# Bis-bidentate *vs.* bis-tridentate imino-heterocycle ligands in the formation of dinuclear helical complexes of Fe(II) †

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By reaction of the bis-bidentate imino-quinoline ligand **1** with the octahedral cation $Fe^{2+}$ in a 3 : 2 metal/ligand molar ratio, a partial hydrolysis of the ligands is observed instead of the formation of the expected triple helicate, due to the excessive crowding of the *trans*-1,2-cyclohexyl spacers. The monomeric $[Fe^{II}(2)_2]^{2+}$ complex is obtained, whose crystal and molecular structure have been determined, in which the amino-imino-quinoline tridentate ligands **2**, originating from **1** by loss of one quinoline aldehyde, coordinate $Fe^{2+}$ with a *mer* disposition. Double helical complexes can instead be obtained by using the bis-tridentate ligand **3**, featuring the same spacer of ligand **1**, *i.e. trans*-1,2-cyclohexyl, and two imino-phenanthroline donor sets. The spectral and electrochemical properties of the low-spin double helical $[Fe^{II}_2(3)_2]^{4+}$ complex have been studied and compared with those of the low spin $[Fe^{II}(4)]^{2+}$ complex, which can be considered the monomeric half of the helicate. Significantly enhanced kinetic inertness and resistance to oxidation were found for the double helical complex.

## Introduction

Syntheses of helical complexes can be programmed relaying on the matching between the denticity of the binding units of the ligands and the coordination preferences of the chosen metal cation. As a rule of thumb, poly-bidentate ligands will form double helical complexes with metal cations preferring four-coordination and tetrahedral geometry (*e.g.* $Cu^+$ and $Ag^+$), while if a metal cation preferring six-coordination and octahedral geometry (*e.g.* $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$) is used with the same kind of ligands, a triple helical complex should be obtained. On the other hand, double helical complexes may be obtained from octahedral cations by the use of poly-tridentate ligands. However, application of this rule does not lead always to the desired results: as an example, oligobipyridine ligand strands with the 2,2′-bipyridines connected at the 6 position by $-CH_2-O-CH_2-$ spacers have been advantageously used to form double-stranded polinuclear helicates with $Ag^+$ and $Cu^+$,[1] but the same ligands failed to form triple-stranded polinuclear helicates *e.g.* with $Fe^{2+}$, as a result of steric crowding among the $-CH_2-$ groups around the metal cation.[2] Connection of the 2,2′-bi-pyridine units in the 4-[3] or 5-[4] position, with a variety of spacers, solves the problem, giving rise to a series of bi- and tri-nuclear triple stranded helicates with metal cations like $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$. Beside, a number of double-stranded helical complexes have been reported between octahedral metal cations and politridentate ligands, with the latter featuring even very short and rigid spacers between the tridentate units. As an example, in the case of sexipyridines a strand of six pyridine rings (connected in the 2 and 6 positions) can be ideally sub-divided into two terpyridine halves, separated by a mere C–C

bond, and these ligands form double helical complex with $Cd^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$.[5] We have recently published a series of papers[6] in which the bis-bidentate *R,R-trans*-1,2-cyclohexane-diminoquinoline ligand **1** and a variety of related ligands (with N-donor heterocycles different from quinoline) have been demonstrated to form double-stranded helical complexes with the tetrahedral cation $Cu^+$.[7] In this work, we have tried to use ligand **1** to form triple-stranded helicates with the octahedral cation $Fe^{2+}$ but we have found that the ligand is too rigid (and it has a too bulky spacer) to arrange around $Fe^{2+}$ to form $[Fe^{II}_2(1)_3]^{2+}$. The ligand undergoes a hydrolytical process to lose one quinoline aldehyde and forming an octahedral complex with ligand **2**, $[Fe^{II}(2)_2]^{2+}$, whose crystal and molecular structure have been determined. To obtain dinuclear helical $[Fe^{II}_2-(ligand)_2]^{4+}$ we had to switch to the bis-*tri*dentate ligand **3**, which mantains the same *R,R-trans*-1,2-cyclohexane spacer but where quinoline has been replaced by phenanthroline connected in the 2-position. The spectral, electrochemical and chemical properties of the $[Fe^{II}_2(3)_2]^{4+}$ helicate have been studied in detail. The mononuclear complex with tridentate ligand **4**, $[Fe^{II}(4)_2]^{2+}$ has also been prepared and studied, for sake of comparison.

## Experimental

### Syntheses

(*R,R*)-*trans*-1,2-cyclohexanediamine and cyclohexylamine were purchased from Aldrich and used without further purification. (*R,R*)-*trans*-1,2-cyclohexanediiminoquinoline (**1**),[6] Fe(CF₃-SO₃)₂·2MeCN[8] and phenanthroline-2-carboxyaldehyde[9] were prepared according to literature methods.

**(*R,R*)-*trans*-1,2-cyclohexanediiminophenanthroline (3).** 200 mg phenanthroline-2-carboxyaldehyde (0.961 mmol) and 55 mg (*R,R*) 1,2-*trans*-cyclohexanediamine (0.481 mmol) were dis-solved in 20 ml $CH_2Cl_2$ to which dry $Na_2SO_4$ (100 mg) was

† Electronic supplementary information (ESI) available: atomic positions, bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, data collection, and crystal parameters for all crystallographically characterized complexes; NMR spectra, including COSY, and CD spectra for ligand **3** and $[Fe^{II}_2(3)_2]^{4+}$. See http://www.rsc.org/suppdata/dt/b2/b210137h/

1

2

3

4
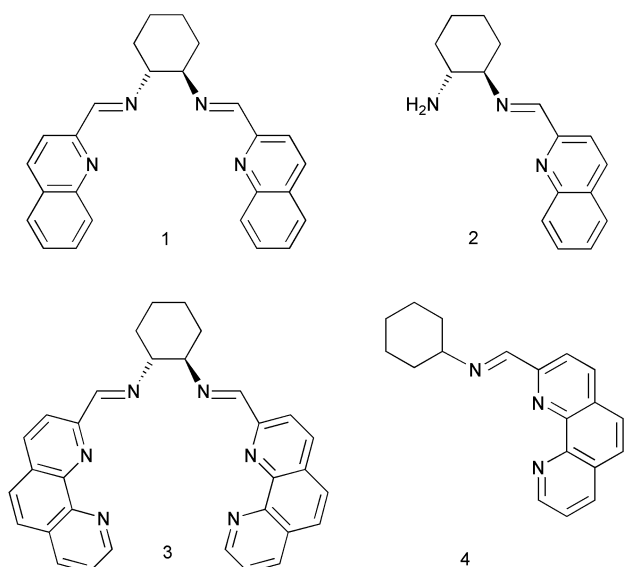
added as a dessicant. The mixture was stirred under nitrogen for 24 h, then filtered and the solvent removed on rotary evaporator. The oily residue was treated with 10 ml diethyl ether to obtain the pure product as a yellowish powder, in 63% yield. IR (NaCl, nujol mull): 1639 cm$^{-1}$ imino C=N stretch. Mass spectrum (ESI technique): $m/z$ = 495, $[3 + H]^+$. Elemental analysis found: C 77.65, H 5.27, N 16.92%. Calculated for $C_{32}H_{26}N_6$: C 77.72, H 5.30, N 16.98%. NMR (CD$_3$CN): $\delta$ 9.05 (dd, 2H) + 8.27 (dd, 2H) + 8.25 (dd, 4H) + 7.75 (dd, 4H) + 7.65 (dd, 2H), H of the phenanthroline rings, 8.56 (s, 2H, imine hydrogens), 3.75 (m, 2H, CH of the cyclohexane ring), 2.0–1.7 (m, 8H, CH$_2$ of the cyclohexane ring).

**Cyclohexyliminophenanthroline (4).** 100 mg (0.480 mmol) phenathroline 2-carboxyaldehyde and 55 µl cyclohexylamine (47.7 mg, 0.480 mmol) were dissolved in 10 ml CH$_2$Cl$_2$, to which dry Na$_2$SO$_4$ (50 mg) was added as a dessicant. The mixture stirred overnight under nitrogen atmosphere, then filtered and the solvent removed on a rotary evaporator. The obtained oily substance was kept at 80 °C under high vacuum (0.01 torr) for further 2 h to remove all residual CH$_2$Cl$_2$. IR (NaCl, oil): 1642 cm$^{-1}$ imino C=N stretch. Mass spectrum (ESI technique): $m/z$ = 290, $[4 + H]^+$. NMR (CD$_3$CN): $\delta$ 9.07 (dd, 1H) +8.25 (3H, m) +7.75 (dd, 2H) +7.66 (dd, 1H), H of the phenanthroline ring; 8.65 (s, 1H, CH=N), 3.75 (m, 1H, CH of the cyclohexyl ring), 2.0–1.0 (m, 10H, CH$_2$ of the cyclohexyl ring).

**[Fe$^{II}$((R,R)-trans-1-amino-2-iminoquinoline cyclohexane)$_2$]-(CF$_3$SO$_3$)$_2$.** [Fe$^{II}$(2)$_2$](CF$_3$SO$_3$)$_2$. 50 mg (0.127 mmol) of ligand **1** were dissolved in 10 ml CH$_3$CN and treated with 37 mg (0.085 mmol) of freshly prepared Fe(CF$_3$SO$_3$)$_2$·2MeCN. To the obtained solution 150 µl of water were added and the resulting blue solution was stirred for 2 h, then it was allowed to slowly evaporate. When the solvent volume was reduced to 2 ml, bulky precipitation of the blue crystalline product was obtained, which was filtered, washed with few drops of a 1/1 mixture of CH$_3$CN/Et$_2$O and then dried under vacuum. Yield 55%. Elemental analysis found C 47.38, H 4.44, N 9.72%; calculated for $C_{34}H_{38}F_6FeN_6S_2O_6$: C 47.45, H 4.41, N 9.76%. Mass spectrum (ESI technique): $m/z$ = 711 $\{[Fe(2)_2] + (CF_3SO_3)\}^+$.

**[Fe$^{II}$$_2$((R,R)-trans-1,2-cyclohexanediiminophenanthroline)$_2$]-(CF$_3$SO$_3$)$_4$.** [Fe$^{II}$$_2$(3)$_2$](CF$_3$SO$_3$)$_4$. 10 mg of ligand were dissolved in 1 ml of dry acetonitrile in a 5 ml vial and treated with the stoichiometric quantity (1 : 1 molar ratio in the case of ligand **3**) of freshly prepared Fe(CF$_3$SO$_3$)$_2$·2MeCN, dissolved in 0.5 ml of acetonitrile. The obtained solution was sonicated for a few minutes and then smoothly heated for 20 min in a water bath (40–50 °C). The 5 ml vial was then sealed in a larger vial,

containing 5 ml of diethyl ether, which was allowed to slowly diffuse, through the vapour phase, in the acetonitrile solution, this yielding after 2–3 days an apparently crystalline deep green solid. After filtration and drying under vacuum, the pure product was obtained in a 65% yield. Elemental analysis found: C 48.08, H 3.12, N 9.86%. Calculated for $C_{68}H_{52}F_{12}Fe_2N_{12}O_{12}S_4$: C 48.13, H 3.09, N 9.90%. Mass spectra (ESI): $m/z$ = 1547, corresponding to $\{[Fe_2(3)_2](CF_3SO_3)_3\}^+$.

**[Fe$^{II}$(cyclohexyliminophenanthroline)$_2$](CF$_3$SO$_3$)$_2$.** [Fe$^{II}$(4)$_2$]-(CF$_3$SO$_3$)$_2$. Synthesis was carried out as for [Fe$^{II}$$_2$(3)$_2$](CF$_3$SO$_3$)$_4$, using a 1 : 2 metal/ligand molar ratio. Deep green microcrystalline solid, 62% yield. Elemental analysis found C 51.58, H 4.10, N 8.98%. Calculated for $C_{40}H_{38}F_6FeN_6O_6S_2$: C 51.53%, H 4.08, N 9.01%. Mass spectra (ESI) on solid samples redissolved in acetonitrile: $m/z$ = 783, corresponding to $\{[Fe(4)_2](CF_3SO_3)\}^+$.

### Spectrophotometric titrations

Titrations were carried out on acetonitrile solutions 0.1 mM in ligand **3** or **4**, by addition of substoichiometric quantities of standard acetonitrile solution of Fe(CF$_3$SO$_3$)$_2$·2MeCN. In a typical experiment, a 40 ml sample of ligand solution was titrated with an iron triflate solution in acetonitrile of such a concentration that a 1 : 1 ligand/Fe molar ratio was reached after the addition of 200 µl. Each addition was of 10–20 µl, and a complete absorption spectrum was recorded each time.

### Electrochemistry

Cyclic voltammetry studies were carried out in anhydrous CH$_3$CN solution, 0.1 mol L$^{-1}$ (t-but)$_4$NClO$_4$). The working electrode was a platinum microsphere and the counter electrode a platinum wire. The potential values were determined by using a platinum wire as the reference electrode and by adding ferrocene to the working solution as an internal standard. (The potential values referred to the Fc$^+$/Fc couple can be transformed into values referred to SCE, or *vice versa*, considering an $E_{1/2}$ value of 425 mV *vs.* SCE, in CH$_3$CN, determined for the Fc$^+$/Fc couple.[10])

### Computational chemistry

Molecular dynamics calculations were run with the Hyper-Chem 3 for Windows package (Hypercube Inc. & Autodesk Inc.) to find the most stable structures for the molecular complexes formed between Fe$^{2+}$ ions and ligands **3** and **4** in 2 : 2 and 1 : 1 stoichiometry, respectively. The geometry optimization was performed using the MM+ force field, which is an extension of MM2, contained in the HyperChem Help Database. Additional calculations were run, including acetonitrile molecules, to evaluate solvent effects on the stability of the complexes.

### X-Ray data collection and processing

The crystal structure of complex [Fe$^{II}$(2)$_2$](CF$_3$SO$_3$)$_2$ was determined by X-ray diffraction methods. Crystallographic and experimental details for the structure are summarized in Table 1. Intensity data and cell parameters were recorded at room temperature (25 °C) on a Bruker AXS Smart 1000 single-crystal diffractometer (MoKα radiation) equipped with a CCD area detector; the raw frame data were processed using SAINT and SADABS to yield the reflection data file.[11] The structure was solved by direct methods using the SIR92 program[12] and refined on $F_o^2$ by full-matrix least-squares procedures, using the SHELXL-97 program.[13] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced into the geometricaly calculated positions and refined riding on the corresponding parent atoms, except for those on N3 and N6 which were located in the difference Fourier $\Delta F$ map. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.0416P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Molecular

**Table 1** Crystallographic data for compound $[Fe^{II}(\mathbf{2})_2](CF_3SO_3)_2$

| | |
|---|---|
| Formula | $C_{34}H_{38}FeF_6N_6O_6S_2$ |
| Fw | 860.67 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$/Å | 10.825(5) |
| $b$/Å | 18.356(5) |
| $c$/Å | 19.223(5) |
| $V$/Å$^3$ | 3820(2) |
| $Z$ | 4 |
| $\mu$/mm$^{-1}$ | 0.5854 |
| $F(000)$ | 1766 |
| Reflns collected | 31878 |
| Independent reflns | 5491 ($R_{int} = 0.060$) |
| Obs. reflns [$I > 2\sigma(I)$] | 4182 |
| Data/restr./param. | 5491/0/651 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0322, wR_2 = 0.0624$ |
| $R$ indices (all data) | $R_1 = 0.0505, wR_2 = 0.0677$ |

geometry calculations were carried out using the PARST97 program.[14] Drawings were made utilizing the ORTEP program[15] in the WinGX suite. All calculations were carried out on a DIGITAL Alpha Station 255 computer.

CCDC reference number 195651.

See http://www.rsc.org/suppdata/dt/b2/b210137h/ for crystallographic data in CIF or other electronic format.
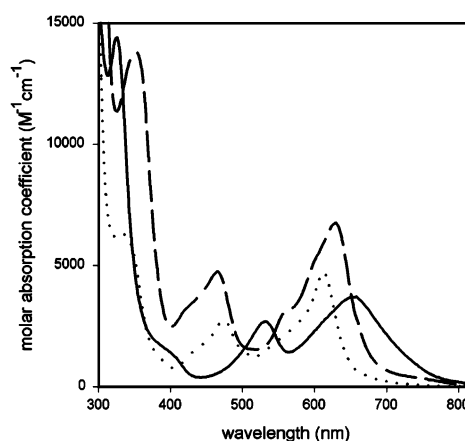
### Physical measurements

UV/Vis spectra were taken on Hewlett Packard HP8453 diode array spectrophotometer. IR spectra were carried out on a Mattson 5000-FT-IR instrument. $^1$H NMR spectra were carried out on a Bruker AMX 400 spectrometer. Mass spectra (ESI) were recorded on a Finnigan MAT TSQ 700 instrument. Circular dichroism spectra were taken on a Jasco J-710 instrument.
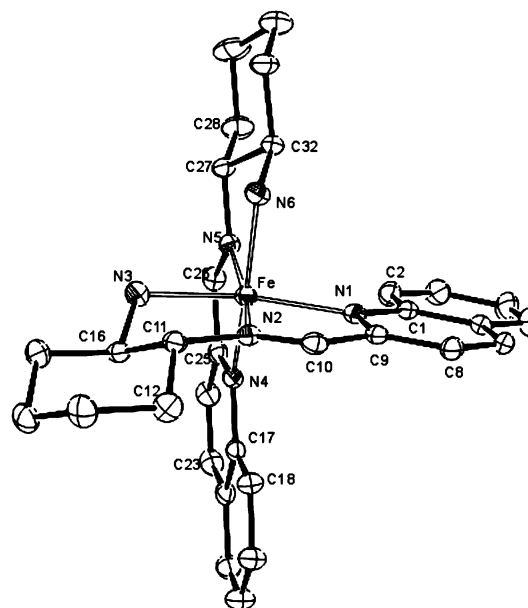
## Results and discussion

### (1) Attempts to prepare triple stranded $[Fe^{II}_2(\mathbf{1})_3]^{4+}$ helical complex

The bis-bidentate bis-iminoquinoline ligand **1** is capable of forming double stranded helical complexes with cations preferring tetrahedral coordination, like $Ag^+$ and $Cu^+$. We tried to use the same ligand to form the triple-stranded helical complex $[Fe^{II}_2(\mathbf{1})_3]^{4+}$ by using $Fe^{2+}$, which prefers octahedral coordination, and by adopting the proper ligand/metal 3 : 2 stoichiometry. Reaction of **1** with 2 : 3 $Fe(CF_3SO_3)_2$ was carried out in commercial acetonitrile (declared water content ≤0.3%), at room temperature. The solutions took for a very short time (1–2 s) the purple–red colour typical of an octahedral, low-spin $Fe^{II}$ cation coordinated by three bidentate ligands featuring a delocalized system which contains two sp$^2$ nitrogen donors. UV/Vis spectra recorded immediately after mixing the reagents displayed a spectrum with $\lambda_{max} = 466$ and 532 nm ($\varepsilon = 1100$, 1190 M$^{-1}$ cm$^{-1}$, respectively), which is reminiscent of the CT band with $\lambda_{max}$ at 520–530 nm (plus a shoulder at 480–490 nm) found for $Fe^{II}$ complexes with monosubstituted bipyridines.[16] However, the colour of the solutions changed in a few seconds into deep blue, due to the disappearance of the bands at 466 nm, to the raise in intensity of the 532 nm band and to the formation of a new intense band with $\lambda_{max} = 654$ nm. Changes lasted ~12 h, after which time superimposable spectra were recorded (see Fig. 1, solid line, for final spectrum).

The transformation corresponds to the hydrolysis of one of the imino groups on two of the coordinated ligands **1**, which lose one quinoline aldehyde to form the mononuclear, octahedral complex $[Fe^{II}(\mathbf{2})_2]^{2+}$ with the amino-imino ligand **2**.[17] The hydrolysis was also carried out with the addition of 50–1000 fold excess water with respect to the $[Fe^{II}_2(\mathbf{1})_3]^{4+}$



**Fig. 1** Absorption spectra for $[Fe^{II}(\mathbf{2})_2]^{2+}$, solid line; $[Fe^{II}_2(\mathbf{3})_2]^{4+}$, dashed line; $[Fe^{II}(\mathbf{4})_2]^{2+}$, dotted line.

concentration, and under these conditions the formation of $[Fe^{II}(\mathbf{2})_2]^{2+}$ followed a pseudo-first order kinetic, with $k_{obs} = k'[H_2O]$ and $k' = 5.64 \times 10^{-2}$ s$^{-1}$ M$^{-1}$ (e.g. $k_{obs} = 6.26 \times 10^{-4}$ s$^{-1}$, $\tau = 26.62$ min, for a solution $6.78 \times 10^{-5}$ M in $[Fe^{II}_2(\mathbf{1})_3]^{4+}$ and $1.11 \times 10^{-2}$ M in $H_2O$). The complex has been isolated in crystalline form and in good yield (40–50% with respect to the starting $Fe^{2+}$) by slow evaporation of the solvent from a 3 : 2 ligand/metal bulk solution, treated with a 100-fold excess of water, and its crystal and molecular structure has been determined, as reported in Fig. 2.



**Fig. 2** ORTEP view of the $[Fe^{II}(\mathbf{2})_2]^{2+}$ molecular cation. Hydrogen atoms and anions have been omitted for clarity. Significant bond lengths and angles: Fe–N1 2.036(3), Fe–N2 1.891(3), Fe–N3 2.010(3), Fe–N4 2.029(3), Fe–N5 1.898(3), Fe–N6 2.015(3), N1–C1 1.382(5), N1–C9 1.353(5), N2–C10 1.282(5), N2–C11 1.474(5), N3–C16 1.482(5), N4–C17 1.381(5), N4–C25 1.353(5), N5–C26 1.281(5), N5–C27 1.474(5), N6–C32 1.482(5). N1–Fe–N2 80.52(12), N1–Fe–N3 163.03(13), N1–Fe–N4 92.95(11), N1–Fe–N5 108.23(12), N1–Fe–N6 89.74(13), N2–Fe–N3 82.80(13), N2–Fe–N4 108.10(12), N2–Fe–N5 167.64(12), N2–Fe–N6 88.39(13), N3–Fe–N4 89.24(13), N3–Fe–N5 88.73(13), N3–Fe–N6 92.93(14), N4–Fe–N5 80.66(12), N4–Fe–N6 163.51(12), N5–Fe–N6 83.04(13).

Noticeably, acetonitrile solutions of the blue crystalline complex $[Fe^{II}(\mathbf{2})_2](CF_3SO_3)_2$ (same batch used for crystal structure determination) display UV/Vis spectra identical to the final ones in the hydrolysis process. Molar extinction coefficients of 2690 and 3700 M$^{-1}$ cm$^{-1}$ are calculated for the 532 and 654 nm bands, respectively.

## (2) Crystal and molecular structure of [Fe$^{II}$(2)$_2$](CF$_3$SO$_3$)$_2$

The Fe$^{II}$ cation is coordinated, in a distorted octahedral fashion, to the nitrogen atoms of two *meridional* tridentate ligands **2**. This type of coordination seems imposed by the cooperative effect between the rigidity of **2** and the metal cation preference for octahedral six-coordination. In the coordination sphere the imino N atoms are mutually *trans* and the quinoline and amine N atoms are mutually *cis*. The average Cu–N$_{imino}$ bond distance [1.895(3) Å], which is significantly shorter than the Cu–N$_{quinoline}$ [2.013(4) Å] and the Cu–N$_{amine}$ [2.033(3) Å] average distance, suggests that the coordination geometry of the complex could be better described as flattened (compressed) octahedral.

The complex is also stabilized by two intramolecular interactions, almost mutually orthogonal to each other, each imino nitrogen (N2 and N5) acting as an acceptor atom in one intramolecular hydrogen bond with an adjacent C–H group belonging to the quinoline moiety of the other meridional ligand (C18–H18 · · · N2 = 3.163 Å, C18–H18–N2 = 148(3)°, C2–H2 · · · N5 = 3.262(6) Å, C2–H2–N5 = 146(3)°). The cationic complex [Fe(2)$_2$]$^{2+}$ is dissymmetric. Its chirality is due to the coordination of two unsymmetrical tridentate ligands and to the conformation of two chelate rings, mutually orthogonal, including chiral carbon centres. The configuration number of the six-coordinate cation is 33 and its chirality is C (clockwise), so [Fe(2)$_2$]$^{2+}$ can be described as an (OC-6-33-C)-[Fe$^{II}$(*R,R-trans*-1-amino-2-iminoquinoline cyclohexane)$_2$] cationic complex. The conformation of both chiral pentaatomic chelate rings is λ.

In the crystal the [Fe(2)$_2$]$^{2+}$ cations interact with CF$_3$SO$_3^-$ anions through intermolecular N–H · · · O hydrogen bonds, which involve both the N–H groups of the two amine moieties of the cations (N3–H3NA · · · O2(1/2 − x, −y, −1/2 + z) = 3.144(5) Å, N3–H3NA · · · O2(1/2 − x, −y, −1/2 + z) = 172(4)°; N3–H3NB · · · O4 = 3.030(5) Å, H3–N3NB–O4 = 161(4)°; N6–H6NA · · · O1 = 2.988(5) Å, N6–H6NA–O1 = 156(3)°, N6–H6NB · · · O4 = 3.161(6) Å, N6–H6NB–O4 = 154(3)°). An unusual aspect of [Fe(2)$_2$]$^{2+}$ concerns the *mutually meridional* arrangements of the ligands **2**. To the best of our knowledge, [Fe(2)$_2$]$^{2+}$ represent the first structurally characterized example of a monomeric iron(II) complex in which two 3N tridentate ligands, involving a central imino atom and terminal sp$^3$ and sp$^2$ nitrogens, are meridionally coordinated to give a chiral six-coordinated (OC-6-33-C) cationic complex. The only other monomeric iron complex with a similar sequence of nitrogen atoms in the coordination sphere (imino nitrogens mutually *trans*, the other ones mutually *cis*) is the [Fe$^{III}${NC$_4$H$_3$-2-CH=NCH$_2$CH$_2$NHCH$_2$)$_2$}]$^+$ complex cation,[18] which shows a distorted octahedral disposition of nitrogen atoms from a 6N hexadentate ligand. However, the presence in the iron(III) complex of five five-membered chelate rings, as opposed to four five-membered ones in [Fe(2)$_2$]$^{2+}$, seems to make comparison inappropriate.

## (3) Solution properties of the double stranded [Fe$^{II}$$_2$(3)$_2$]-(CF$_3$SO$_3$)$_4$ helical complex

Ligand **1** does not appear feasible to form triple stranded helical complexes with Fe$^{2+}$. As a matter of fact, most probably due to the steric crowding of the three large and rigid imino-quinoline moieties around the metal cations, the [Fe$_2$(1)$_3$]$^{4+}$ form is not stable, and a reaction leading to a less-crowded species is observed. In order to avoid steric crowding and obtaining helical complexes maintaining the *R,R-trans*-1,2-cyclohexanediimine framework, we prepared the bis-tridentate ligand **3**. Spectrophotometric titrations experiments (addition of standard Fe$^{II}$ trifluoromethanesulfonate solutions to the ligand solution), carried out in acetonitrile, indicated a preference for 2 : 2 stoichiometry when coupled to ESI measurements. Plots of absorbance *vs.* added metal display profiles with inflection points at ligand/metal molar ratio of 4 : 1 and 2 : 1, with a

final sharp change to a plateau at a 1 : 1 molar ratio. Solutions containing Fe/ligand **3** in a 1 : 1 molar ratio revealed the authentic 2 : 2 stoichiometry of the obtained species by means of mass spectra ESI experiments, which show the expected peak for the {[Fe$_2$(3)$_2$] + (CF$_3$SO$_3$)$_3$}$^+$ cation at *m/z* 1547. From these solutions, several batches of crystalline solids were obtained, both by solvent diffusion and by slow evaporation. The crystalline solids gave correct elemental analysis for [Fe$^{II}$$_2$(3)$_2$]-(CF$_3$SO$_3$)$_4$ but unfortunately were not suitable for X-ray diffraction, so that the double helical nature of the prepared complexes can only be demonstrated in solution.

Spectral data are consistent with those found for octahedral Fe$^{II}$ complexes featuring tridentate ligands with N-donors belonging to heterocycle ligands. As shown in Fig. 1 (dashed line) green acetonitrile soutions of [Fe$^{II}$$_2$(3)$_2$](CF$_3$SO$_3$)$_4$ display a main band at 626 nm (ε = 6700), with a shoulder at 560 nm, plus a less intense band at 465 nm (ε = 4700), which can be compared with what found for [Fe(terpy)$_2$]$^{2+}$ solutions in DMF (terpy = 2,2′:6′,2″ terpyridine), which display an intense CT band at 562 nm (ε = 12000), a shoulder at 550 nm and a less intense band at 370 nm (ε = 6000), or with a series of Fe$^{II}$ 1 : 2 complexes with rigid tridentate ligands featuring sp$^2$ N donors of imino-heterocyclic nature.[19] In particular, in the latter case meridional complexes are obtained, which display a two-band spectrum, like in our complex, with λ$_{max}$ ranging in water from 585 to 659 nm (more intense band) and from 466 to 564 (less intense band). Moreover, spectral comparison to prove the octahedral and meridional geometry around the metal centres can be made also with the 2 : 1 ligand/Fe$^{II}$ complexes of ligand **4**. Ligand **4** can be considerd as a tridentate "half" of ligand **3**, and it forms the mononuclear complexes and [Fe$^{II}$(4)$_2$]-(CF$_3$SO$_3$)$_2$, as indicated by correct elemental analysis and ESI mass spectra. For this complex, although we were not able to obtain crystals suitable for X-ray diffraction, an octahedral geometry with meridional ligand disposition is expected, due to the simple tridentate and rigid nature of **4**, to the stoichiometry and by considering the absence of any further ligand (*e.g.* solvent) in the obtained solid.[20] In acetonitrile solution, for the green [Fe$^{II}$(4)$_2$](CF$_3$SO$_3$)$_2$ a spectrum very similar to that of [Fe$^{II}$$_2$(3)$_2$]$^{4+}$ is found, with bands at 473 nm (ε = 2700) and at 612 nm (ε = 4700), as reported in Fig. 1 (dotted line).

Beside UV/Vis data, which give indications on the local Fe$^{II}$ geometry, the helical nature of the dimeric Fe$^{II}$ complex with ligand **3** is strongly supported by molecular modelling. Stable and symmetric conformation was found using the molecular dynamics force field MM+. In this structure, which is shown in Fig. 3, the cyclohexyl rings are in the stable chair conformation, and the imine group is co-planar with the phenanthroline ring, while imino-phenanthroline systems at each coordination centre are perpendicular. The helicity of the calculated structure is M. Noticeably, we also found a P helical complex with both cyclohexyl rings in a boat conformation, and other non-helical structures, but these structures were less
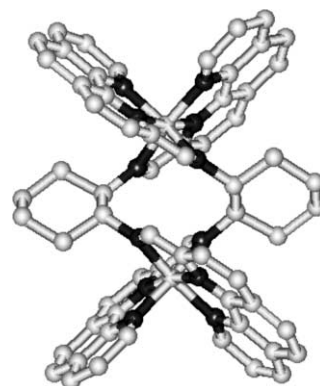


**Fig. 3** Calculated structure (MM+) for the [Fe$^{II}$$_2$(3)$_2$]$^{4+}$ molecular cation.

**Table 2** Proton chemical shifts for ligand **3** and $[Fe^{II}_2(3)_2]^{2+}$. $\Delta\delta$ values refer to the shifts observed on complexation

| $^1$H-NMR($\delta$) | H$_{1/1'}$ | H$_{2/2'}$ | H$_3$ | H$_4$ | H$_5$ | H$_6$ | H$_7$ | H$_8$ | H$_9$ | H$_{10}$ | H$_{11}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ligand **3** | 1.8/1.8 | 1.6/1.8 | 3.75 | 8.56 | 8.25 | 8.25 | 7.75 | 7.75 | 8.27 | 7.65 | 9.05 |
| $[Fe^{II}_2(3)_2]^{4+}$ | 0.15/0.75 | −0.80/0.60 | 2.15 | 8.15 | 9.40 | 9.55 | 8.70 | 8.35 | 7.10 | 7.30 | 8.45 |
| $\Delta\delta$ | −1.65/−1.05 | −2.4/−1.20 | −1.60 | −0.41 | +1.15 | +1.3 | +0.95 | +0.60 | −1.17 | −0.35 | −0.60 |

energetically favored with respect to the structure displayed in Fig. 3 ($\Delta E$ values are in the range of 10–20 kcal mol$^{-1}$, with respect to the structure reported in Fig. 3). Moreover, the M helical complex was found to be stable also under acetonitrile influence as the calculated geometry of the isolated macromolecule was not significantly modified by solvent effects.

Noticeably, the calculated structure resembles that found for the 2 : 2 complexes of ligand **1** with Cu(I).[6a,b] In particular, in that case, considering one of the two ligands intertwined in the double helicate, its two imino-heterocycle halves were lying in almost perpendicular planes, with divergent nitrogen donor sets, while the ligand followed an M helical disposition, towards which ligand **1** is preorganized, due to the presence of the *R,R-trans*-1,2-cyclohexane spacer.[6b] A similar reciprocal disposition of the iminophenanthroline halves of a single ligand is found for the structure calculated of $[Fe^{II}_2(3)_2]^{4+}$, and the M helicity is mantained, as expected by considering that **3** contains the same *R,R-trans*-1,2-cyclohexyl spacer as **1**.

Significantly, the calculated structure is consistent with the $^1$H NMR spectrum measured at 25 °C in CD$_3$CN[21] (the spectrum is available in the ESI).† $[Fe^{II}_2(3)_2](CF_3SO_3)_4$ is diamagnetic, as very sharp signals are obtained in CD$_3$CN, distributed over the chemical shift range −0.7 ppm < $\delta$ < 9.5 ppm. A single set of signals is found for the phenanthroline and imine protons, confirming the symmetrical nature of the $[Fe^{II}_2(3)_2]^{4+}$ molecular cation, in which not only one ligand is equivalent to the other, but also each half of a single ligand is equivalent to the other half (it has to be noted that any exchange between the ligands is prevented by the d$^6$, low spin, kinetically inert nature of the iron centres). Moreover, the existence of only on set of signals indicates the significantly higher stability of the obtained form with respect to other possible forms, *e.g.* the less stable ones found by molecular modelling. This represents an interesting difference with comparable systems described by us[6a] and other authors,[22] in which some less stable species were instead detected by NMR beside the most stable one. The chemical shift of the protons and their assignation (made by COSY experiments, available in the ESI) are summarized in Table 2 both for ligand **3** and for $[Fe^{II}_2(3)_2]^{4+}$, together with the $\Delta\delta$ values observed on complexation. Scheme 1 displays the used proton labelling scheme.

A downfield shift of the imine and phenanthroline protons (H4–H11) is observed on complexation of the tridentate imino-phenanthroline units to the +2 charged iron centres. Beside, a dramatic upfield shift is instead observed for the CH and CH$_2$ protons of the cyclohexane rings. In particular, H2,2′ protons are upfield shifted by −2.4 and −1.2 ppm, reaching unusual
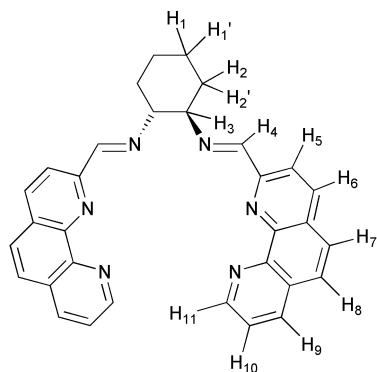


**Scheme 1** Proton labelling scheme for ligand **3**.

chemical shifts values of −0.80 and 0.60. Such a shift can accounted for by the shielding exerted by the phenanthroline rings on the 2,2′ protons. The cyclohexyl rings, and the 2,2′ protons in particular, lie in close proximity to the phenanthroline planes and are "sandwiched" between them, according to the calculated structure displayed in Fig. 3. Moreover, by comparing the $^1$H NMR spectra of the "half ligand" **4** with that of $[Fe^{II}(4)_2]^{2+}$, upfield $\Delta\delta$ of the cyclohexyl protons of only ~0.5 ppm are observed on complexation, with lower value signals found at 0.5 ppm. This confirms the special disposition found for the cyclohexyl rings in the Fe$^{II}$ helicate with ligand **3**. At this regard, it is also important to note that a 2 : 2 side by side disposition of the two ligands in dimeric complexes based on the *R,R-trans*-1,2-cyclohexyl spacer bearing imino-heterocycle rings has been found only in the solid state for a Cu(I) complex with 6-methyl-pyridine as the heterocycle, and in the reported structure[6d] the cylohexane spacers were located in separate space regions with respect to the heterocycle rings.

The chiral helical nature of complex $[Fe^{II}_2(3)_2]^{4+}$ is confirmed also by circular dichroism measurements, carried out in acetonitrile: intense bands with positive $\Delta\varepsilon$ values are found in the visible region at 470 nm ($\Delta\varepsilon = +7.5$), 566 nm ($\Delta\varepsilon = +5$), 598 nm ($\Delta\varepsilon = +5$) and 654 nm ($\Delta\varepsilon = +25$). The full CD spectrum and, for comparison, the spectrum of ligand **3** are available in the ESI.†

Finally, the solution properties of complex $[Fe^{II}_2(3)_2]^{4+}$ have been examined also as regards its kinetic inertness: treatment of CH$_3$CN solutions with 70% perchloric acid (final acid concentration: 2 M) leaved the complex intact for two weeks. Beside the intrinsic inertness due to the low spin nature of the d$^6$ Fe$^{2+}$ cations in this complex, it has to be noted that, as already found in the literature,[23] inclusion in an helical complex seems to enhance the kinetic inertness of the metal centres: under the same conditions, slow decomposition (50% after 6 h, on the basis of spectral measurements) has instead been observed for the "half" complex $[Fe^{II}(4)_2]^{2+}$.

### (4) Electrochemical properties of $[Fe^{II}_2(3)_2]^{4+}$

The redox behaviour of $[Fe^{II}_2(3)_2]^{4+}$ double helical complex has been examined by cyclic voltammetry experiments carried out on its trifluoromethanesulfonate salt, dissolved in an acetonitrile solutions made 0.1 M in tetrabutylammonium perchlorate. Beside reversible reductions taking place at very low potentials ($E_{1/2}$ < 1.0 V *vs.* Fc$^+$/Fc), most probably centred on the ligand system as typical of polypyridine complexes of transition metal cations, two reversible and separated monoelectronic oxidative processes were observed. Fig. 4 illustrates the CV profile obtained for the Fe$^{II}$ dimeric helical complex. $E_{1/2}$ values of 995 and 1110 mV *vs.* Fc$^+$/Fc can be evaluated from Fig. 4, although the separation between the two events is not so pronounced to avoid partial superimposition of the signals. However, it has to be stressed that two identical and independent redox centres would give origin to redox events which are separated only by the statistical term (36 mV) and which appear as a single, sharp wave in the CV profile.[24] In our case, the presence of two separated oxidation waves indicates that the metal centres influence each other and are subject to separate oxidative events.

Moreover, the complexes $[Fe^{II}(4)_2]^{2+}$ display only one reversible, monoelectronic oxidation wave, centred at 830 mV *vs.* Fc$^+$/Fc, respectively: in the helical dimer the oxidation of the first $[Fe^{II}(imino-phenanthroline)_2]^{2+}$ centre is remarkably more

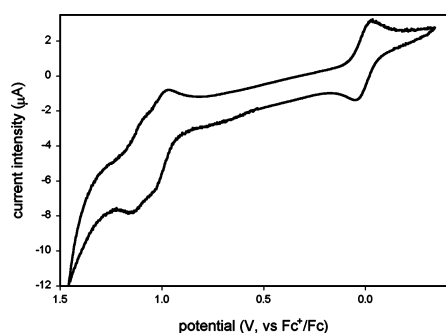**Fig. 4** Cyclic voltammetry profile for $[Fe^{II}_2(\mathbf{3})_2]^{4+}$ in acetonitrile, on a solution containing ferrocene as internal standard ($E_{1/2}$ Fc$^+$/Fc = 0.0 V).

difficult than in the separate $[Fe^{II}(\mathbf{4})_2]^{2+}$ situation, most probably due to the unfavourable electrostatic effect exerted by the other proximate metal centre. Beside, oxidation of the second metal centre takes place at even higher potentials, as one electron has to be abstracted from a +2 centre which has a proximate +3 metal cation. Interestingly, the first oxidation in $[Fe^{II}_2(\mathbf{3})_2]^{4+}$ and the oxidation of $[Fe^{II}(\mathbf{4})_2]^{2+}$ are also significantly more difficult than in the case of the $[Fe^{II}(terpy)_2]^{2+}$ complex (terpy = 2,2′:6′,2″ terpyridine) as literature reports an $E_{1/2}$ value of 710 mV *vs.* Fc$^+$/Fc.[10] Finally, also the CV experiments carried out on $[Fe^{II}(\mathbf{2})_2]^{2+}$ disclosed one reversible oxidation wave, centred at $E_{1/2}$ = 495 mV *vs.* Fc$^+$/Fc. The changes in the donor set (four sp$^2$ and two sp$^3$ N donors, instead of six sp$^2$ N donors) account for the lower potential.

## Acknowledgements

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