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A new look at molecular and electronic structure of homoleptic diiron(III,II) complexes with N,N-bidentate ligands: Combined experimental and theoretical study


Abstract: Paddlewheel-type dinuclear complexes featuring metal–metal bonding have been the subject of widespread interest due to fundamental interest in their electronic structures and potential applications. Here, we explore the molecular and electronic structures of diiron(III,II) complexes with N,N'-diarylformamidinate ligands. While a paddlewheel-type diiron(III,II) complex with N,N'-diphenylformamidinate ligands (DPhF) exhibits the centrosymmetric [Fe₂(μ-DPhF)₄]₂⁻ structure, a minor alteration in the ligand system, i.e. switching from phenyl to p-tolyl N,N'-substituted formamidinate ligand (DTolF), resulted in the isolation of an unprecedented non-centrosymmetric [Fe₂(μ-DTolF)₂Fe(μ₂-DTolF)] complex. Both complexes were characterized using single-crystal X-ray diffraction, magnetic measurements, ⁵⁷Fe Mössbauer spectroscopy, and cyclic voltammetry along with high-level ab-initio calculations. The results provide a new view on a range of factors controlling the ground-state electronic configuration and structural diversity of homoleptic diiron(III,II) complexes. Interestingly, the Mayer bond orders for the Fe–Fe interactions are significantly lower than 1 and equal to 0.15 and 0.28 for [Fe₂(μ-DPhF)₄] and [Fe₂(μ-DTolF)₂Fe(μ₂-DTolF)], respectively.

Introduction

Since the seminal Cotton’s achievements in the characterisation of multiple bonding between rhenum atoms,¹,² transition metal complexes incorporating the metal-metal (M–M) bond have been a subject of widespread interest driven by several perspectives, including fundamental curiosity and potential applications in heterogeneous or enzymatic catalysis and small molecules activation.³–⁵. The direct electronic communication between metal centres allows tuning the reactivity at coordination sites and controlling multielectron redox processes as well as modulating magnetic properties of the multimetallic core. Among the most intensively developed groups of the metal-metal bonded compounds are paddlewheel-type dinuclear complexes supported by appropriate bridging ligands such as amidinates.³ These versatile N,N-donor ligands have steric and electronic factors naturally supporting the formation of symmetric, metal-metal bonded complexes surrounded by two, three, or four bridges. The mentioned class of complexes generally shows strong metal-metal interactions, leading to a low-spin bimetallic core, often with a multiple bonding between metal atoms, reaching up to five for dichromium and dimolybdenum systems.¹⁰–¹⁶ When the metal-metal interplay decreases, the probability of ferromagnetic or antiferromagnetic exchange increases.¹⁷,¹⁸ In the case of the first-row transition metals, for which compounds incorporating the M–M bonding are far less known than their second- and third-row counterparts, the most common are low-spin complexes with strong antiferromagnetic interactions.³,⁶ However, metal-metal bonded bimetallic complexes containing iron or cobalt centres generally show a high-spin ground state, challenging the common wisdom according to which strong metal-metal interactions should be antiferromagnetic.⁵,¹⁹–³⁷

We note that diiron metal-metal bonded complexes lacking strongly r-acidic ligands are rare and show a vast diversity in the oxidation states, coordination numbers, and geometries.⁶ Most of them are centrosymmetric dimers, resulting from the utilisation of symmetric N,N-bidentate ligands (cf. complexes I and II, Fig. 1)¹⁹–²² or trans-located ligands with different donor atoms (complex III, Fig. 1).²⁸ To our knowledge, the non-centrosymmetric systems are known only for heteroleptic compounds or for some examples of non-centrosymmetric ligands (complex IV, Fig. 1).³⁵ Remarkably, diiron complexes can exhibit different, often very high, spin states up to S = 9/2.³⁸,³⁹ While the majority of high-performance single molecular magnets (SMMs) achieve their high ground state by superexchange coupling mechanism at low temperatures,⁴⁰–⁵³ the Fe–Fe bonded complexes may be an alternative pathway to the design of SMMs combining high spin ground state even at room temperature due to the direct overlap
of the metal valence orbitals with significant magnetic anisotropy. Indeed, Betley and co-workers investigated mixed-valent tri- \((S = 11/2)\) and hexanuclear \((S = 9/2 \text{ to } S = 11)\) multiiron clusters, which show slow magnetic relaxation and maintain a thermally persistent high-spin ground state owing to both direct and double exchange mechanisms between the iron centres.\(^{54-57}\)

Fig. 1. Selected examples of structurally characterised diiron(II,II) complexes with distances between Fe centres (Å, in red) along with their oxidation states of diiron cores and ground spin states.

Herein, we examined the nature of the metal-metal interactions in high-spin diiron formamidinates \([\text{Fe}_2\mu-(\text{DPhF})_4]\) \((1)\) \((\text{DPhF} = N,N'-\text{diphenylformamidinate})\) and \([\text{Fe}\mu-(\text{DTolF})_3\text{Fe}(\kappa^2-\text{DTolF})]\) \((2)\) \((\text{DTolF} = N,N'-\text{di(p-tolyl)formamidinate})\), and an influence of their molecular structure on a slow magnetic relaxation. Particularly, we present how subtle changes in the character of aromatic subunit \(N,N'-\text{diarylformamidinate}\) ligand can dramatically affect the molecular and electronic structure of diiron \(\text{Fe}-\text{Fe}\) bonded complexes. Thus, a minor alteration in the ligand system, i.e. switching from phenyl to \(p\)-tolyl \(N\)-substituted formamidinate ligand, results in major structure change – the formation of an unprecedented non-centrosymmetric complex \(2\) incorporating variously coordinated \(N\)-bidentate symmetric ligands. Finally, we also provide a new view on the ground state electronic structure of diiron formamidinate complexes \([\text{Fe}_2\mu-(\text{DPhF})_4]\) and \([\text{Fe}\mu-(\text{DTolF})_3\text{Fe}(\kappa^2-\text{DTolF})]\) (Fig. 2) including the origin of \(D_{2h}\) to \(D_{2d}\) symmetry lowering, based on both combined high-level \(ab\text{-initio}\) calculations, and supported by magnetic measurements, Mössbauer spectroscopy, and cyclic voltammetry.

Fig. 2. Simplified molecular orbital diagrams for diiron(II,II) formamidinates. (a) The electronic structure of \(1\) considered so far and (b) that assigned this work, and (c) the electronic structure of \(2\).

Results and Discussion

Synthesis of diiron(II,II) formamidinates. The general synthesis method of the paddlewheel-type complexes proposed by Cotton and Murillo consisted of two steps: the reaction of \(\text{MCl}_2\) \((\text{M} = \text{Fe, Co, Ni})\) with a neutral amidine \((\text{AH})\) leading to a \([\text{M}_2\text{Cl}_2(\text{AH})_2]\) precursor and its subsequent reaction with \(n\text{-BuLi}\).\(^{20}\) To simplify the synthesis, we elaborated a new approach based on the transmetalation reaction between \(\text{FeCl}_2\) and a potassium formamidinate salt at ambient temperature, which led to the isolation of \([\text{Fe}_2\mu-(\text{DPhF})_4]\) \((1)\) and \([\text{Fe}\mu-(\text{DTolF})_3\text{Fe}(\kappa^2-\text{DTolF})]\) \((2)\) in high yields (Scheme 1). Then, we performed a comparative analysis of the molecular structure and magnetic properties of compounds \(1\) and \(2\) based on single-crystal \(X\)-ray diffraction, IR and UV-VIS spectroscopy, \(^{57}\text{Fe}\) Mössbauer spectroscopy, AC and DC magnetic measurements, and cyclic voltammetry.

Scheme 1. Synthesis of diiron(II,II) \(N,N'\)-diarylformamidinates.
Molecular and supramolecular structures. To demonstrate how subtle changes in the character of \(N,N'-\)diarylf ormamidinate ligands can dramatically affect the molecular structure and geometrical parameters of the examined diiron(II,II) complexes, we reinvestigated the molecular and supramolecular structure of 1 and structurally characterised compound 2 using single-crystal X-ray diffraction. As previously reported by Cotton and co-workers,\(^\text{20}\) the molecular structure of 1 can be described as a distorted paddlewheel-type system with a bimetallic core and four formamidinate bridging ligands (Fig. 3a.). The structure shows a distortion from the \(D_{3h}\) symmetry, frequently found in this class of complexes, towards the \(D_{3d}\) symmetry, which is preassembly triggered by the Jahn-Teller effect.\(^\text{27}\) Each of the two parallel pairs of formamidinate bridges is pulled in opposite directions along the two-fold axis bisecting the Fe-Fe vector. Additionally, the Fe-N bonds are not equal; there are two longer (2.161(2) and 2.170(2) Å) and two shorter (2.011(2) and 2.015(2) Å) Fe-N distances. The Fe-Fe distance is 2.4584(8) Å, which is relatively long compared to that in most of Fe(II)-Fe(II) bonded compounds reported so far,\(^\text{6}\) but significantly shorter by about 0.4 Å than in paddlewheel-type tetracarboxylate-bridged diiron complexes.\(^\text{58,59}\)

Compound 2 has an extraordinary asymmetric molecular structure incorporating the \([\text{Fe}_2]\text{Cl}_4\) core bridged by three \(N,N'-\)ditolylformamidinate ligands and the fourth formamidinate ligand that chelates the Fe2 centre (Fig. 3b). As a result, there are two non-equivalent iron(II) centres where one (Fe1) has an approximate trigonal pyramidal coordination sphere, and the other (Fe2) shows pseudooctahedral geometry. At first sight, the structure resembles a zwitterionic complex, but a thorough analysis of the Fe-N distances shows that the Fe-N bonds are significantly stronger at the Fe1 centre, suggesting a more balanced distribution of electronic density; to explain this phenomenon, \(^\text{60}^{\text{60}}\)Fe Mössbauer analysis and quantum chemical methods are applied in the following part of the article. Strikingly, the Fe-Fe bond distance of 2.5166(10) Å is only slightly longer than that observed in 1. As in structure 1, the Fe-N distances fall into two ranges 1.957(2)-1.985(2) Å and 2.133(2)-2.203(2) Å, but in the case of 2 all the short Fe-N bonds are around the four-coordinate centre Fe1. The chelating formamidinate ligand coordinates to the Fe2 centre, and is quasi-coplanar to one of the bridging ligands. We note that similar non-centrosymmetric bimetallic complexes have been observed so far only for compounds containing various ligands, diverse metals, or having multidentate ligands, which naturally force the formation of non-centrosymmetric systems (e.g. Fig. 1, IV).\(^\text{60-62}\)

The second-sphere non-covalent interactions often operate in concert with the primary donor-acceptor bonds, which provides opportunities for the rational manipulation of the molecular and supramolecular structure of metal complexes.\(^\text{83,64}\) It seems reasonable that the intermolecular non-covalent interactions are one of the key factors determining such differentiation of both structures. The paddlewheel-type complex 1 crystallises in the \(P2_1/c\) space group, and its supramolecular arrangement is governed via a system of cooperative intermolecular C-H-π interactions (Fig. 3c). In turn, complex 2 crystallises in the \(P\) space group with much lower symmetry, and the most important non-covalent forces are localised between parallel tolyl subunits (Fig. 3d). The introduction of methyl substituent to the \(N\)-bonded aromatic rings of stabilising ligand has a profound impact on the geometry and energy of non-covalent interactions. As is well known, in phenyl systems the T-shaped arrangement with C-H-π interactions is the most privileged, while tolyl subunits favour the antiparallel π-stacking arrangement.\(^\text{65-67}\) This difference in preferred geometry of π-aromatic intermolecular interactions is probably responsible for the various molecular structures of 1 and 2 and the unprecedented form of compound 2.
**Electrochemistry.** The redox behaviour of 1 and 2 were investigated by cyclic voltammetry (CV). To help interpret the results, we also made the characterisation of neutral formamidines (Fig. S7). As shown at Fig. 4, both complexes display one quasi-reversible oxidative event at 0.53 V (vs Fc+/Fc) for 1 and 0.44 V for 2. These may correspond to the removal of an electron from a high-lying δ* orbital and the formation of a [FeL]⁺ cation. However, the poor reversibility of the observed redox process can be explained by a breakup of the oxidised dinuclear cation and forming a Fe(III) trischelate [FeL₃]⁺. Analysing the reduction potentials, both diiron compounds show one irreversible reductive process at -2.25 V for 1 and -2.15 V for 2. These one-electron reduction acts may be connected with the dissociation of one formamidinate ligand and the formation of a trigonal paddlewheel-type complex with mixed-valent [FeL]ᵖ⁺ core. Compound 2 displays another reductive event at -2.58 V, but such an increase in current value impedes straightforward interpretation; probably the peak refers to formamidinate ligands decomposition (see Fig. S7). For 1 a similar peak was not observed.

To summarise the electrochemical measurements, both examined complexes display one reductive and one oxidative process, probably centred at the Fe-Fe core, confirming similar energy levels of involved electronic states. The small differences in the observed redox potentials trace back to the different symmetry of both compounds. The non-centrosymmetric complex has relatively long Fe-N distances at chelating ligand, so this form can be more ‘flexible’ in potential follow-up reactions of the electrochemically oxidised/reduced product.

**Fig. 4.** Cyclic voltammograms for 1 and 2 in 0.1 M [TBA(PF₆)]/THF at room temperature; scan rate 100 mV/s.

**Mössbauer spectroscopy.** To investigate the electronic structure of both complexes, zero-field ⁵⁷Fe Mössbauer spectra were collected at 78 K (Fig. 5). The Mössbauer spectrum of 1 displays a single symmetric quadrupole doublet centred at δ = 0.600 mm/s (|ΔEQ| = 0.786 mm/s), confirming the equivalence of both iron centres. Such value of the isomer shift and narrow quadrupole splitting are typical rather for low-spin Fe(II) centres, but previous reports showed a large diversity of Mössbauer spectra parameters for Fe(II) centres, strongly depending on the nature of surrounding ligands and a geometry of the coordination sphere. Furthermore, in the literature there were found relatively low isomer shifts for systems with significant metal-metal interactions; for example, phosphamide diiron(II,II) complexes with Fe-Fe distances in the range of 2.58-2.87 Å have isomer shift values about δ = 0.6 mm/s, almost identical to 1. Interestingly, another non-centrosymmetric diiron(II,II) compound (see Fig. 1, IV), stabilized by three N-C-N donor groups, shows two distinct quadrupole doublets centred at δ = 0.58 mm/s (|ΔEQ| = 0.38 mm/s) and δ = 0.48 mm/s (|ΔEQ| = 1.31 mm/s), despite the high spin state S=3, which is convergent to our results. The low quadrupole splitting in 1 can be explained in terms of crystal field calculations on high-spin ferrous ions.

The Mössbauer spectrum of 2 displays a broad unsymmetrical quadrupole doublet, best fitted as two overlapping signals of equal intensity. The two quadrupole doublets are centred at similar isomer shifts: δ = 0.709 mm/s (|ΔE_Q| = 2.658 mm/s) and δ = 0.912 mm/s (|ΔE_Q| = 2.724 mm/s), which clearly suggests the presence of two high-spin Fe(II) centres. Obviously, the iron atoms cannot be equivalent due to completely different coordination spheres, but the electronic density is distributed similarly for both of them. It corresponds with the significantly longer Fe-N bonds at the six-coordinated centre Fe2 than those at Fe1. Analysing Mössbauer spectrum for phosphinoamide diiron(II,II) complex with a similar geometry to 2, we suppose that the quadrupole doublet centred at δ =0.912 mm/s can be assigned to the four-coordinated centre Fe1, and another doublet corresponds to the Fe2 centre. The diversity of 1 and 2 spectra are caused probably by the packing in the crystal network, various symmetry of the compounds, and the different coordination environment of iron centres. Unlike for the mononuclear complexes, there are few Mössbauer spectra for multiron clusters, so spectra analysis for these systems is very challenging, especially in the presence of metal-metal bonds.
The high-spin ground state and the suspected magnetic anisotropy prompted us to investigate 1 and 2 as promising candidates for single molecule magnets similar to a recently reported metal-metal bonded triiron molecule. Therefore, we performed dynamic magnetic susceptibility measurements for both of them, but no out-of-phase signal was observed under the zero DC field, most probably due to the fast quantum tunnelling (QTM). This effect is efficiently quenched by applying a constant DC magnetic field, which led to the observation of the slow magnetic relaxation for 1 and 2, as presented in Fig. S8-11. The AC magnetic susceptibility signals were fitted using the generalised Debye model for a single relaxation process. The increasing DC field elongates the magnetic relaxation time $\tau$ for 2 until it reaches 0.15 T, when it starts to accelerate the relaxation, due to the onset of the direct relaxation process. On the other hand, magnetic field variation from 0.15 T to 1 T does not seem to visibly move $\chi''$ peaks, leading mostly to the strong broadening of the signal. Indifference of the magnetic relaxation time under a strong magnetic field $>0.45$ T in compound 1 may be a sign of a phonon bottle-neck process, which limits the influence of the direct relaxation pathway and prevents the shortening of the relaxation time at higher magnetic fields. Therefore, thermal dependence of the magnetic relaxation time for 1 and 2 was recorded under the optimal DC field of 0.15 T (Fig. S12-15) for both compounds. Compound 1 seems to obey the Arrhenius law with $T_0=2.4(2) \times 10^{-10}$ s and $U_{\text{eff}}=53.5(2)$ K down to 2.6 K, when the QTM process starts to govern the relaxation of the magnetisation (Fig. 7). As a result, complex 1 shows a butterfly-shaped magnetic hysteresis loop at 1.8 K (Fig. 8), which remains open only in the 1-6 T field range, when QTM remains suppressed by the strong magnetic field. A hysteresis loop of this type is in line with the suspected phonon bottle-neck effect in compound 1. On the other hand, magnetic relaxation of complex 2 under applied 0.15 T DC field follows the Arrhenius law in the investigated temperature range and can be described purely by the Orbach relaxation mechanism, with $T_0=7.5(6) \times 10^{-9}$ s and $U_{\text{eff}}=27.9(2)$ K. However, the relatively small value of the magnetisation reversal barrier and the resulting relatively fast

Magnetic measurements. The spin state of both diiron compounds was further probed by magnetic measurements. The $\chi T$ values of 10.1 cm$^3$ K mol$^{-1}$ for 1 and 10.7 cm$^3$ K mol$^{-1}$ for 2 at 250 K strongly exceed 6.0 cm$^3$ K mol$^{-1}$ calculated for two isolated (non-interacting) $g = 2.0$ iron(II) centres (Fig. 6). The experimental results exceed slightly the $\chi T$ value of 10.0 cm$^3$ K mol$^{-1}$ calculated for $g = 2.0$ and $S = 4$, suggesting very strong ferromagnetic interactions between the Fe(II) centres and $S = 4$ ground spin state for both molecules in the whole 1.8-250 K temperature range. Both compounds show a distinct decrease of the $\chi T(T)$ dependence at low temperatures approaching 2 K, which is assumed to result from a significant magnetic anisotropy. Moreover, the $\chi T(T)$ for 1 exhibits a flat maximum at 42 K, which probably results from the partial alignment of the sample along an easy magnetisation axis despite freezing the sample in the paraffin oil before applying the magnetic field.
relaxation preclude the appearance of the magnetic hysteresis loop down to 1.8 K (Fig. 8).

![Figure 7](image)

Figure 7. Arrhenius plot of the relaxation time $\tau$ (logarithmic) versus $1/ T$ for 1 (full circles) and 2 (open circles) under $H_{dc} = 0.15$ T. Red lines are the best fits to the equations presented in the figure.

![Figure 8](image)

Fig. 8 M(H) plot for 1 (full circles) and 2 (open circles) at $T = 1.8$ K.

Comparison of the effective magnetisation reversal barrier $U_{eff} = 53.5$ K for 1 (approximate axial $D_{4d}$ symmetry) with $U_{eff} = 27.9$ K for 2 (no symmetry) clearly demonstrates that highly axial diiron complexes have the potential to be very good SMMs. Further ligand modification towards perfectly axial geometry with $D_{4d}$ symmetry (or higher) may further enhance the slow relaxation of the magnetisation, leading to the opening of the magnetic hysteresis loop even at zero magnetic field for this class of compounds. Another strategy could involve the preparation of higher-nuclearity clusters with metal-metal bonds as demonstrated by Betley et al., or the oxidation of the diiron(II,II) compounds to a non-integer spin systems diiron(II,III). Theoretical investigations. While the majority of [M$_2$L$_4$] paddlewheel-type complexes exhibit a $D_{4h}$ symmetry, the tetragonal diiron(II,II) complex 1 has a lower $D_{2h}$ symmetry and a putative high-spin electronic configuration $\left(3\sigma^2(\pi^*)^4(\delta^*)^1(\delta)^1(\delta^*)^1\right)$ (Fig. 2a), supported by previous density functional theory (DFT) calculations. However, so far neither comprehensive experimental characterisation nor high-level $ab$-initio calculations have been taken to examine the electronic structure of this complex. Our preliminary geometry optimisations of the molecules 1 and 2 in the gas phase revealed a large dependency of Fe-Fe distance on the employed approximate density functional. This typically is a sign of electronic structure change upon functional alternation. To avoid such uncontrolled behaviour, we first turned our attention to model systems $1^H$ and $2^H$ (Fig. 9), for which application of high-level wavefunction-based methods of controlled accuracy is possible. As pointed out by Timmer et al., the distortion from ideal $D_{4h}$ to observed $D_{2h}$ point group in $1^H$ may originate in the Jahn-Teller effect. According to their DFT calculations, the distortion lifts the degeneracy of $n_{z^2}$ and $n_{x^2-y^2}$ molecular orbitals and yields altered geometry with decreased energy and non-degenerate electronic configuration described as $\left(\sigma^2(\pi^*)^4(\delta^*)^1(\delta)^1(\delta^*)^1\right)$ (Fig. 2a). Our DFT calculations (vide infra 1-coupling calculations) show that in $D_{2h}$-$1^H$ this configuration is preferred indeed when GGA functionals are used (e.g. BP86). However, once the Hartree-Fock exchange is turned on, the most stable configuration becomes $\left(\sigma^2(\pi^*)^4(\delta^*)^1(\delta)^1(\delta^*)^1(\delta^*)^1\right)$. To decide which configuration is correct as well as to track the origin of electronic configuration changes in a sequence $D_{4h}$-$1^H \rightarrow D_{2h}$-$1^H \rightarrow C_2$-$2^H$, we decided to carry out state-of-the-art multireference calculations. Herein, we employed the multireference average quadratic coupled-cluster (MRAQCC) method based on the complete active-space self-consistent field (CASSCF) reference that captures orbital degeneracies well and at the same time provides a balanced description of all relevant spin-states. Schematic representation of high-spin natural orbitals’ ordering and occupation obtained in these calculations is provided in Fig. 10. The ground state of $D_{4h}$-$1^H$ is a doubly-degenerate $^4E_g$ state (it has two components $B_{2g}$ and $B_{3g}$ in $D_{2h}$ point group used in calculations). The non-degenerate $\tilde{A}_g$ state is $984$ cm$^{-1}$ above $^4E_g$. We note the correct electronic structure of $^4E_g$ state cannot be captured by single-reference methods such as common approximated DFT approaches. The molecular distortion $D_{4h}$-$1^H \rightarrow D_{2h}$-$1^H$ increases the energy of $n_{z^2}$
and π_e orbitals, making them singly occupied. Alongside, the energy of σ* gets down and σ* becomes doubly occupied. Altogether, this brings the non-degenerate 3A_e state lower in energy than 5E state. Upon D_{2h}→1^h structure π_e and π_e* orbitals experience less repulsion, so their energies go down. At the same time, the presence of an axial nitrogen atom increases the energy of σ*. Thus, we can now assign unambiguously the ground state electronic configurations of 1^h and 2^h as (σ)^4(σ*)^2(δ_i)^2(δ_j)^2(e^2)(e^*^2)(δ_e)^2 and (σ)^4(π_e)^2(π_e*)^2(σ*)^2(π_e)^2(δ_i)^2(δ_j)^2(δ_e)^2(δ_e*)^2, respectively. Remarkably, the Mayer bond orders for Fe-Fe interactions are significantly lower than 1 and equal to 0.15 and 0.28 for 1^h and 2^h, respectively.

Having the electronic structure of 1^h and 2^h at hand, we can obtain some insights into the electronic coupling between the two iron centres. We used isotropic Heisenberg-Dirac-van Vleck Hamiltonian:

\[ H_{BDVV} = -2JS_A S_B \]

where \( J \) is the exchange coupling constant, positive for ferromagnetic interactions and negative for antiferromagnetic coupling. \( S_A \) and \( S_B \) denote the local spins of the coupled centres A and B. The extraction of \( J \) values from multireference calculations is rather straightforward as the energy difference between states of multiplicity 9 and 1 should equal 20J. In the DFT calculations, the low spin states are approximated with the broken symmetry approach\(^{76,77}\) and to obtain \( J \) one needs to account for this approximation. Here, we used Yamaguchi formula\(^78\)

\[ J = \frac{E_{HS} - E_{BS}}{<S^2>_{HS} - <S^2>_{LS}} \]

that employs energies of high-spin (\( E_{HS} \)) and broken-symmetry (\( E_{BS} \)) solutions along with their spin expectation values (\( <S^2> \)).

The results of \( J \)-coupling calculations with various methods are presented in Table 1. We stress that MRAQCC calculations should be considered as a reference. For structure 2^h, all methods provide the positive value of \( J \)-coupling, although the magnitude varies considerably. The reference value is 139.8 cm\(^{-1}\), and the hybrid density functionals (TPSSH\(^{79,80}\) and PBE0\(^{81}\)) provide similar results. CASSCF and fully-internally contracted n-electron valence state perturbation theory (FIC-NEVPT2)\(^{82}\) result in somehow smaller, but still positive, coupling. The picture is different for 1^h, where the MRAQCC calculations provide a small positive \( J \) value of 15.1 cm\(^{-1}\). CASSCF and FIC-NEVPT2 feature small negative couplings (-4.7 and -14.2 cm\(^{-1}\), respectively). The first look at the DFT results provides intriguing observation – the BP86 and TPSS are the only functionals that provide positive \( J \)-couplings, although way too large compared to the reference calculations. Hybrid functionals display small negative \( J \)-couplings. However, the BP86 and TPSS\(^{79}\) feature incorrect electronic configuration \( (\sigma)^2(\pi_e)^2(\delta_{ij})^2(\delta_e)^2(e^2)(e^*^2)(\delta_{de})^2(\delta_{de*})^2 \) (1), respectively. At the same time, TPSSh and PBE0 operate on the same configuration as the reference calculations \( (\sigma)^2(\sigma*)^2(\delta_{ij})^2(\delta_{e})^2(e^2)(e^*^2)(\delta_{de})^2(\delta_{de*})^2 \).

**Table 1.** \( J \)-coupling values in cm\(^{-1}\) for model compounds 1^h and 2^h obtained with different wavefunction- (1-3) and DFT-based (4-7) methods.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Method</th>
<th>1(^h)</th>
<th>2(^h)</th>
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<tbody>
<tr>
<td>1</td>
<td>CASSCF*</td>
<td>-4.7</td>
<td>+34.8</td>
</tr>
<tr>
<td>2</td>
<td>FIC-NEVPT2*</td>
<td>-14.2</td>
<td>+64.9</td>
</tr>
<tr>
<td>3</td>
<td>MRAQCC*</td>
<td>+15.1</td>
<td>+139.8</td>
</tr>
<tr>
<td>4</td>
<td>BP86</td>
<td>+163.0</td>
<td>+288.3</td>
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<td>5</td>
<td>TPSS</td>
<td>+90.2</td>
<td>+223.5</td>
</tr>
<tr>
<td>6</td>
<td>TPSSh</td>
<td>-48.2</td>
<td>+152.8</td>
</tr>
<tr>
<td>7</td>
<td>PBE0</td>
<td>-33.8</td>
<td>+109.8</td>
</tr>
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*active space of 12 electrons distributed over 10 orbitals
Our calculations show that none of the tested functional can simultaneously account for proper electronic structure and provide accurate J-coupling values. It is a consequence of correlation effects that are not captured in a balanced way at the DFT level. Thus, any further calculations performed with DFT on experimental molecules 1 and 2 should not be interpreted with great care. First of all, we are stuck to structures derived from crystallographic measurements (with only positions of H atoms optimised). Secondly, we prefer a functional that provides an electronic configuration similar to the reference calculations. Thus, we decided to use PBE0 for calculations on 1 and 2. Moreover, as the high-spin wavefunctions of 1th and 2th were rather a single-reference character, we employed a coupled electron pair approximation method (CEPA/1)\(^8\) to compute better estimates of the energy difference between centrosymmetric and non-centrosymmetric model structures. In these computations, we explored the virtual orbital space compression with localised pair natural orbitals (LPNO)\(^8\).

The model structures feature the same simplified ligand to compare their energies (in a high-spin state) directly. Reference LPNO-CEPA/1 and DFT/PBE0 methods point to the symmetric structure 1\(^\text{th}\) as the most stable (relative energy \(\Delta E_{12}\) of the 2\(^\text{nd}\) was 7.2 kcal/mol and 8.2 kcal/mol with the two methods, respectively). We have also carried out a kind of ‘Gedankenexperiment’ on experimental structures: eight hydrogen atoms attached in para-position of phenyl rings in 1 were replaced with methyl groups, and accordingly eight methyl groups were replaced with hydrogen atoms in 2. After re-optimising the changed atoms, we could calculate \(\Delta E_{12}\) for the ligands used experimentally. Due to the size of the system, these calculations could only be performed at the DFT level. The \(\Delta E_{12}\) values for non-centrosymmetric systems were found to be 3.5 kcal/mol and -1.6 kcal/mol for 1 and 2, respectively. Thus, the non-centrosymmetric structure is preferred when methyl groups are present in the para-position of phenyl rings in the examined ligands, in accordance with the experiment. We also note the reduction of the magnitude of \(\Delta E_{12}\) when going from simplified ligands in 1\(^\text{th}\)/2\(^\text{nd}\) to bulk ligands in 1/2. It suggests that crystal packing effects will influence the final geometry of the complex.

The computations of absolute reduction/oxidation potentials could be used to distinguish between various possible electronic configurations, but these are rather challenging to calculate. However, one can easily compute the oxidation potential difference (exp. 0.09 V) and reduction potential difference (exp. -0.1 V) between 1 and 2. DFT/PBE0 method provides oxidation potential difference of 0.13 V and reduction potential difference of -0.05 V with an electronic configuration of 1 set to \((\sigma^2)(\sigma^2)^2(\delta^2)(\delta^2)^2(\delta^2)^2(\delta^2)^2 \cdots \). When the latter is artificially set to \((\sigma^2)(\delta)(\delta^2)^2(\delta)^2(\delta)^2 \cdots \) as proposed by Timmer et al.,\(^{22}\) these numbers become -0.28 and 0.73 V, respectively. Thus, not only magnitude but also the sign changes. In our view, this is strong evidence in favour of the newly proposed electronic configuration. Another evidence could be provided by computing zero-field splitting parameters and directly comparing them with experimental values, but in our opinion this would require the application of highly-correlated methods such as MRAQCC to large structures 1 and 2, preferably with crystallographic surrounding, which is currently impossible.

Conclusion

In summary, we revealed new factors determining the molecular and electronic structures of Fe-Fe bonded diiron(II,II) complexes, leading to the isolation of the unusual non-centrosymmetric metal-metal bonded complex \([\text{Fe}(\mu-\text{DTOF})_2\text{Fe}(\kappa^2-\text{DTOF})]\) (2). Comprehensive experimental characterisation of 2 and the paddlewheel-type complex \([\text{Fe}(\mu-\text{DPhF})_2]\) (1) along with the high-level calculations provided new insight into the electronic structure of this class of metal-metal bonded complexes. Examination of magnetic properties revealed strong ferromagnetic interactions between the Fe(II) centres and \(S = 4\) ground spin state for both complexes in the 1.8-250 K temperature range. Moreover, compounds 1 and 2 exhibit field-induced slow magnetic relaxation with the effective magnetisation reversal barrier \(U_{\text{eff}} = 53.5\ \text{K}\) and \(U_{\text{eff}} = 28.9\ \text{K}\), respectively. These results demonstrate that magnetic anisotropy of the Fe-Fe bonded compounds is enhanced within the highly symmetrical coordination environment and support a view that highly axial diiron complexes are great candidates for SMMs. Furthermore, calculations of ground state electronic structures of model diiron(II,II) formamidinate compounds with \(D_{\text{ib}}\), \(D_{2h}\), \(C_5\) symmetry revealed the differentiation in a sequence of the close-lying orbitals with eight unpaired electrons, and in each case the Fe-Fe bond order was significantly lower than one. Remarkably, the comparison of calculated energies for paddlewheel-type and non-centrosymmetric systems with \(N,N'\text{-di}(\text{phenyl})\text{formamidinate}\) and \(N,N'\text{-di}(p\text{-tolyl})\text{formamidinate}\) ligands indicated that the energy difference between the two geometrical isomers is rather low (up to 3.5 kcal/mol). Clearly, the factors that govern the structure and physicochemical properties of diiron(II,II) formamidinate complexes have yet to be delineated fully. The reported study sets the stage for further advances in the fundamental chemistry of metal-metal bonded complexes and their applications in catalysis and molecular magnetic materials.

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Conflict of interests

There are no conflicts to declare.

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