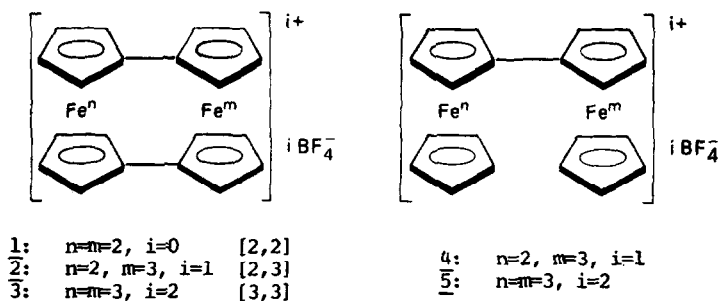


BISFULVALENEIRON [Fe(III)-Fe(III)] - BIS-TETRAFLUOROBORATE: EVIDENCE FOR METAL-METAL INTERACTIONS THROUGH THE π -LIGANDS OF A METALLOCENOPHANE.

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In our recent communication¹ concerning bisfulvalenediiron (1, "BFD") and its iron(II)-iron(III) derivative 2 we suggested the [2,3] species* to be a true mixed valence system rather than a delocalized fully conjugated compound. Based on an analysis of the near infrared transition in [2,3], Cowan and LeVanda² found the interaction parameter³ α to be small ($\alpha \approx 0.2$), so that



[2,3] would be a Class II mixed valence compound according to the classification by Robin and Day⁴. We now wish to report the unusual electronic properties of the iron(II)-iron(III) system [3,3], which reflect strong interactions between the iron atoms and which let us consider the electronic structure of BFD and its oxidized systems in a different light.

Oxidation of a slurry of [2,2] in benzene or acetonitrile by one equivalent of benzoquinone and boron trifluoride etherate produced¹ the dark green crystals of [2,3]. When [2,2] or [2,3] were oxidized in acetonitrile by excess benzoquinone and BF_3 etherate the yellow-brown [3,3] was

(* The notation [2,2] for the iron(II)-iron(II) oxidation state of BFD is used for reasons of simplicity. Similarly, [2,3] stands for the mixed valence monocation of BFD and [3,3] denotes the doubly oxidized dication. This communication concerns only the tetrafluoroborate salts of these systems.

formed, which was precipitated either by slow cooling to -30° (shiny thin leaflets) or upon addition of dry ether (microcrystalline powder) in analytical purity ($C_{20}H_{16}B_2F_8Fe_2$ calculated: C 44.35%, H 2.98%; found: C 44.38%, H 2.85%). Pure [3,3] appears to be stable in air at room temperature but darkens above 250° without melting. In the absence of an oxidizing agent, solutions of [3,3] in acetonitrile or water decompose rapidly, [2,3] being formed, which is easily detected by its green color and its near infrared bands^{1,2} at 1550 nm. Pure [3,3] shows no absorption in this region. As is indicated by the yellow-brown color of [3,3], its electronic spectrum (λ_{max} 465 (ϵ 2755), 428 (ϵ 2405), 320 (shoulder), 270 (ϵ 14700), 239 (ϵ 14715) nm in acetonitrile) also does not show the typical ferrocenium absorption around 600 nm (λ_{max} 617 (ϵ 420) nm for ferrocenium tetrafluoroborate⁵), which was found^{1,2} in [2,3] (λ_{max} 600 (ϵ 370) nm) and which is present in biferrrocene[Fe(III)-Fe(III)]-bis-tetrafluoroborate⁶ 5 (a solid nujol mull shows λ_{max} 760 nm), the non-rigid analogue of our [3,3] compound.

This observation lead us to suspect that [3,3] might be diamagnetic. Magnetic susceptibility measurements⁷ at 22° proved [2,2] to be diamagnetic and showed the expected spin 1/2 paramagnetism (μ_{eff} =1.85 B.M.) for [2,3], while for [3,3] only a small but detectable susceptibility was found. Our suspicion that this residual paramagnetism might be due to impurities was supported by the fact that different samples showed varying but always minor susceptibilities. It was therefore not surprising that nmr spectra of all samples of [3,3] in CD_3CN showed only broad nondescript signals. In spite of the instability of aqueous solutions of [3,3], we were, however, able to record nmr spectra of [3,3] in D_2O by virtue of the fact that [2,3] is essentially insoluble in water*. They show two sharp peaks at τ 3.64 and 5.92 with a width at half height of 6Hz and a 1:1 proton ratio. Both peaks rapidly broaden (the high field part faster than the low field portion) until after a few minutes only ill defined broad bands, shifted slightly to lower field, can be found, similar to the signals of [3,3] in CD_3CN . Understandably, our efforts to detect the expected resolution of the two peaks into triplets** were not successful. We consider these observations as valid proof for the diamagnetism of the [3,3] dication.

As reasons for the diamagnetism of [3,3] we have to consider either direct metal-metal bonding or metal-ligand-metal interactions. A metal-metal bond has recently been implied⁸ to be responsible for the diamagnetism of bis(pentalenedi)cobalt, in which a Co-Co distance close to 2 Å can be assumed, while the paramagnetism of bis(as-indacene)dicobalt was considered⁸ to result from a Co-Co distance too large to allow bonding interactions. If this interpretation alone were applicable to the BFD system, we should expect [3,3] to be paramagnetic, since, if we extrapolate

(*) The nmr spectra were recorded with sodium 2,2-dimethyl-2-silapentane sulfonate as internal standard. D_2O containing the standard was added to [3,3], the solution was filtered into an nmr tube, and the spectra were recorded within one minute after dissolving the sample.

(**) A. Davison and J. C. Smart (J. Organometal. Chem., in press) have prepared the bis-hexafluorophosphate salt of the dicobalt analogue of [3,3] (nmr in CD_3CN : triplets ($J=1Hz$) at τ 2.52 and 4.52), which is isoelectronic with BFD (nmr in benzene- d_6 : triplets ($J=2Hz$) at τ 4.78 and 6.27).

from the Fe-Fe distance⁹ of 3.984 Å in [2,2] and of 3.887 Å in bis(as-indacene)diiron¹⁰, the Fe-Fe distance in [3,3] should be considerably larger than the highest known Fe-Fe bond length¹¹ of 3.05 Å. For these reasons, and because it is known¹² that metal-metal bonds are preferred in low oxidation states, we reject the idea that a direct Fe-Fe bond is responsible for the diamagnetism in [3,3] and propose that it is due to spin pairing by interactions of the two iron atoms through the coplanar ligands. It has been established, mainly through the work of Taube¹³ that two metals can interact strongly through conjugated π -electron systems, although full delocalization or resonance stabilization¹⁴ have not been described so far in organometallic systems. The observation by Cowan¹⁵ that 5 is paramagnetic indicated that alternatives to find potential energy minima are available, so that the high spin configuration is energetically favored in 5 over the singlet resulting from electron pairing through the potentially conjugated fulvalene ligand*. The coplanarity of the fulvalene ligands in BFD naturally favors interactions over the entire system. Thus we believe that [3,3] represents a delocalized cyclic conjugated system of D_{2h} symmetry.

These results still do not clarify the questions concerning the electronic structure of the [2,3] system. Since there is little reason to assume that the observed interactions between the iron atoms in the [3,3] case should be lost in the [2,3] compounds, our earlier suggestion¹ not to regard [2,3] as a delocalized symmetric system might possibly require a revision. Preliminary Mössbauer and ESCA data indeed indicate the equivalence of the two iron atoms in the mixed valence system¹⁶. If this can be confirmed, the near infrared bands in [2,3] might have to be assigned to a $\pi \rightarrow \pi^*$ like transition rather than a [2,3] \rightarrow [3,2] electron transfer absorption. Our hesitation to adopt this view is based on the knowledge that in delocalized systems the spectral characteristics of the constituents are no longer discernible, but that the electronic spectrum of [2,3] does show the 600 nm absorption of the ferrocenium salts with nearly the same intensity as in ferrocenium tetrafluoroborate⁵. This observation still has to be reconciled with the evidence for delocalization and symmetry of the BFD system.

(*) In this case, however, the interaction between the two ferrocenium halves may be diminished by twisting of the central bond caused by steric and electronic repulsions, although a C_{2h} arrangement would promise complete conjugation so that the singlet state could, in principle, be energetically preferred.

REFERENCES:

1. U. T. Mueller-Westerhoff and P. Eilbracht, *J. Amer. Chem. Soc.*, **94**, 9272 (1972)
2. D. O. Cowan and C. LeVanda, *ibid.*, **94**, 9271 (1972)
3. N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967)
4. M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967)
5. R. Prins, *Chem. Commun.*, 280 (1970)
6. D. O. Cowan, R. L. Collins and F. Kaufman, *J. Phys. Chem.*, **75**, 2025 (1971)

7. We thank Dr. K. Lee of this laboratory for these measurements.
8. T. J. Katz, N. Acton and J. McGinnis, J. Amer. Chem. Soc., 94, 6205 (1972)
9. M. R. Churchill and J. Wormwald, Inorg. Chem., 8, 1970 (1969)
10. R. Gitany, I. C. Paul, N. Acton and T. J. Katz, Tetrahedron Lett., 2773 (1970). The Fe(III)-Fe(III) derivative of this compound should be an interesting test case for our assumptions.
11. L. F. Dahl, E. R. Gill and R. D. Feltham, J. Amer. Chem. Soc., 91, 1653 (1969)
12. F. A. Cotton, Accounts Chem. Res., 2, 240 (1969)
13. (a): H. Taube and E. S. Gould, ibid., 2, 321 (1969); (b): C. Creutz and H. Taube, J. Amer. Chem. Soc., 91, 3988 (1969), 95, 1086 (1973); (c): R. H. Magnuson and H. Taube, ibid., 94, 7213 (1972); (d): B. Maych and P. Day, ibid., 94, 2885 (1972); (e) E. S. Gould, ibid., 94, 4360 (1972).
14. Ref. 5, p. 248
15. D. O. Cowan, G. A. Candela and F. Kaufman, J. Amer. Chem. Soc., 93, 3889 (1971), found $\mu_{\text{eff}} = 3.5$ B.M. for 5 and $\mu_{\text{eff}} = 2.2$ B.M. for the corresponding Fe(II)-Fe(III) salt 4.
16. Footnote 10 of ref. 3.