the numerical coincidence with the number of electron pairs available for the bonding in the Cr−Cr fragment[25] seems to be straightforwardly compatible with the anticipated quintuple multiplicity of the Cr−Cr bond. The inspection of the actual values in the Table 1 shows, however, that that above parallel is not completely satisfactory. The reason is that the straightforward association of these eigenvalues and the corresponding eigenvectors with Cr−Cr bonding electron

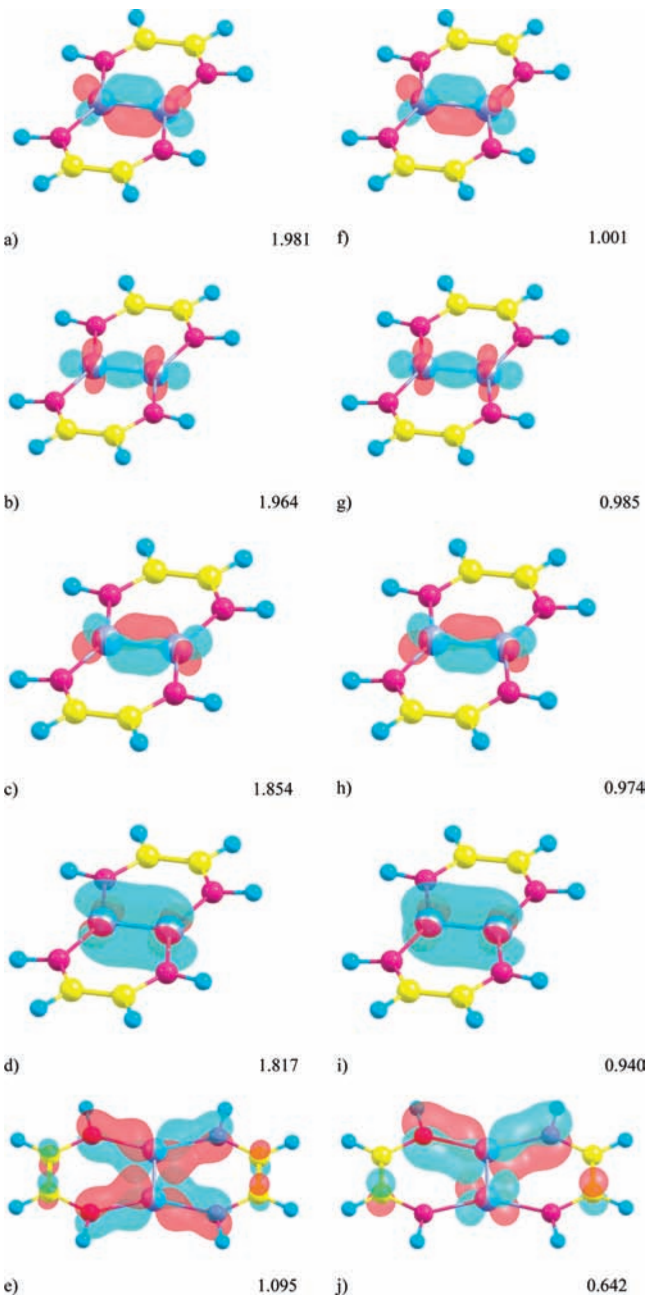


Figure 3. Results of the DAFH analysis for complex I. Selected eigenvectors of the Fermi holes corresponding to electron pairs and broken valences of the Cr−Cr bond for the holes averaged over the fragment Cr−Cr (left column) and the domain involving one Cr atom (right column), respectively.

pairs is possible only for four of five eigenvalues, whose values are reasonably close to 2 (Figure 3a−d).

The situation with the remaining nonzero eigenvalue is, however, more complex because, as a result of the dramatic drop of the population of the corresponding eigenvector to a value close to 1, its straightforward association with the fifth bonding electron pair is evidently questionable. In order to gain insight into the nature of this questionable component of the Cr−Cr bond, it is useful to display the graphical form of the corresponding eigenvector (Figure 3e). As is possible to see, this eigenvector is very reminiscent of the MO (HOMO−2; Figure 1), whose extended delocalization beyond the region of the Cr−Cr bond has been considered by the authors of the study[25] as the main cause of the uncertainties concerning the classification of the multiplicity Cr−Cr bond. This result is very interesting because it demonstrates that earlier qualitative expectations attributing the observed reduction of the calculated bond order to the partial depletion of the electron density from one of the electron pairs participating in the Cr−Cr bonding are, in principle, correct, but in contrast to a simple MO description,[25] where the above depletion could be anticipated only indirectly via the extended delocalization of one of the MOs toward the ligands, the proposed DAFH analysis provides a more detailed quantitative estimate of the extent of depletion via the projection of the corresponding electron pair into the effective population of the domain of the metal−metal bond. Given the considerable extent of this depletion, the dramatic decrease of the bond order detected using various earlier approaches is not at all surprising, and consistent with earlier suggestions,[42,45] we also prefer to characterize the Cr−Cr bond in complex I as an effectively quadruple bond.

In connection with the above classification, it is, nevertheless, useful to point out another peculiar feature emerging from the DAFH analysis of the Cr−Cr bond. The discrepancy between the number of electron pairs involved and the effective multiplicity of the bond is, namely, observed in the realm of metal−metal bonding quite frequently, but what makes the Cr−Cr bond unusual is the mechanism of the reduction of the bond order, which is in this case different from what was observed previously in the DAFH analysis of Re−Re and Ga−Ga bonds.[30,37] Thus, for example, while the reduction of the effective Re−Re bond order was found to be due to the partial population of an antibonding δ^* orbital of the Re−Re bond,[30] no similar population of an antibonding δ^* orbital is observed here and the decrease of Cr−Cr bond order is primarily found to be due to depletion of the electron density from one of the δ electron pairs. In this connection, it is perhaps interesting to remark that independent proof for the existence of such a depletion has recently been provided by the QTAIM study,[45] and the specific position of one of the available δ electron pairs was also reported in the study,[27] in which the authors reported the different topologies of the localization indicator ELI-D for closely related complex II. While for four of the available pairs (one σ, two π, and one δ), the maxima of ELI were localized in the region between the Cr atoms, the pattern of pELI-D distribution for the remaining δ component is different and suggests a tendency toward intraatomic localization of one of the metal δ−d orbitals. Such a localization results in a reduction of the overlap of the corresponding δ−d orbitals on the metal atoms, which is a situation favorable for the switch of the bonding interactions from ordinary sharing to antiferromagnetic coupling.[60−63]

The above picture of the bonding is also independently corroborated by the closely related DAFH analysis of the complementary hole averaged over one of the metal atoms only. In such a case, the main benefit of the DAFH analysis can be expected to come from providing the straightforward information about the number and nature of the electron pairs (chemical bonds) whose formal splitting is required for isolation of the Cr atom from the rest of the molecule. The most interesting in this respect are, of course, the “dangling” valences corresponding to formally split electron pairs involved in Cr−Cr bonding, and as will be shown, the results of the analysis, summarized in Table 2, are completely consistent with the picture of the bonding provided by the results of the DAFH analysis of the hole averaged over the domain involving both Cr atoms.

Inspection of Table 2 shows that the DAFH analysis yields 16 (essentially) nonzero eigenvalues of which five, equal to 2.00, correspond to electron pairs of completely filled 1s, 2s, and 2p

TABLE 2: Numerical Results of the DAFH Analysis of Complex I[a]

eigenvalue	degeneracy	interpretation
2.000	5	Electron pairs of completely filled K and L inner shells on Cr
1.996	1	$3s^2$ electron pairs on Cr
1.995	1	$3p_z^2$ electron pair on Cr
1.983	1	$3p_x^2$ electron pair on Cr
1.982	1	$3p_y^2$ electrron pair on Cr
1.001	1	Broken valence of $(d-d)_\pi$ bond
0.985	1	Broken valence of $(d-d)_\sigma$ bond
0.974	1	Broken valence of $(d-d)_\pi$ bond
0.940	1	Broken valence of $(d-d)_\delta$ bond
0.642	1	Broken valence of partially populated $(d-d)_\delta$ bond
0.257	2	Broken valences of Cr-ligand bonds

[a] The calculated eigenvalues of the Fermi hole averaged for the fragment involving one Cr atom, together with the interpretation of the corresponding eigenvectors.

inner shells on Cr and the another four, ranging between 1.982 and 1.996, to electron pairs of completely filled 3s and 3p valence shells of Cr atom (Figure 2d,e). These electron pairs are not, of course, involved in metal−metal bonding, and in the following discussion can be discarded. The main discussion thus has to be again focused only on the remaining seven nonzero eigenvalues and the associated eigenvectors. The simplest situation is with the group of two eigenvalues equal to 0.257, for which inspection of the associated eigenvectors shows that they correspond to free or broken valences of formally broken polar Cr−ligand bonds (Figure 2f). This implies that the dangling valences of the Cr−Cr bond thus again have to be associated with the remaining five nonzero eigenvalues and associated eigenvectors, and inspection of the corresponding data (Table 2 and Figure 3f−j, respectively) shows that the picture of the bonding that they provide is straightforwardly consistent with the complementary picture resulting from the analysis of the DAFH averaged over the domain involving both metal atoms. Thus, for example, the existence of four bonding electron pairs detected in the analysis of the domain Cr−Cr (Figure 3a−d) is completely confirmed by the presence of four broken valencies (Figure 3f−i) characterized by occupation numbers close to 1, expected to arise from the symmetrical splitting of four evenly shared electron pairs of the homopolar Cr−Cr bond. Such an interpretation is also straightforwardly confirmed by the close resemblance of the form of the corresponding eigenvectors (Figure 3a−d vs Figure 3f−i), which is typical for the chemical bonds well described by the classical Lewis model of ideally shared electron pairs.[48] The situation is, however, again a bit more complex for the remaining broken valence (Figure 3j), originating from the splitting of a delocalized electron pair, whose projection into the region of the Cr−Cr bond results in a reduced population of the corresponding DAFH eigenvector (Figure 3e). As expected, the population of the broken valence is indeed roughly half of that for the population of the eigenvector (Figure 3e), but what makes this dangling valence unusual is the form of the associated eigenvector (Figure 3j), which lacks the close resemblance observed in the remaining cases and displays an increased localization toward one of the metal atoms. This result is very interesting because the increased tendency toward localization of one of the δ-bonding electron pairs is something that was also detected in the previous ELI-D study of closely related complex II[27] and the agreement of both of the above methodologies thus clearly confirms that one of the δ components of the Cr−Cr bond is indeed different from the remaining four. In order to gain more detailed insight into the nature of this peculiar component of the Cr−Cr bond, it is useful to refer to a recent DAFH study of dissociation of the F−F bond in F_2, in which a similar asymmetry in the DAFH eigenvectors was observed even for interatomic distances close to equilibrium.[64] According to a general interpretation,[48] the asymmetry of the DAFH eigenvectors is, namely, closely related to the partial splitting of the bonding electron pairs, and the existence of an analogous situation in the case of the Cr−Cr bond can thus also be regarded as an indication of the partial splitting of the delocalized electron pair of the corresponding δ component of the Cr−Cr bond. The fact that the partial splitting of one δ component of the Cr−Cr bond is observed despite the extremely short interatomic distance can apparently be attributed to the reduced population of the associated DAFH eigenvector (Figure 3e), which, of course, will be reflected in the reduced strength of this component of the Cr−Cr bond. Such a conclusion is also straightforwardly corroborated by the existence of the close link between the asymmetry of the DAFH eigenvectors (Figure 3j) and the reduced overlap of the corresponding functions on individual Cr atoms, due to which it seems tempting to attribute the weakness of this particular component of the Cr−Cr bond to the operation of antiferromagnetic coupling,[60−63] similar to that recently reported in the Cr_2 cluster.[65]

Complex II. The importance of this model complex for the chemistry of multiple Cr−Cr bonding is due to its close relation to the recently reported stable species,[27] in which the corresponding metal−metal bond for the first time broke the limit 1.80 Å considered as a milestone in the chemistry of complexes with ultrashort Cr−Cr bonds.[25,26] The picture of the bonding in this model complex was recently discussed using theoretical analysis, in which the specific role of one of the δ electron pairs involved in Cr−Cr bonding was independently confirmed using the electron localization indicator ELI-D.[27] Our aim in this study is to show that a similar peculiarity of Cr−Cr bonding, independently detected in the above-reported analysis of complex I, emerges from the DAFH analysis also in this case. Because of the close similarity of both systems, we focus in the forthcoming discussion only on the presentation of the results concerning the decisive role of the electron pairs for the nature of Cr−Cr bonding. Discarding the presence of electron pairs of completely filled inner shells and the broken valences of Cr−ligand bonds, the analysis of DAFH averaged over the domain involving both Cr atoms as well as over the domain of one Cr atom only detected the presence of five nonzero eigenvalues (Table 3), whose relation to the bonding electron pairs and/or broken valences can straightforwardly be deduced from inspection of Figure 4.

Such an inspection shows that four of the five eigenvectors (Figure 4a−d vs Figure 4f−i), well localized in the region of the Cr−Cr bond, are remarkably reminiscent of the eigenvectors (Figure 4a−d vs Figure 4f−i) detected in the analysis of complex I, and because of the closeness of the associated eigenvalues, they can evidently be regarded as corresponding to electron pairs and/or broken valences of the quadruple Cr−Cr bond. Slightly different is, however, again the situation with the remaining eigenvector (Figure 4e), which displays extensive delocalization toward the ligands and whose associated eigenvalue 1.624 again suggests similar, albeit not so deep, depletion of the electron density from the region of the Cr−Cr bond. The existence of the above depletion then also allows us to expect a reduction of the Cr−Cr bond order, and such an expectation is indeed confirmed by the values of both the Wiberg−Mayer

TABLE 3: Numerical Results of the DAFH Analysis for Complex II[a]

DAFH(Cr−Cr)		DAFH(Cr)	
eigenvalue	interpretation	eigenvalue	interpretation
1.974	electron pair of the $(d-d)_\pi$ bond	0.996	broken valence of the $(d-d)_\pi$ bond
1.959	electron pair of the $(d-d)_\sigma$ bond	0.982	broken valence of the $(d-d)_\sigma$ bond
1.878	electron pair of the $(d-d)_\pi$ bond	0.957	broken valence of the $(d-d)_\pi$ bond
1.817	electron pair of one component of the $(d-d)_\delta$ bond	0.928	broken valence of the $(d-d)_\delta$ bond
1.624	partially populated component of the $(d-d)_\delta$ bond	0.909	broken valence of the partially populated $(d-d)_\delta$ bond

[a] Comparison of selected eigenvalues of the Fermi holes directly involved in metal−metal bonding. Left column: Fermi hole averaged over the fragment Cr−Cr. Right column: Fermi hole averaged over one Cr atom only.

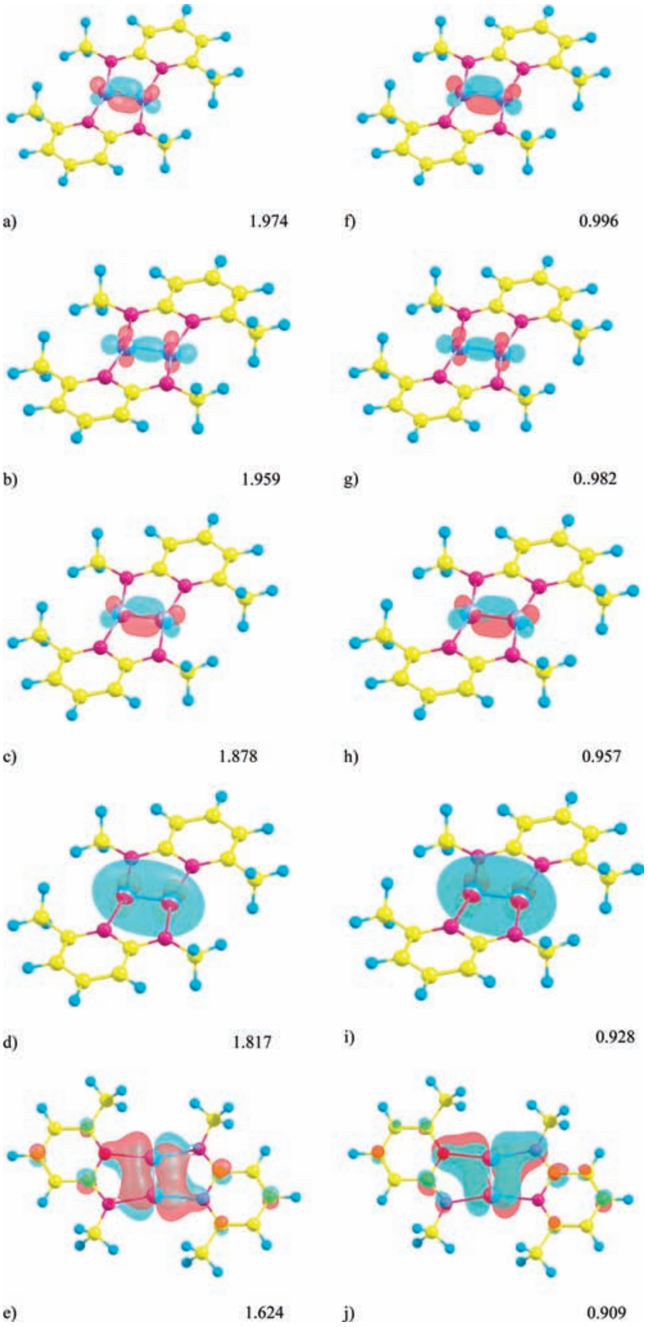


Figure 4. Results of the DAFH analysis for complex II. Selected eigenvectors of the Fermi holes corresponding to electron pairs and broken valences of the Cr−Cr bond for the holes averaged over the fragment Cr−Cr (left column) and the domain involving one Cr atom (right column), respectively.

bond order (4.38) and its AIM generalized counterpart SEDI (4.17), which both nearly coincide with the value 4.2 of the delocalization index δ(CrCr) reported by Noor et al.[27] Consistent with the above interpretation is also the form of the associated broken valence (Figure 4j), whose clear localization toward one of the Cr atoms fits well with the tendency toward intraatomic localization detected by a pELI-D localization indicator and suggests, similar to that in the case of the previous complex I, that the nature of the bonding interactions revealed by the DAFH analysis of both complexes is very similar and the corresponding Cr−Cr bonds can also be classified as a quadruple bond with the contribution of antiferromagnetic coupling of metal atoms via one of the δ-bonding electron pairs.

Conclusions

The nature of the bonding interactions in an ultrashort presumably quintuple Cr−Cr bond has been analyzed and discussed using analysis of the domain-averaged Fermi holes. The new interesting insights provided by this analysis have allowed us to reveal the origin of the observed discrepancy between the number of available electron pairs and the calculated bond order. According to the reported analysis, the dominant contribution to Cr−Cr bonding is due to four shared electron pairs, while the fifth available pair is involved via the contribution of antiferromagnetic coupling of the metals.

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