

## X-Ray Photoelectron Spectroscopy of Ferrocene Compounds<sup>1</sup>

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*Summary* X-Ray photoelectron spectra of a number of ferrocene compounds have been measured and the results have been used to help elucidate the electronic structure and interactions in the novel mixed valence organometallic compound, biferrocene  $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$  picrate.

X-RAY photoelectron spectroscopy not only affords the possibility of probing the electronic structure of organometallic compounds (ionizations from the valence band region) but also the possibility of studying the electronic environment of the constituent atoms of the molecule (ion-

ization of the core electrons) To learn more about the interactions in and electronic structure of mixed valence ferrocene compounds<sup>3</sup> we have measured X-ray photoelectron spectra for the following six ferrocene compounds on a AEI ES-100 electron spectrometer using Al- $K_{\alpha}$  radiation ferrocene, biferrocene, ferroceneFe<sup>III</sup> picrate, ferroceneFe<sup>III</sup> fluoroborate, biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate, and biferroceneFe<sup>III</sup>Fe<sup>III</sup> fluoroborate

The preliminary results of this study can be summarized as follows First Since the ionizations from the valence band region of ferrocene and biferrocene are almost identical there can be little interaction between the two ferrocene moieties in biferrocene or in the biferrocene ions formed by the Al- $K_{\alpha}$  radiation This is consistent with the observation that the uv spectra of these two compounds are very similar<sup>2</sup> However, the line width of the Al- $K_{\alpha}$  radiation limits the size of interaction that can be observed For weak interactions (less than 1 eV) He(I) gas phase photoelectron spectroscopy should prove useful These measurements are in progress and will be reported elsewhere Ionizations from the valence band region of the ferrocene salts are complicated by the transitions due to the picrate and fluoroborate ions

Second If there is only weak interaction between the two ferrocene units in biferrocene, then upon formation of biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate from biferrocene the charge should be relatively localized on one ferrocene ring In the closely related series of ferrocene compounds described here the binding energies of a specific iron core level are expected to vary approximately linearly with the charge on these atoms, because neighbouring charges are expected to be small If our postulate that biferrocene Fe<sup>II</sup>Fe<sup>III</sup> picrate can be described as a mixed valence compound is correct then we should observe two transitions for each Fe core level Figure 1 gives the spectrum of the transitions

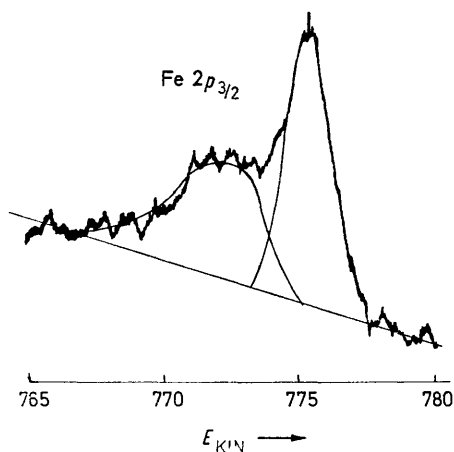


FIGURE 1 Iron  $2p_{3/2}$  region of the X-ray photoelectron spectra of biferrocene, Fe<sup>II</sup>Fe<sup>III</sup> picrate, ordinate, kinetic energy of photoelectrons

assigned to ionizations from the Fe  $2p_{3/2}$  core levels for biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate The transition at a binding

† The effect of exchange interaction on other transitions will be discussed in the full paper The  $2p_{3/2}$  level was chosen because the signal to noise ratio was good and the energy separation between this level and the valence levels was not as great as for the other transitions with good signal to noise ratios

energy of 707.7 eV (kinetic energy of ejected electron  $775.5 \pm 0.1$  eV) corresponds in shape and position to Fe  $2p_{3/2}$  bands found in ferrocene and biferrocene while the transition at a binding energy of 711.1 eV (kinetic energy of ejected electron  $772.1 \pm 0.2$ ) corresponds in position and approximate shape to the Fe  $2p_{3/2}$  bands observed in ferroceneFe<sup>III</sup> picrate, ferroceneFe<sup>III</sup> fluoroborate, and biferroceneFe<sup>III</sup>Fe<sup>III</sup> fluoroborate In addition the relative areas indicate that a 1:1 stoichiometry of Fe<sup>II</sup> and Fe<sup>III</sup> for this compound is reasonable The Fe core ionizations observed for the inorganic mixed valence compound Prussian blue,<sup>4</sup> K Fe<sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>], are very similar to those observed for biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate The separation between the Prussian blue Fe<sup>II</sup>  $2p_{3/2}$  and Fe<sup>III</sup>  $2p_{3/2}$  states is 4.4 eV while the corresponding separation for biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate is 3.4 eV

Third Since ferrocene, biferrocene, and the Fe<sup>II</sup> portion of biferrocene Fe<sup>II</sup>Fe<sup>III</sup> picrate are diamagnetic any exchange interaction of the core electrons with the valence electrons cannot produce a net energy stabilization However, when a partially filled valence shell is present spin-unrestricted Hartree-Fock calculations<sup>5</sup> predict that exchange interactions of the core electrons with the unpaired valence electrons will affect the spin-parallel (core and valence) electrons but not the spin-antiparallel electrons This exchange interaction should broaden or produce multiple bands<sup>6</sup> for the ferroceneFe<sup>III</sup>  $2p_{3/2}$  line† depending on the unpaired spin density on the iron atom The  $2p_{3/2}$  line widths of the ferroceneFe<sup>II</sup> compounds studied were narrow, 1.3–1.4 eV, while the ferroceneFe<sup>III</sup> compound had much broader  $2p_{3/2}$  lines, 2.5–4.0 eV Since the Mossbauer quadrupole splitting (Q.S.) in these compounds can be related to the electric field gradient at the iron atom due to the valence shell electrons<sup>7</sup> we have compared the Mossbauer quadrupole splitting and the  $2p_{3/2}$  line widths (Figure 2)

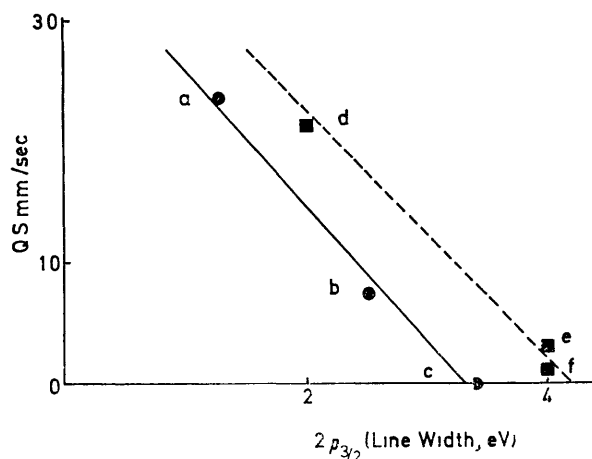


FIGURE 2 Comparison of Mossbauer quadrupole splitting (Q.S.) and iron  $2p_{3/2}$  line widths (a) ferrocene, (b) ferroceneFe<sup>III</sup> fluoroborate, (c) ferroceneFe<sup>III</sup> picrate (d) Fe<sup>II</sup> portion of biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate, (e) Fe<sup>III</sup> portion of biferroceneFe<sup>II</sup>Fe<sup>III</sup> picrate, (f) biferroceneFe<sup>III</sup>Fe<sup>III</sup> fluoroborate

A reasonable correlation is obtained as long as a very similar set of compounds are compared. This tends to confirm our opinion regarding the origin of the  $\text{Fe}^{\text{III}}$   $2p_{3/2}$  line width and suggest that the PES line width may be a useful probe in studying the electronic structure of other organometallic compounds.

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<sup>1</sup> For previous paper in the series 'The Organic Solid State', see D. O. Cowan, G. A. Candela, and F. Kaufman, *J. Amer. Chem. Soc.*, 1971, **93**, 3889.

<sup>2</sup> D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, 1970, **92**, 219, 6198.

<sup>3</sup> D. T. Clark, D. Kilcast, and D. H. Reid, *Chem. Comm.*, 1971, 638; K. Siegbahn, C. Nordling, G. Johansson, J. Herdman, D. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werne, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North Holland, Amsterdam, 1969.

<sup>4</sup> G. K. Wertheim and A. Rosencweig, *J. Chem. Phys.*, 1971, **54**, 3235.

<sup>5</sup> J. H. Wood and G. W. Pratt, *Phys. Rev.*, 1957, **107**, 995; T. E. Watson and A. J. Freeman, *Phys. Rev.*, 1960, **120**, 1134; P. S. Bagus and B. Kiu, *Phys. Rev.*, 1966, **148**, 79.

<sup>6</sup> C. S. Fadley and D. A. Shirley, *Phys. Rev. Letters*, 1968, **21**, 980; J. Hedman, P. F. Heden, C. Nordling, and K. Siegbahn, *Phys. Letters*, 1969, **29A**, 178; C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Letters*, 1969, **23**, 1397; I. W. Drummond and H. Harker, *Nature*, 1971, **232**, 71.

<sup>7</sup> R. L. Collins, *J. Chem. Phys.*, 1965, **42**, 1052; D. O. Cowan, R. L. Collins, and F. Kaufman, *J. Phys. Chem.*, 1971, **13**, 2026.