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J. Guillin, M. Desbois, M. Lacoste, Dominique Astruc, F. Varret. MAGNETIC PROPERTIES AND ELECTRON TRANSFER IN BINUCLEAR ORGANO-IRON SANDWICHES. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-837-C8-838. 10.1051/jphyscol:19888377 . jpa-00228561

HAL Id: jpa-00228561

<https://hal.science/jpa-00228561>

Submitted on 1 Jan 1988

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MAGNETIC PROPERTIES AND ELECTRON TRANSFER IN BINUCLEAR ORGANO-IRON SANDWICHES

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Abstract. – Bi-iron electron reservoirs complexes, of sandwich structure, have been studied in the 36, 37, 38 e[−] states, by Mössbauer spectroscopy in external magnetic fields. The nature of the various couplings between the 19 e[−] subunits has been elucidated, and correlated to the electron transfer to the bridge in the mixed valence state.

1. Introduction

Fe(I) organometallic complexes, so called "Electron Reservoirs" exhibit unusual properties by comparison to the more stable Fe(II) (18 e[−], *S* = 0) compounds [1]: The additional – unpaired – electron is located in an antibonding orbital *e*₁^{*} (*d*_{zx}, *d*_{zy}). Mössbauer spectrometry yields larger isomer shift (IS) values and, in many cases, a temperature dependent quadrupole splitting (QS) because of the thermal population of the two orbitals of the *e*₁^{*} level which is split by a rhombic distortion [1]. At low temperature, 6 T Mössbauer spectra reveal an anisotropic hyperfine field (consistent with *S* = $\frac{1}{2}$), a negative QS contrary to 18 e[−] compounds, different orientations for the total electric field gradient (EFG) and the hyperfine field tensors.

We report here the Mössbauer study with and without external field, in a large range of temperatures, of two series of binuclear organometallic complexes [C₆Me₆Fe(C₅H₄)₂FeC₆Me₆]^{*n*+} and [C₅Me₅Fe(C₆H₅)₂FeC₅Me₅]^{*n*+}, respectively denoted A^{*n*+} and B^{*n*+} where *n* = 2, 1, 0 and Me = CH₃. We compare the results for identical oxydation states, particularly for monoreduced (*n* = 1) and bireduced (*n* = 0) states. Also a "perethylated" A⁰ was studied.

The synthesis of the complexes, X-rays data (Fig. 1), sample preparation and other instrumental data have been reported in references [2, 3].

Fig. 1. – Schematized structures of A^{*n*+}, B^{*n*+}; arene distortions for B⁺, B⁰ are α = 5°, 23° respectively (X-rays data [2a]). B²⁺ and A^{*n*+} are undistorted. The bridge is C–C for all dimers, except for B⁰ (C = C).

2. Complexes with *n* = 2, A²⁺ and B²⁺

Zero field spectra yield IS values and temperature independent QS typical for 18 e[−] complexes [2, 4, 5].

The parameters of A²⁺ are identical to those obtained for its monomer parent [C₅H₅FeC₆Me₆]⁺ [2b, 5]. 6 T spectra (Fig. 2a) reveal that A²⁺ and B²⁺ are diamagnetic with a positive EFG main component like in all 18 e[−] compounds.

3. Complexes with *n* = 1

Between 4.2 K and 300 K, only one doublet is seen on the zero field spectra indicating that A⁺ and B⁺ are delocalized mixed-valence compounds at the Mössbauer time scale [2]. The IS values are in between those of 18 e[−] and 19 e[−] compounds. The increase of the IS values from B²⁺ to B⁺ is smaller than from A²⁺ to A⁺ and is interpreted as a weaker increase of electron density on the iron atom upon reduction. QS is temperature independent because of the electronic interaction between the *d*_{zx} orbitals of the two iron atoms which lifts the degeneracy of the *e*₁^{*} level of the monomers [1]. The energy difference between the resulting orbitals is large and does not allow a sizeable thermal population like in 19 e[−]. Under an external field, the spectra (Fig. 2b) show negative EFG, large asymmetry parameter, paramagnetic behaviour with anisotropic, temperature-dependent hyperfine field. The isotropic part of the magnetic hyperfine tensor, *A*_{iso}, equals the fermi contact term because [*g*] ~ 2. We measured *A*_{iso} = −5.0 T, −3.3 T for resp. A⁺, B⁺ (Refs. [2a, b]). The expected value is −25.4 T for a spin 1 on the free ion. This yields for each iron atom a density of unpaired spin 1/2 equal to 25 % for B⁺ and 40 % for A⁺. This shows that in B⁺ a large part of the extra electron density is transferred to the biphenyl bridge (as suggested by the lower IS).

4. Complexes with *n* = 0, A⁰ and B⁰

The Mössbauer data of B⁰ are typical for 18 e[−] complexes [2a]: IS values, QS positive and practically temperature independent. The hyperfine field is negligible (Fig. 2c). This indicates that the addition of two electrons (starting from the stable 18 + 18 e[−] complex) does not affect the iron atoms but results in a total

Fig. 2. - Typical spectra of dimers under longitudinal magnetic field of 6T (at 4K): (a) diamagnetic (B^{2+}); (b) paramagnetic with spin 1/2 (B^+ , temperature dependent hyperfine field) (delocalized mixed valence); (c) chemically coupled dimer (B^0); (d) antiferromagnetically coupled spins 1/2 (A^0): a minor contribution originates from spins remaining uncoupled [2b]; (e) paramagnetic, uncoupled spins 1/2 (perethylated A^0).

electronic transfer to the biphenyl ligand. These data, together with the observation of a structural distortion by X-rays (decoordination of one C by arene ring and creation of a C = C bond) is well described in terms of "chemical coupling" [2a]. Similar distortion was previously observed in some oxydized monomers [5].

A^0 and "perethylated" A^0 show behaviours quite different from the "chemically coupled" B^0 and reminiscent of the uncoupled parent monomers $Fe(I)$ ($19 e^-$, $S = \frac{1}{2}$); precisely at low temperature under external field, a negative EFG, an anisotropic hyperfine field and a rotation of the hyperfine tensor with respect to the EFG axes [1] are expected. This is exactly observed in "perethylated" A^0 (Fig. 2e).

The behaviour of A^0 is much more complex [2b]: at high temperature, zero-field spectra yield parameters expected for $19 e^-$ complexes: large IS values, temperature dependent QS. Lowering the temperature in the range 50-30 K, a second doublet of lower IS progressively substitutes the former one; the small decrease in IS values indicates a partial electron transfer to the bridge. 4 K, 6 T spectrum (Fig. 2d) shows a major contribution with negligible hyperfine field and a negative QS, together with a minor contribution typical of uncoupled $19 e^-$ system. On the other hand, magnetic measurements show an antiferromagnetic coupling below 40 K [2b] which explains the absence of hyperfine field. All these data suggest a structural transition with partial electron transfer, giving rise to a sizeable antiferromagnetic interaction between the two unpaired spins.

5. Conclusion

The bireduced series shows the coupling between 2 paramagnetic subunits, at various degrees: negligible (perethylated A^0 , high-temperature A^0), antiferromagnetic (low-temperature A^0), "chemical" (B^0 at any temperature). The strength of the coupling is correlated with the degree of transfer of the unpaired electronic density to the bridge in the mixed valence state. Molecular orbital calculations are in progress to provide quantitative explanations.

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