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A new insight from qualitative MO theory into the problem of the Fe–Fe bond in $Fe_2(CO)_9$

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Abstract

A revision of EHMO calculations with FMO analysis has provided new qualitative insight into the bonding network in $Fe_2(CO)_9$ and reconciled the previous diverging interpretations. After separation of all of the $Fe-(CO)_{bridge}$ bonding/antibonding levels (12 electrons for six Fe–C bonds) there remains a two-electron/two-orbital interaction (σ/σ^*) that is ultimately responsible for a direct (through-space) Fe–Fe bond. However, predominant repulsive interactions via the CO bridges (through-bond) may hide the linkage.

Introduction

The nature of metal–metal bonding in transition metal binuclear and polynuclear clusters is still a matter of controversy. It is unresolved even for well-known compounds that have received the closest attention from theoreticians and that could serve as models for the interpretation of intricate molecules.

One example is the dimer $Fe_2(CO)_9$. The short Fe–Fe separation of 2.523(1) Å [1] could be a structural manifestation of bonding , and the brilliant golden colour of the compound may provide spectroscopic evidence for it [2]. Chemical intuition also suggests the presence of such a bond. The two metal have a formal 17 electron count, and since the compound is not paramagnetic there should be a direct bond between them. However, no clear-cut theoretical evidence for the presence of a Fe–Fe σ bond has yet been provided [3*]. Summerville and Hoffmann [4] concluded that direct metal–metal interactions can not play a role in determining the geometry of the bi-octahedron: The metals would then be held in close proximity by the three-centered Fe–C–Fe linkages. Since in the corresponding delocalized MOs

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* Reference number with asterisk indicates a note in the list of references

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the metal d_π–d_π antibonding character predominates, the Fe–Fe interaction is more repulsive than attractive. Although most of the conclusions were reached from the powerful analysis of the fragment molecular orbitals (FMO) [5], identification of the presence of direct Fe–Fe bonding is evidently difficult. One reason is that the dimer cannot be properly separated into fragments containing all of the metal–ligand bonds already preformed so that one can focus upon the residual metal-metal interactions, if any.

Even more drastic proposals were made by other authors [6,7], who, in the light of results of ab-initio calculations conclude that there is no direct Fe–Fe bond in $Fe_2(CO)_9$. Bauschlicher [6] has introduced quite new concepts in respect of the bonding abilities of transition metal atoms, and in particular he has pointed out that the high lying s and p metal functions have little relevance for the bonding and the energetics of carbonyl complexes such as $Ni(CO)_4$ and $Fe(CO)_5$ [8], and so of the title dimer [6].

Criticism of Bauschlicher's calculations are beyond the scope of this note, but exclusion of the s and p metal orbitals appears to be in conflict with the eighteen electron rule, which is based on the availability of nine orbitals for metal atoms. The occasional exclusion from bonding of one or more p metal orbitals (as in square planar d^8 or linear d^{10} complexes) is well understood in terms of symmetry arguments [9]. In other cases, careful examination has shown that weak interactions (often with non-canonical electron donors) can be present and preserve the essence of the above rule (e.g. the agostic interactions with a C–H bond) [10]. This can be restated as the "rule of nine orbitals", implying a specific assignment for each one of them, i.e. either they participate in interatomic bonding (or antibonding) interactions or remain unaffected at low energy as filled or half-filled [11*] non-bonding MOs. The interactions between ligand lone pairs and metal s, p orbitals are favoured by a large overlap (diffuse orbitals on both sides) but disfavoured by a large energy gap and by the intermediate presence of d orbitals, which act as buffers. Whatever the nature and the strength of the metal–ligand bonds [12*], the s and p metal orbitals are the most likely orbitals to accept part of the electron density from the ligands. If electronically-unsaturated (electron number < 10), some d orbitals can also function as acceptors (e.g., e_g levels in d^6 octahedral complexes). Otherwise, they remain either non-bonding or used in clusters for direct metal–metal interactions.

Results and discussion

We have refined the EHMO analysis [13*] of the bonding in $Fe_2(CO)_9$, largely by reference to the interaction diagram (Fig. 1) originally reported by Summerville and Hoffmann [4].

Essentially the diagram shows the interaction between the FMOs of the fragments $(CO)_3Fe \cdots Fe(CO)_3$ and $(\mu\text{-}CO)_3$. On the left side, in ascending order, are the in-phase and the out-of-phase combinations of the frontier orbitals of typical L_3M fragments [9], [14]. In the lower group the levels $1a_1'$, $1e'$, $1e''$, and $1a_2''$ have σ, δ, $\delta^\star$, and $\sigma^\star$ character, respectively. In octahedral coordination the latter levels (combinations of t_{2g} sets) are expected to remain non-bonding. At higher energies the levels $2e'$, $2a_1'$, $2e''$, and $2a_2''$ have π, σ, $\pi^\star$ and $\sigma^\star$ character, respectively. The latter σ and $\sigma^\star$ partners are different mixtures of terminal ligands

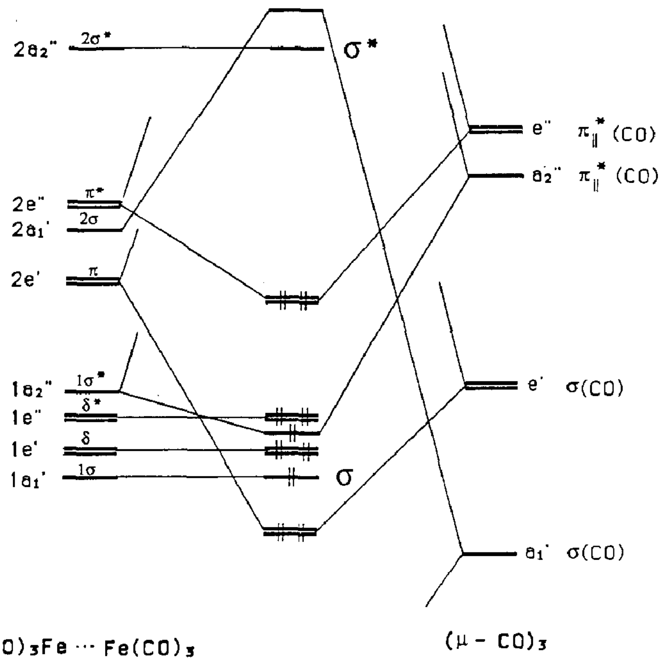
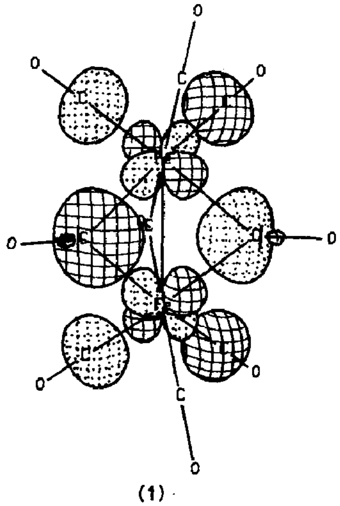


Fig. 1. Diagram for the orbital interactions between the $Fe_2(CO)_6$ and the (μ-CO)$_3$ fragments.

and metal s, p_z, d_{z^2} orbitals. On the right side, only the combinations of σ lone pairs (a_1' and e') and of the $\pi_\parallel{}^*$ orbitals (e'' and a_2''), parallel to the Fe–Fe vector, for the CO bridges, are reported. For clarity, the combinations of the CO $\pi_\perp^*$ orbitals are omitted, because the a_2' combination is symmetry-excluded from bonding and the e' set is at most mixed with other important e' combinations.

Mulliken population analysis identifies the main interactions between the FMO bases [15]. Even if there is consistent mixing of δ and π character and rehybridization of the σ metal orbitals, the overlaps $\langle 2e' | e' \rangle$, $\langle 2e'' | e'' \rangle$, $\langle 2a_1' | a_1' \rangle$ and



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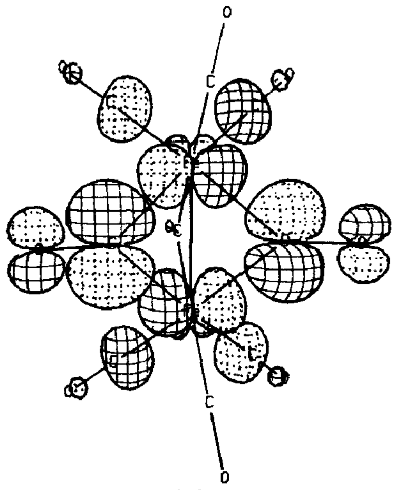

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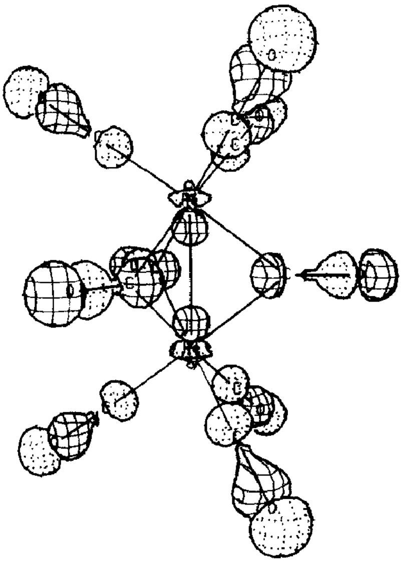

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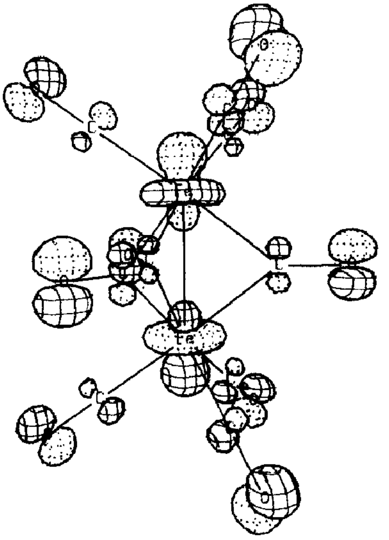


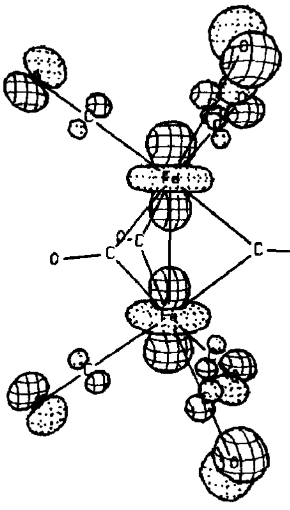
(4)

$\langle 1a_2'' \mid a_2'' \rangle$ predominate, since the corresponding OP values, of 0.43 ($\times 2$), 0.52 ($\times 2$), 0.38 and 0.18, are by far the most positive in the system. Among these, the e' and e'' interactions (selected antibonding members are shown in **1** and **2**, [16*]) are the largest, and fully consistent with the results of ab-initio calculations. Indeed, the synergistic donation (e' type) and backdonation (e'' type) effects determine most of the metal-bridge bonding.

The a_1' and a_2'' interactions (the bonding MOs in **3** and **4**) are also relevant. In fact, they raise to six the total number of the major Fe–C_{bridge} bonding interactions (involving twelve electrons). Other authors seem to have underestimated one or both of these interactions. Bauschlicher [6] considers only those of e' and e'' type (eight electrons involved) while Heijser, Baerends and Ros [7] (LCAO Hartree–Fock–Slater calculations) and also Minot and Criado-Sancho [17] (EHMO calculations), disregard the metal → CO a_2'' type back-donation **4**. Accordingly, they predict the presence of only five Fe–C_{bridge} bonds, with a total of ten electrons (six from the σ-CO lone pairs a_1', e' and four from the metal d_π levels, $2e''$).

It should be noted that disregarding the a_1' and the a_2'' interactions limits the full operation of the CO bridges as donors and that of the metals as back-donors. In $Fe_2(CO)_9$, as in the precursor $(CO)_3Fe \cdots Fe(CO)_3$ fragment, there would be two σ/σ^* pairs, one fully populated (four electrons) and one empty. By contrast, since the filled $1a_2''$ ($1\sigma^*$) and the empty $2a_1'$ (2σ) FMOs are used to complete bridge-bonding, the $1a_1'$ (1σ) and $2a_2''$ ($2\sigma^*$) are forced to coexist in the final MO picture of the dimer as unperturbed filled σ and empty σ^* levels (**5**, **6**). This reflects the formal requirement to have a σ bond, no matter how weak it might be [18*]. Notice that FMOs $1a_1'$ and $2a_2''$, formerly non-bonding, have diversified their role by acquiring metal-metal and metal–ligand bonding character, respectively.

In any case the EHMO calculations reveal a slightly negative Fe–Fe reduced OP of -0.02 [19*]. By definition, the value is the resultant of all of the inter-metal



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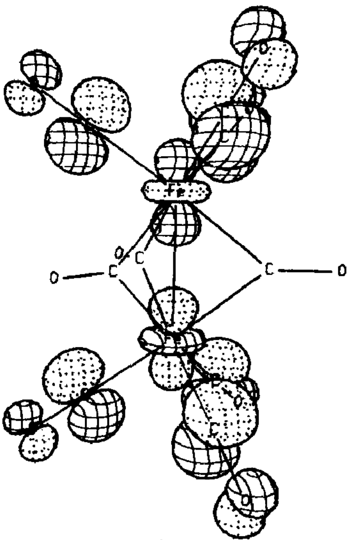

(6)

orbital interactions, occuring either through-space (direct) or through-bond (via the bridges) [20]. As already mentioned, Summerville and Hoffmann found that the e' and e'' interactions, through the bridges, involve different percentages of metal d_π character, with a predominant antibonding effect ($e'' > e'$). This argument can be extended to couplings of a_1' and a_2'' symmetry, occurring through the bridges, so that a net repulsion between the metals can reasonably be expected. However, the essential point is that the through-bond intermetal repulsion does overcome the attractive Fe–Fe interaction, occurring through-space.

More quantitative evidence for an Fe–Fe σ bond can be obtained as follows. In the calculations, the σ/σ^* pair (**5**, **6**) can either be depopulated or forced to accept a total of four electrons. In any case the effect is that of making the Fe–Fe OP value more negative (-0.09 and -0.14, respectively), with no variation in the strength of the Fe–C_{bridge} linkages. Accordingly it can be stated that the geometry of the bioctahedron is influenced by the Fe–Fe bond, at least in the sense that its elongation is minimized. The same conclusion can be reached by analyzing the results of calculation based on fragmentation of $Fe_2(CO)_9$ into three pieces, i.e. two terminal $(CO)_3Fe$ moieties and one bridging $(\mu\text{-}CO)_3$ grouping. Again the OP values clearly indicate six Fe–C_{bridge} bonding interactions. Furthermore, the OP values are positive ($+0.08$) for the direct interaction between metal σ-FMOs (essentially, p_z and d_{z^2}) and negative (-0.15) for the d_π–d_π interactions, with the latter predominating.

It seems clear from the above argument that the Mulliken Population analysis becomes most informative when the numerical quantities are not attributed an absolute significance but instead are considered in terms of the components and their trends.

Conclusions

The Fe–Fe interactions in $Fe_2(CO)_9$ have a through-bond and a through-space character, since the metals have enough orbitals for the existence of both. Owing to the predominance of the former type of interaction, the net effect is a repulsion which will be consistent with the presence of a weak direct Fe–Fe linkage.

More generally, it can be argued that the well known weakness of the metal–metal bonds in bridged carbonyl metal clusters is attributable to the intermetal antibonding interactions generated via the stabilizing participation of CO π^* orbitals in the bridge-bonding network (through-bond coupling).

Acknowledgements

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References and notes

1 F.A. Cotton and J.M. Troup, J. Chem. Soc. Dalton Trans., (1974) 800.

2 W.C. Trogler, J. Chem. Educ., 57 (1980) 424.

3 VB calculations better than MO predict the existence of a Fe–Fe single bond. See: L. Pauling and Z.S. Herman, J. Chem. Educ., 61 (1984) 582; Z.S. Herman, Int. J. Quantum Chem., 23 (1983) 921.

4 R.H. Summerville, R. Hoffmann, J. Am. Chem. Soc., 101 (1979) 3821.

5 R. Hoffmann, H. Fujimoto, J.R. Swenson and C.-C. Wan, J. Am. Chem. Soc., 95 (1973) 7644.

6 C.W. Bauschlicher Jr., J. Chem. Phys., 84 (1986) 872.

7 W. Heijser, E.J. Baerends and P. Ros, Faraday Symp., 14 (1980) 211.

8 C.W. Bauschlicher Jr. and P.S. Bagus, J. Chem. Phys., 81 (1984), 5889.

9 T.A. Albright, J.K. Burdett and M.-H. Whangbo, Orbital Interactions in Chemistry, John Wiley&Sons, New York 1985, p. 381.

10 (a) M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395; (b) O. Einsenstein and Y. Jean, J. Am. Chem. Soc., 107 (1985) 1177; (c) C. Mealli and D.M. Proserpio, Comments Inorg. Chem., 9 (1989), 37.

11 For example tetrahedral high-spin 16 electrons complexes differ from the 18 electron conformers in having the *e* set half rather than fully populated.

12 Although of long standing, the problem of metal–ligand interaction is currently receiving much attention and recently Epiotis has proposed the concept of orbital dispersion and bond cooperativity for organometallic compounds, since the canonical covalent and ionic models appear insufficient. See: N.D. Epiotis, New J. Chem., 12 (1988) 231, 257.

13 All MO calculation were of the extended Hückel type [13a]. The atomic parameters were taken from ref. 13b. The geometry of the model was that revealed by an X-ray diffraction study [1]. (a) R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36 (1962) 2179, 3489; R. Hoffmann, ibid., 39 (1963) 1397; (b) T.A. Albright, P. Hofmann and R. Hoffmann, J. Am. Chem. Soc., 99 (1977) 7546.

14 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058; M. Elian, M.M.-L. Chen, D.M.P. Mingos and R. Hoffmann, Inorg. Chem., 15 (1976) 1148.

15 M.-H. Whangbo, H.B. Schlegel and S. Wolfe, J. Am. Chem. Soc., 99 (1977) 1296.

16 Drawings made with the program CACAO (Computer Aided Composition of Atomic Orbitals) written by these authors and presented in: C. Mealli and D.M. Proserpio, J. Chem. Ed., in press.

17 C. Minot and M. Criado-Sancho, New J. Chem., 8 (1984) 537.

18 An evaluation of the intermetal bond strength is obtainable via an empirical relationship with bond distance. In particular, the calculated Fe–Fe bond energy is only 70 kJ mol^{-1} a value that accounts for only ca. 6% of the heat of disruption of $Fe_2(CO)_9$. See: (a) C.E. Housecroft and K. Wade, J. Chem. Soc. Chem. Comm., (1978) 765; (b) J.A. Connor in B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley & Sons, Chichester, 1980, p. 345.

19 Negative Fe–Fe overlap population are reported by several authors, for example see: B. Jezowska-Trzebiatowska and B. Nissen-Sobocinska, J. Organomet. Chem., 342 (1988) 353. The EHMO value reported in ref. 17 is larger than ours probably on account of the somewhat different molecular geometry and orbital parameters.

20 R. Hoffmann, Acc. Chem. Res., 4 (1971) 1.